# PROCEEDINGS OF THE CHEMICAL SOCIETY

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# EARLY 18TH CENTURY CROP NUTRITION, THEORY, AND PRACTICE By G. E. FUSSELL

It is tempting to assess the late 17th-century works of Grew, Malpighi, and Woodward, inter alia, higher than their really great value deserves. Too easily can their language be mistranslated into modern terms, and meanings given to their hypotheses that are not applicable. Already these men had postulated the absorption of liquid nutriment by the roots from the soil, and of some form of "gaseous" food by the leaves, the value of light to all life, and the circulation of the sap, mistakenly compared with the circulation of the blood in animals and man (partly the continuing result of the impact of Harvey's work on scientific thought).

Experiment had begun to replace speculation in analysing vital processes. It had been initiated by van Helmont on plants, and continued by Boyle and his contemporaries. Nevertheless, between 1700 and 1740 there was more speculation than experiment, or than deduction from practice, despite the numerous descriptions of laboratory processes and their application supplied by Boerhaave in his Elementa Chemicae,<sup>1</sup> of which an English translation appeared in 1727.2 This work became the standard handbook of biochemistry for some decades.

For Boerhaave a vegetable was a body generated of the earth or of something arising out of the earth, to which it was attached by roots; through the roots the vegetable received its nourishment and increase. The vegetable consisted of juices and vessels everywhere distinguished from each other. It was an organised body. The vessels or containing parts were earth bound or connected by oil as a gluten. If exhausted by fire, air, age, or the like, the plant mouldered or returned again to earth or dust. Nutritious juice in a very crude form was drawn into the plant through the roots from the earth. In the plant these juices were elaborated, secreted, and assimilated to the substance of the different parts. where by circulation something suitable was deposited in each, stem, branch, leaf, flower, etc. This circulation had motion, as had blood in animals, a belief based on Malpighi and his two series of vessels. It rose upward till it reached the plant extremities, and then the excess descended through the bark.

The juice was composed of some fossil parts with others derived from the air and rain. Putrified animals, plants, etc., contributed a quota. Conse-

<sup>&</sup>lt;sup>1</sup> Cf. Charles A. Browne, "A Source Book of Agricultural Chemistry," Chronica Botanica, Waltham, Mass., 1944. Vol. VIII, Part 1, p. 106. <sup>2</sup> H. Boerhaave, "A New Method of Chemistry," tr. by P. Shaw, M.D. and E. Chambers London, 1727, pp. 142–148.

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quently plants contained all kinds of salts, oil, water, earth, and probably all kinds of metals, too, "inasmuch as the ashes of vegetables always yield something that the lodestone attracts." The nutrients entered as a fine and subtile water, which changed as it passed through the plant. The leaves performed the respiratory function of lungs.<sup>2</sup>

Marietti had observed the force exerted by the ascending sap. Malpighi realised the importance of leaf function. Almost every writer dealt with root action: but all their work was narrowly circumscribed by the confining influence of tradition, and by the wrongheadedness of alchemy. Boyle had broken out of these limits: Hales based his conclusions on careful experimental work,3 and made a marked advance on Malpighi. He could not with the apparatus and knowledge available confirm it, but he demonstrated that "air is wrought into the composition of plants," which Sir Frederick Keeble called a bold and widely discredited conjecture, proved by much later experience to be correct.<sup>4</sup> The substance, as has now been known for a century and a half, is the carbon dioxide of the atmosphere. Hales showed that "air" entered through the leaves and rind of the plant.

In many ways Hales possessed a modern outlook though this must not be too heavily emphasised. His "Staticks" were really statistical; they were measurements. His earliest experiment was on transpiration, from which he passed to other functional activities within the living plant. His guiding idea was to explain these. For example, he measured the quantity of water taken in by the roots and that transpired by the leaves. He showed the relation between the amount of water in the soil, and root absorption. By an ingenious system of calculation of leaf area and main stem, he determined the velocity at which "liquor" rose in plant stems, and showed it to be related to the rate at which the roots absorb and the leaves transpire it. He found the rate of sap flow varied in different plants, and attempted to demonstrate that this internal movement was explained by their structure. He did not agree with Boerhaave's theory of sap circulation. Howard S. Reed<sup>5</sup> reasonably commented that Hales used the three methods of estimating transpiration employed in modern times.

Hales did not realise that the soil water absorbed by the roots contained in solution minerals necessary to the plant and consumed in its metabolic processes. He could hardly have done so in the then condition of inorganic chemistry, but his work was far in ad-

vance of his time, and for the next fifty years no one showed his genius for devising rewarding experiments,<sup>5</sup> nor did his results have any effect on practical farming, because it had long been known from experience that the health and development of plants was largely determined by the volume of water in the soil, and their need for periods of sunshine.

Hales' difficulty in determining exactly what entered the leaves from the atmosphere resulted from current ignorance of the composition of air. Chemists knew that a small bird or animal confined in an air-tight container found the conditions mortal. The living thing consumed the "vital air," and changed it into something noxious. Something similar happened to matter burned in a confined space. This led Stahl, following Becher, to the phlogiston theory, an attempted explanation of the processes of combustion, erroneous it is true, but at once generally accepted.

Becher, a late 17th-century German, who subscribed to the theory that water was the whole food of plants, their whole substance even to their seeds, called plants nothing but coagulated rain water. He renamed the three iatrochemical principles (sulphur, mercury, and salt) fatty, mercurial, and strong earth, and believed all combustibility rested in the fattyearth constituent of everything. There is a slight Aristotelian flavour about his thinking.

His pupil, G. E. Stahl, adopted the name phlogiston for the combustible part of matter in his "Fundamenta Chymiae," Nuremburg, 1723, translated as "Philosophical Principles of Universal Chemistry," London, 1730. Stahl's phlogiston theory explained the phenomena of flame and combustion. Flame and smoke always occurred when something was burnt: something disappeared into the atmosphere, or perhaps into nothingness. Before Stahl the alchemists and iatrochemists had named this sulphur, not in the precise sense of the word today, but as indicative of some quite undefined subtle principle; the word disguised a lacuna in knowledge. Stahl changed the name but not the principle: the word phlogiston did no more to explain the results of combustion than the word sulphur. Becher named the combustible part of any substance, in particular vegetation, terra pinguis; with Stahl this became phlogiston. For him. phosphorus was a compound of phosphoric acid and phlogiston: charcoal, because it left on combustion very little ash, was nearly pure phlogiston: and metals, because only slightly consumed when

<sup>&</sup>lt;sup>a</sup> Stephen Hales, "Vegetable Staticks," London, 1727.
<sup>4</sup> Sir Frederick Keeble, "The Life of Plants," Oxford, 1946, p. 59.
<sup>5</sup> Howard S. Reed, "A Short History of the Plant Sciences," Chronica Botanica, Waltham, Mass., 1942, pp. 103—105; cf. Charles Singer, "A History of Biology," New York, 1950, p. 363; A. R. Hall, "The Scientific Revolution, 1500—1800," 1954, pp. 286—7, 291.

burned, were almost entirely free from phlogiston.<sup>6</sup> The dominance of this theory-until Lavoisier exploded it-acted as a brake on the greater understanding of plant nutrition that should immediately have followed upon Hales's work and theories.

Jethro Tull, whose experiments, inventions, and writings played a very great part in the development of practical agriculture in the 18th century, still believed in the four elements, Earth, Air, Fire, and Water. He was already a well-known farmer in the first years of the 18th century, but his books did not appear until the fourth decade.

Tull's idea was one many people had shared. He believed earth was the food of plants. Minute particles were assimilated, and the smaller these particles were, the more readily the plants could absorb them. The main function of applied manure was to split up the soil into minute crumbs. His conclusion was that pulverising the soil without manuring it may be better than manuring it without pulverising it. Such pulverisation allowed air, dew, and rain to reach the roots of plants more effectively, and increased the nutrients available to their lateral growths. He tried to devise a scientific theory to support his husbandry. It was only after he had practised his methods in the fields for a good many years that he agreed to write his books, and he very quickly and rather contemptuously dismissed other people's theories,<sup>7</sup> but he owed them a debt as everyone does in every age.

Tull's theory was that the roots range far in search of a supply of nourishment, to which nitre, water, air, fire, and earth, all contributed. This was generally agreed, but there was no agreement about which of these things was the "very Increase or Food". In his view nitre was useful to divide and prepare the food: water always contained "in its Intervals a charge of Earth." He thought van Helmont's water contained a lot of earth. Air was "as necessary to the Life of Vegetables, as the Vehicle of water is." Richard Bradley and others who believed water the food of plants were mistaken. Tull did not agree with the commonly held opinion that different crops took different materials from the soil. If it were true this would prove that air was not the food of plants, because it could not supply the changes of food-it was "Homogenous." Stahl had believed that both earth and water were the food of plants, but Tull

may not have been aware of this: he does not trouble to discuss it.

After the roots had found the pabulum by means of the pressure of the soil which forced fine particles of earth into them, the stalks and leaves received it, and discharged into the atmosphere such part as was unfit for nutrition. The leaves acted as lungs. purified the sap of the noxious parts of the food, and perhaps some decayed particles that flew off the vessels through which the blood and sap passed. "Besides which the Nitro Aerous Particles may there enter to keep up the vital Ferment or Flame." Tull cites Mr. Papin, who showed that air passed in at the leaves of plants and out through the roots, but that water would not pass in at the leaves. Browne has suggested that this idea may owe something to Mayow. He refers also to Grew's air bladders in leaves, which may perform the same function as the vesicles in lungs. A similar function of the leaves, described by Georg Andreas Agricola, whose work was translated by Bradley, comes astonishingly close to the understanding of the action of the stomata, but Agricola felt that it was "impossible to express or even to conceive how Plants drew their Nourishment, and how that is digested because it is performed by an internal Movement"8-a council of despair.

Tull thought that nitre (saltpetre) applied to the roots of plants would kill them. Indeed the only reason why the salts in dung, brine, and urine did not kill field crops or garden plants was that their force was spent in acting upon and dividing the parts of earth. None of the salts, or very little, ever reached the roots. This was the true reason why manures appeared to feed the crop: they assisted comminution. The more this was accomplished the more accessible became the plant nutrients.9

It would be the easiest thing in the world to interpret Tull's words in modern terms, and to imagine that he, as indeed he seems to have done, had come pretty close to the modern hypothesis that plants absorb the minerals contained in the soil solution as part of their nutrient.

In support of his theories Tull appealed to classical practice. The dry land farmers of the Mediterranean littoral were obliged to keep their soil in a fine state of comminution so as to preserve the proper degree

<sup>6</sup> Sir William Cecil Dampier, "A History of Science," 1948, p. 182; Russell M. Garnier, "History of the England Landed Interest: Modern Period," London, 1893, p. 426. 'T. K. Wolfe and M. S. Kipps, "Production of Field Crops," 1953, p. 134; A. Wolf, "History of Science Technology and Philosophy in the 16th and 17th Centuries," 1935, p. 455; Archibald and Nan Clow, "The Chemical Revolution," 1952, p. 465; T. H. Marshall, "Jethro Tull and the New Husbandry," *Econ. Hist. Rev.*, Jan., 1929; cf. Ernle, "English Farming Past and Present," London, 1932, p. 169. Ernle's is a rather too fulsome and over-enthusiastic estimate of this man more justified in respect of his practice than his theory. Marshall comes down too heavily on the other side

\* Jethro Tull, "Horse Hoeing Husbandry," 4th edn., London, 1762. Chaps. I, II, and III; the argument is continued throughout the book; G. A. Agricola, "Philosophical Treatise of Husbandry and Gardening," tr. by R. Bradley, London, 1721, pp. 22, 37.

<sup>9</sup> Tull, op. cit., pp. 11, 22-27.

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of soil moisture to maintain the growth of the crops. In a way, therefore, Tull was right when he said that the "sarrition" of the ancients, *i.e.*, hoeing twice in the growing corn, and weeding once; stirred the earth and so provided more plant pasture. Inter-row hoeing had, he declared, the effect of a summer fallow. Farmers of classical times were only able to grow a crop every other year, something Tull overlooked, but on his own farm he was able to grow a crop year after year. He has, however, a long argument on the deficiencies of the system of ploughing described by Virgil. Both his soil and climate were rather different from those of the Mediterranean lands; but it was this argument that produced the term Semi-Virgilian husbandry later in the century.

Stephen Switzer was one of the most virulent of Tull's opponents, but his theory of plant nutrition was not so very different. It was derived from a reading of the 17th-century scientists as well as from practical experience. Switzer was a professional gardener and seedsman, who wrote gardening and farming textbooks. Besides giving practical instruction he ventured into the somewhat nebulous realm of plant-nutrition theory. For him there were only two qualities of soil, the light, sandy, and loose, or the stiff, clay, and close. Both possessed animate and inanimate qualities. "For the better Understanding of the Specifick Parts of which Earth is compos'd, I am to premise, That there are (simply) two Parts; one the Body, Bed or Couch, wherein lies latent or is contain'd the other, I mean those nitrous and prolifick Salts, being the Spiritus Mundi, which by the co-operation of Rain and Water, Sun and Air, sets, or rather is by them set, to hasten forward the great Work of Vegetation, whilst the other Part is only a lifeless inanimate, dead Lump . . ." The nitrous salts were present in all soils, but more easily extracted (by plants) from some than others. Some method must, therefore, be adopted of renewing the vigour of the lifeless lump earth. The process was, of course, manuring.

After discussing the action of rain in dissolving the salts in the earth, and the theories that water alone, earth only, or water carrying particles of earth were the food of plants, Switzer proceeded to the effects of the sun and air. The sun was the *primum mobile* of all vegetative motion. It drew out the crude and unwholesome vapours sometimes present in the soil, warmed and cheered the surface of the earth, helped to dissolve the latent salts and prepare them for the inhibition or suction of the root fibres. He thought this obvious to all experienced men. Air was the principle cause of the vegetation of plants. It in-

sinuated itself into the surface of the earth and amongst the liquids it contained, and by the genial force of the sun caused ascending motion or fermentation. It mixed its "aereal Substance" into the liquid sap, and rose throughout the tissues of the plant "as Milk, or any other liquid rises by Fire to the top of any Tube" . . . thus permeating all parts of the plant.<sup>10</sup> All this seems fairly orthodox in terms of that day. It was much more simply stated by Agricola, who laid it down that the growth and nourishment of a tree consists in a regular and uniform reception of the nourishing juice, and that the root drew the juice or sap from the earth and conveyed it to the trunk and other parts.<sup>11</sup>

Nearly two decades later Switzer made a virulent attack on Tull. In the 1730's, possibly before, Switzer was a prominent member of a Private Society of Husbandmen and Planters. This Society formulated a grandiose scheme for producing an agricultural encyclopaedia. Switzer was the mainspring of the enterprise, though he had collaborators, "all practical men." There is little out of the ordinary in the only two volumes printed except the compilers' acid criticism of their contemporaries.

Richard Bradley, the translater of G. A. Agricola, was another contemporary whom Switzer condemned as roundly as he did Tull. Bradley was the first Professor of Botany at Cambridge. He made experiments, possibly not always well-designed, and described them in his books, most of which were intended as textbooks for the practical man, though they also contained his theories. Dr. Hamshaw Thomas has emphasised the importance of his discovery of "the rôle of pollination in the formation of seeds," and his proof of the sexuality of plants, as well as his observations on the occurrence of variegated leaves as a sign of what had been known for only the past three decades as virus diseases.<sup>12</sup>

Naturally Bradley enters into controversy since most of the early 18th century hypotheses were based on reasoning rather than knowledge. He was opposed to the theory that earth was the principal element that concerned vegetation. Soil alone could not cause any seed to germinate or sprout without the help of water, air, and heat. He suggested experiments to prove this. Earth was, for him, the nidus or nest to keep the plant steady, a repetition of an older contention. It had no other effect: he strongly opposed Laurence's opinion that earth had more in it than he admitted. If a plant was shut up in an airtight vessel it would decline and eventually die, notwithstanding it has sun and heat and earth to stand in. In addition to air a plant must have heat in some

<sup>&</sup>lt;sup>10</sup> Stephen Switzer, "Ichnographia Rustica," London, 1718, Vol. I, pp. 100-184.

<sup>&</sup>lt;sup>11</sup> Agricola, op. cit., p. 36.

<sup>&</sup>lt;sup>12</sup> H. Hamshaw Thomas, "Richard Bradley, an 18th Century Biologist," Bull. Brit. Soc. for the History of Science, May, 1952.

degree or other according to its nature. The sun was not essential, but plants grown in covered glasshouses tasted flat and insipid. The earth received water, air, and heat, the best sort readily, and it distributed them slowly; therefore strong clays were too closely bound together, and sands too loose to retain them.13

Garnier, in 1893, made some play with Bradley's preoccupation with nitre. Bradley was doing no more here than follow authority. Bacon had considered this substance a plant stimulant, and Boyle that it was an essential part of all life. To Bradley nitre and saltpetre were the same with the reservation that the one was a purer form of the other. It was the constituent of all manures that supplied plant food, a salt that could be found in all the comprehensive miscellany of waste and other products then commonly used or recommended. "Bradley's experiments were not altogether mischievous," acknowledged Garnier. "The mere fact of thus resorting to scientific aid set philosophic thought in motion.' Bradley recognised that practical men were not likely to pay much attention to these theories. They still worked on traditional lines that had been worked out empirically centuries before. Unfortunately philosophers often lacked practical experience, and many forged "Systems in the Air" not founded on any true basis.14

John Laurence, in his "New System of Agriculture," 1726, gave air an important place in the life of plants. External air (atmosphere) carried off the vegetable perspiration. Winds shook the trees to hinder the secretory glands being obstructed, and blew away the noxious air resulting from fermentation and putrefaction. Internally air constantly ascended in the tubes of plants, and a great part remained there plumping up the fruit, and filling the vessels as water did. Air was useful to vegetation "to carry up the Juices to open and support the Vessels against the pressure of external Air, and to swell the Fruit . . . by mingling with the Soil to replenish it with what is so necessary to the growth of Plants ....' This statement he expanded. "When by internal and external Heat it expands itself it ascends; and by ascending carries with it the surrounding films of water, saturated with vegetable Salts (& qua data porta ruit) enters into every open Orifice, and consequently into all the subterranean Pores of Plants . . ."

It contained an "Acid Spirit," the principal thing by which it became manure. This "uniting with Salt of Lime forms a Nitre. Tis this which feeds flame being blown on a dull Fire." Evidently the term Nitre was a spacious one. Laurence believed in the circulation of the sap. He accepted Evelyn's theory of soils, and tried to explain the composition of earth. It was sand "held apart by a sort of Glew . . . as well as the minute Terrestrial Food of the Plant.' He also relied on Woodward's theory that the food of plants was contained in the water in the soil; he nevertheless thought that vegetables were formed of a certain terrestrial matter, not of water. George Rye put this even more clearly. "By modern Experiments it is found that the Nourishment of all Plants consists in some Portions of Matter or Earth swimming in a Fluid; prest by the weight of the Atmosphere, and rarefied by the Sun into the Pores of Plants, and circulating in their Tubes. As the Pores and Tubes differ in their Dimensions so they are capable of admitting different Parts and Sizes of Matter into them." This was the underlying reason why crop rotation was possible and successful. Laurence held the same view . . . "most of the Materials used for the Improvement of Land do it by sending earthy Particles into the Plants by the help of Nitre: the Spirit of the Air and Moisture they receive from without . . . The Materials most ready to receive this Nitre . . . are best Dungs."15

Few novel manures were being brought before farmers in the first thirty years of the 18th century. Most writers prefaced their advice by theories, but there was little new in their practical suggestions. There was a permanent shortage of animal manure, and compost had been made with part dung, part earth, household waste, lime, chalk, and so on, ever since classical times. Much of the animal excrement was voided on the wastes, woodland, and commons where they were then grazed. Some was saved when beasts were housed at night, or when sheep were folded on the open field stubble or fallows. In some places there were enclosed lands, and on these the droppings and urine could be more carefully conserved. Laurence had already perceived that the value of dung was "in great Measure according to the Food eaten."

The most miscellaneous materials were used in the compost heap. Various soils were collected; chalk, lime, and marl were used alone or in the mixture. Street sweepings, a mixture of earth and animal droppings, were collected; coal and wood ash were used. Pigeon, poultry, and pig manure were highly esteemed supplements to other animal products, or used unmixed. Paring the surface of moorland, and burning the vegetation with part of the soil, enriched

<sup>13</sup> Richard Bradley, "Complete Body of Husbandry," London, 1727, pp. 1–14. (I have used this book because it may be considered a compendium of his views.)

 <sup>&</sup>lt;sup>14</sup> Garnier, op. cit., pp. 282–289.
 <sup>15</sup> John Laurence, "New System of Agriculture," London, 1726, pp. 3–13, 70; George Rye, "Considerations on Agriculture," Cork, 1730, p. 2.

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these grounds, and made them fruitful. Most of these things and others like seasand, seaweed, the soil of river beds, pond mud, had been recommended for a century, some for hundreds of years.

Little was yet known of soil science. The farmer classified his land in the rough generalisations that had served his ancestors, despite Evelyn's "Terra," Dr. Lister's Tables of clay and sand<sup>16</sup> and other late 17th century work. Rye's distinction between clay, sand, and gravel is rather narrow: most farmers distinguished qualities of these, and used the term loam as well. Bradley attempted to classify soils and their attributes, and the effect of rainfall on slopes. He made some experiments on the results of drying different soils.17 Each soil ameliorated the others if added to them, except perhaps gravel. Claying was practised in the Fens; marl was used in some parts of the country, but became a famous restorative of sandy soils and light lands only after the publicity given to its use in West Norfolk. Lime and chalk suited heavy soil.

Switzer laid it down that heavy land required "fiery and sprightly" manures to break it up. He suggested a mixture of almost everything available, turned monthly to mix it well and help fermentation. For light lands a mixture of three loads each of natural soil, pond or ditch earth, loam and dung was proper.<sup>18</sup> These suggestions are characteristic, expanded in some works, restricted in others.

Edward Laurence, reasonably enough, thought it undesirable that tenants should dry cow dung and use it for fuel as they did in Lincolnshire and Yorkshire, and indeed in some other counties he does not mention. Paring and burning he considered a bad thing in the long run. Tenant farmers ought to use all the natural manures available on an estate, lime, marl, coal ash, kelp ash, ware, shells or seasand. To the mixture of earth and dung used in Essex he suggested the addition of leaves to make it "fat and serviceable in vegetation . . ." He was a great advocate of green manure; clover ploughed in "by its Salts gives an uncommon fertility to Soil," and on a lower scale so did peas, beans, vetches, lentils, and buckwheat, a comment on the value of ploughing in legumes that was not new but that needed repeating.<sup>19</sup>

Bradley added a trifle to the list of materials, quoting local practice. Oil cake, linseed, rape, etc., powdered and spread at the rate of 1,000 cakes for three acres were "much used" in some parts of North Essex and Cambridge. Again in Buckingham, Hertford, and some parts of Essex the farmers used woollen rags chopped very small and spread at 25-30 bushels per acre just after the corn was sown. This material had been tried in some western counties, but Bradley did not know it. Waste fish was used in Cornwall. Bradley supposed that the parts of these fish helped to bind light land, and contributed to fertility. He has much to say about the more usual manures.20

George Rye does not add much to our knowledge of the practice of manuring, but does a little to the composition of that all-powerful agent, Nitre. He defined it as "a compound Salt made of Alkali, Urine and Salts of the Air . . . so that Ground burnt or limed and well folded by Sheep or other Cattle must generate Nitrous Salts." He thought this was perhaps one reason why grounds are generally fertile after great snows or frosts.<sup>21</sup> This reflexion is the only real attempt that any of these writers made to connect practice with theory that was then being so widely discussed.

All join in advising the farmer to have a care in the preparation of his dung heap, leystall, or compost. The rays of the sun could withdraw valuable fertilising agents contained in the fermenting material, and rains could wash them away. Probably the farmer was well aware of this as he was of the fact that he could, if circumstances, village organisation, and so on allowed, grow several different crops in succession on the same land and obtain good yields without interpolating a fallow year, because the crops used different nutrients-if he troubled to think so far.

Many of the writers discussed their theories as well as the practice they proposed, had experienced, or had observed: but the connecting link between the two is missing. The theory, too, is often mere speculation, if no worse, and the few experiments made, afforded less information than they could have if the current state of biochemistry and soil science had been more developed.

<sup>21</sup> George Rye, op. cit., pp. 10-11.

 <sup>&</sup>lt;sup>16</sup> Lister, *Phil. Trans.*, 1684, 14, 489.
 <sup>17</sup> R. Bradley, "Ten Practical Discourses Concerning Earth," London, 1727; cf. his "Complete Body of Husbandry," <sup>18</sup> Switzer, *op. cit.*, pp. 104—106.
 <sup>19</sup> E. Laurence, "Duty of a Steward to his Lord," London, 1727, pp. 23—31, 182—193, 202.
 <sup>20</sup> R. Bradley, "Complete Body of Husbandry," pp. 58—107.

#### **PEDLER LECTURE\***

#### Polyacetylenes

By E. R. H. JONES

THE first Pedler Lecture, given by W. H. Perkin in 1929, was on "The Early History of the Synthesis of Closed Carbon Chains."1 His revolutionary ideas on the possibility of making small-ring compounds were evolved and brought to fruition during the period (1882-1886) he spent in the Munich school, at that time the organic chemical centre of the world. There the great Baeyer, seeking a change after his exhausting studies on indigo, wondered about the properties of polyacetylenes, compounds containing chains consisting only of carbon atoms; would they have physical properties like those of ordinary compounds or would they be "explosive diamonds?" In his Baeyer Memorial Lecture Perkin wrote, "It was the author's good fortune to be allowed to take part in and watch these experiments on polyacetylenes and the experience of the experimental skill with which Baeyer carried out these very ticklish operations with no other apparatus than test tubes and glass rods, is to this day a very lively recollection." Baeyer's synthetical work,<sup>2</sup> well in advance of the availability of the essential techniques, yielded substances of great instability, but it is only fair to relate that diacetylene, which he was the first to make, is still regarded as a dangerous, unstable compound and that the preparation of tetra-acetylenedicarboxylic acid, the handling of which he related in such agonising terms, has not yet been satisfactorily achieved. Their explosive properties led to the brief enunciation, in his second and last paper on polyacetylenes, of the strain theory, one of the fundamental concepts of organic chemistry.

In 1870 Glaser<sup>3</sup> had described how, when kept in air, the red cuprous phenylacetylide was converted into a colourless crystalline substance which proved to be diphenyldiacetylene, thus discovering the basic reaction for polyacetylene synthesis and incidentally one of the easiest ways of forming carbon-carbon bonds. Over the years quite a number of extensions of the scope of the reaction and variations in the

nature of the oxidising agent have been made<sup>4</sup> and the process, which usually gives very high yields, is one of considerable generality. Mixed coupling, originally achieved by Baeyer<sup>5</sup> between phenyl- and nitrophenyl-acetylenes, is of course possible<sup>6</sup> but it is an expensive procedure when difficultly accessible components are involved. The major variation, if not a new reaction, recently developed by Cadiot and Chodkiewicz<sup>7</sup> is therefore greatly to be welcomed. Instead of employing two ethynyl compounds in an oxidation, elimination of hydrogen bromide, catalysed by a cuprous salt, is brought about between an ethynyl compound and an  $\alpha$ -bromo-acetylene in the presence of a base. A little hydroxylamine serves to keep the cuprous salt in that condition. Very high

yields of unsymmetrical products are obtained, comparable with those produced in symmetrical couplings. Little is known about the mechanisms of these reactions but it appears that they occur within a copper complex since no interaction with solvent or other species present can ever be observed.

Dehydrohalogenation has long been a standard method of forming the acetylenic bond<sup>8</sup> and a development from this constitutes the other main reaction for polyacetylene synthesis.

Starting from the observation that dichlorobutyne gave some diacetylene on treatment with alkaline reagents<sup>9</sup> the scope of this reaction has gradually been enlarged so that it can now be applied where several triple bonds intervene between the two

\* Delivered before the Society at the Imperial College of Science and Technology, London, on February 12th, 1959.

- <sup>1</sup> Perkin, J., 1929, 1347. <sup>2</sup> Baeyer, Ber., 1885, **18**, 674, 2269.
- <sup>3</sup> Glaser, Annalen, 1870, 154, 159.

- <sup>6</sup> Baeyer and Landsberg, *Ber.*, 1882, **15**, 87. <sup>6</sup> Cf., *e.g.*, Bell, Jones, and Whiting, *J.*, 1958, 1313. <sup>7</sup> Cadiot and Chodkiewicz, *Compt. rend.*, 1957, **245**, 1634; Chodkiewicz, *Ann. Chim.* (*France*) 1957 **2**, 819.
- <sup>8</sup> Cf. Jacobs, Organic Reactions, 1949, 5, 1.
   <sup>9</sup> Keyssner and Eichler, G.P. 750, 637; Johnson, J., 1946, 1009, 1014.

<sup>&</sup>lt;sup>4</sup> Sondheimer and Amiel, J. Amer. Chem. Soc., 1957, 79, 5817; Eglinton and Galbraith, J., 1959, 889, and references cited therein.

reacting centres,<sup>10</sup> e.g.:

Bohlmann and Herbst<sup>11</sup> have recently made the surprising observation that mixed ethylenic-acetylenic systems lead, on dehydrohalogenation, to unsymmetrical rather than symmetrical products; the mechanism is obscure.

$$CH_3 \cdot CHCI \cdot CH = CH \cdot [C = C]_2 \cdot CH = CH \cdot CHCI \cdot CH_3$$

By various combinations of these two basic reactions it has now been possible to synthesise the series of polyacetylenes indicated below, but this necessarily bald statement does scant justice to the ingenuity and determination of Dr. M. C. Whiting and our zealous colleagues in Manchester and Oxford during the last ten years and the elegant complementary studies of Professor Bohlmann and his collaborators at Brunswick.

> $CH_3 \cdot [C = C]_n \cdot CH_3 \qquad n = 1 - - 6$  $Ph \cdot [C \equiv C]_n \cdot Ph$  n = 1 - - 6, 8 $Me_3C \cdot [C \equiv C]_n \cdot CMe_3$  n = 1 - - - 8, 10

Many modifications of normal techniques and of conventional ways of handling organic compounds had to be made in order to cope with substances whose lifetime in light at room temperature could sometimes be measured only in seconds. In addition, for the syntheses of these compounds and also for those of the remarkable naturally occurring members, much effort had to be put into the preparation of the requisite intermediates. Thus the discovery of the elimination reaction leading to the formation of cis- and trans-pentenynes,12 and of a preparative route to the inaccessible cis-pentenynol,<sup>6</sup> were essential for the synthesis of the Compositae esters.

The development of a method of making the simplest acetylenic Grignard reagent,13 and of making penta-1,4-diyn-3-ol by its reaction with ethyl formate, was vital for syntheses of some of the rather spectacular compounds in this series. By operating in acetylene-

$${}_{3}^{\mathsf{CHCL}}\mathsf{CH} = \mathsf{CH} \cdot [\mathsf{C} = \mathsf{C}]_{2}^{\mathsf{C}} \mathsf{CH} = \mathsf{CH} \cdot \mathsf{CH} \mathsf{CL} \cdot \mathsf{CH}_{3} \xrightarrow{\mathsf{Na}\mathsf{NH}_{2}} \mathsf{CH}_{3}^{\mathsf{C}} \mathsf{CH} = \mathsf{CH}_{2}^{\mathsf{C}} \mathsf{C} = \mathsf{CH}_{3}^{\mathsf{C}} \mathsf{CH}_{3}^{\mathsf{C}}$$

saturated tetrahydrofuran solution and adopting a reverse-addition technique, solutions consisting essentially of ethynylmagnesium bromide can be obtained and, from these, ethynylcarbinols derived from compounds such as acetylenic aldehydes and halogenated ketones can be made entirely free from the former major products of such reactions, the acetylenic glycols.

HC≡C·MgBr + H·CO₂Et ---- HC≡C·CH(OH)·C≡CH

Apart from the relations with the natural products. attention has centred mainly on the stabilities and the light absorption properties of the synthetic polyacetylenes. Triacetylene was found to be more unstable than diacetylene, and tetra-acetylene could not be isolated; in general, compounds containing free ethynyl groups are much less easy to handle than the disubstituted analogues. Most polyacetylenes are sensitive to light in the solid state although in dilute solution they may be quite stable; thus crystals of diacetylenic compounds often become coated with a scarlet polymer after an hour or so in daylight while the yellow crystals of dimethylhexa-acetylene after a few minutes at 20° become black and insoluble. This

$$CH_{3} \cdot CH(OT_{5}) \cdot CH_{2} \cdot C \equiv CH \xrightarrow{KOH-EtOH} CH_{3} \cdot CH = CH \cdot C \equiv CH (60\% \text{ cis}; 40\% \text{ trans})$$

$$CH_{2} = CH \cdot CH(OH) \cdot C \equiv CH \xrightarrow{HCI-CaCI_{2}} CH_{2} = CH \cdot CHCI \cdot C \equiv CH (23\%)$$

$$CH_{2} = CH \cdot CH(OH) \cdot C \equiv CH \xrightarrow{HCI-CaCI_{2}} CH_{2} = CH \cdot CHCI \cdot C \equiv CH (23\%)$$

$$CH_{2} - CH = CH \cdot C \equiv CH (57\% \text{ trans}; 20\% \text{ cis})$$

$$HOCH_{2} \cdot CH \stackrel{\text{cis}}{=} CHC \equiv CH$$

P-C6H4 Me-502

- <sup>10</sup> Cook, Jones, and Whiting, J., 1952, 2883.
- <sup>11</sup> Bohlmann and Herbst, *Chem. Ber.*, 1958, 91, 1631.
   <sup>12</sup> Allan and Whiting, *J.*, 1953, 3314.
   <sup>13</sup> Jones, Skatteböl, and Whiting, *J.*, 1956, 4765.

striking phenomenon is probably dependent upon the closeness of the packing of the polyacetylene chains in the crystal lattice; X-ray measurements reveal that the linear chains have a closest approach to one another of 3.8-4 Å in dimethyltriacetylene and diacetylenedicarboxylic acid. It occurred to Bohlmann<sup>14</sup> that more bulky terminal groups might prevent the close approach of the carbon atoms, an idea which was tested by the preparation of a range of di-t-butylpoly-ynes (up to n = 7). In marked contrast to the compounds of the dimethyl series it was found that the t-butylhepta-acetylene is remarkably stable, decomposing only slowly above 150°. We have recently been able, since penta-1,4-divn-3-ol became available, to synthesise<sup>15</sup> the octa- and decaacetylenes of this series and have found that the

Melting or decomposition points of methyl- and t-butyl-polyacetylenes.

n	Methyl	t-Butyl
2	64°	130—132°
3	128°	70°
4	Decomp. 80°	99—100°
5	Unstable $-5^{\circ}$	129—130°
6	Unstable - 5°	140°
7		Decomp. 150°
8		Decomp. ca. 130°
10		Decomp. ca. 100°

stability is maintained even with these highly carbonaceous materials, the latter having a linear arrangement of twenty-two carbon atoms. The limit

 $Me_{C}C \equiv C \cdot C \equiv C \cdot CHO + HC \equiv C \cdot CH(OH) \cdot C \equiv CH$ 2 Et MgBr  $Me_3C \cdot C \equiv C \cdot C \equiv C \cdot CH(OH) \cdot C \equiv C \cdot CH(OH) \cdot C \equiv C$ SOCL2 - Py Basic Al203 

of reasonable stability has certainly been reached in the dimethyl and probably in the diphenyl series, but the stability of the di-t-butyldeca-acetylene and the high yields in the later stages (40% from the glycol) suggest that still higher members could be made.

When we began to study the polyacetylenes no solution spectra even of diacetylenes had been

14 Bohlmann, Chem. Ber., 1953, 86, 657.

measured, although diacetylene itself and dimethyldiacetylene had been examined in the gas phase. With a series of diacetylenic glycols it was found<sup>16</sup> that in the region where dienes and vinylacetylenes absorb intensely (log  $\epsilon = \sim 4$ ), they showed fine



FIG. 1 Light absorption of dimethyltetra-acetylene (in alcohol).

structure but only of very low intensity (log  $\epsilon = \sim 2$ ). It was not until a tetra-acetylene was made<sup>17</sup> that we had the first indication of the remarkable spectra of the compounds of this series: the low-intensity bands were now shifted towards longer wavelengths (2800-3500 Å) and were succeeded by bands of very high intensity in the 2000-2400 Å region, corresponding to the high-intensity bands at about 1600 Å observed when diacetylene and its dimethyl derivative were examined in the gas phase. The accompanying Fig. 1 of the spectrum of dimethyltetraacetylene shows the low-intensity A bands and the very-high-intensity (log  $\epsilon = \sim$ 5) L bands; their frequency spacing is characteristic of the polyacetylene series, being about 2000 cm.<sup>-1</sup> compared with about 1500 cm.<sup>-1</sup> for the polyene series. The remarkable absorption (Fig. 2) of the deca-acetylene with its 18 maxima reveals yet another series of high-intensity bands emerging into the measurable region. (It was a slight disappointment that the  $\epsilon$  value of the main peak failed to reach the million mark.) Compounds containing three conjugated acetylenic linkages can be recognised by the high-intensity L maximum, and those with two or three when conjugated with an ethylenic or carbonyl group can be characterised and identified readily by the unique spacing and high

<sup>&</sup>lt;sup>15</sup> Jones, Lee, and Whiting, J., in the press. <sup>16</sup> Armitage, Cook, Entwistle, Jones, and Whiting, J., 1952, 1998; Bowden, Heilbron, Jones, and Sargent, J., 1947, 1579.

<sup>&</sup>lt;sup>17</sup> Armitage, Jones, and Whiting, J., 1952, 2014.

intensity of the A bands; work on the natural substances of this class has thereby been greatly facilitated.

FIG. 2 Light absorption of di-t-butyldeca-acetylene (in hexane).

Although they are essentially different from the fully conjugated polyacetylenes so far discussed, mention must be made of the remarkable linear and cyclic compounds which have resulted from the studies of Sondheimer<sup>18</sup> and Eglinton<sup>19</sup> on the coupling of diacetylenes, e.g.,  $HC \equiv C \cdot [CH_2]_n \cdot C \equiv CH$ , using the novel and most valuable cupric acetatepyridine coupling procedure devised by the latter

They<sup>20</sup> succeeded in isolating the major component and found that it reacted very violently with bromine. Quite a considerable quantity of this highly unsaturated substance, lachnophyllum ester, seems to have been available and it was proved quite conclusively to have structure (I), *i.e.*, to be a divnenecarboxylic ester, the cis-stereochemistry of the

C<sub>10</sub> Compounds from Compositae plants

$$CH_{3} \cdot CH_{2} \cdot CH_{2} \cdot C \equiv C \cdot C \equiv C \cdot CH \stackrel{\text{\tiny (I)}}{=} CH \cdot CO_{2}Me \qquad (I)$$

$$CH_3 \cdot CH \stackrel{\text{\tiny (iii}}{=} CH \cdot C \equiv C \cdot C \equiv C \cdot CH \stackrel{\text{\tiny (iiii}}{=} CH \cdot CO_2 Me \qquad (II)$$

$$CH_3 C \equiv C \cdot C \equiv C \cdot C \equiv C \cdot C H \stackrel{\text{\tiny def}}{=} CH \cdot CO_2 Me \qquad (II)$$

ethylenic bond following from the isolation of maleic acid on degradation by alkali. From another plant of the Compositae family Sörensen and Stene<sup>21</sup> isolated, in 1941, the more unsaturated matricaria ester for which they suggested the formula (II) of a dehydrolachnophyllum ester. After the war Sörensen at Trondheim renewed the investigation of these constituents of Compositae plants, now using spectrographic methods, and discovered<sup>22</sup> that a substance, recorded as long ago as 1826 as being deposited from the essential oil of Artemisia vulgaris, was in fact a dehydromatricaria ester (III). Systematic studies revealed that these three esters are widely distributed in this plant family and that some related  $C_{10}$  compounds, including the alcohol (IV) and an

$$HC \equiv C \cdot [CH_{2}]_{n} \cdot C \equiv C \cdot [CH_{2}]_{n} \cdot C \equiv C \cdot [CH_{2}]_{n} \cdot C \equiv C + (n = 2 - 6)$$

$$\begin{pmatrix} C \equiv C - C \equiv C \\ [CH_{2}]_{n} \\ C \equiv C - C \equiv C \end{pmatrix} \qquad (n = 2 - 6)$$

$$(n = 3, 4, \text{ and } 5) \qquad (n \geq 10)$$

$$\begin{pmatrix} [C \equiv C \cdot C \equiv C \cdot [CH_{2}]_{4}]_{6} \\ [CH_{2}]_{4} \cdot C \equiv C \quad C \equiv C \end{pmatrix} \qquad (c \equiv C - C \equiv C)$$

author. Not only are the compounds of much inherent interest, but also, being readily accessible, they may well provide simple routes to very long straight-chain and large carbocyclic systems.

Workers at an Agricultural College near Moscow in the 1930's were somewhat surprised to find that the essential oil from Lachnophyllum gossypinum decomposed on distillation at atmospheric pressure.

amazing series of highly unsaturated C13 compounds, mainly hydrocarbons, are also to be found in certain genera. It is only possible to refer briefly to the most interesting and significant work of the Sörensens and their colleagues, but attention must be drawn to the intriguing structural similarities in the C<sub>13</sub> compounds, where open-chain compounds, cyclic isomers of the benzenoid series, and heterocyclic analogues

- <sup>19</sup> Eglinton and Galbraith, J., 1959, 889; Behr, Eglinton, and Raphael, *Chem. and Ind.*, 1959, 699.
   <sup>20</sup> Willjams, Smirnov, and Goljmov, *Zhur. obshchei Khim.*, 1935, 5, 1195.
   <sup>21</sup> Sörensen and Stene, *Annalen*, 1941, 549, 80.
   <sup>22</sup> Stavholt and Sörensen, *Acta Chem. Scand.*, 1950, 4, 1567.



<sup>&</sup>lt;sup>18</sup> Inter al., Sondheimer and Amiel, ref. 4; Sondheimer and Wolovsky, J. Amer. Chem. Soc., 1959, 4755.

of the furan and thiophen series are produced by closely related plant species (see Table).\*

C<sub>13</sub> Compounds from Compositae plants.

CHy=CH·CH=CH·C≡C·C≡C·CH<sup>™</sup>CH·CHyOAc  $C_{g}H_{5} \cdot C \equiv C \cdot C \equiv C \cdot C H \cong C H \cdot C H_{2} \cdot O A c$   $C_{g}H_{5} \cdot C H_{2} \cdot C \equiv C \cdot C = C H \cdot C H = C H$ CH=CH·C≡C·C≡C·C≡C·C≡C·CH<sup>™</sup>CH·CH, C<sub>6</sub>H<sub>5</sub>·C≡C·C≡C·CH<sup>™</sup>CH·CH<sub>3</sub>

$$\begin{array}{c} \mathsf{CH}_2 = \mathsf{CH} \cdot \mathsf{C} \equiv \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + \mathsf{C} + \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + \mathsf{C} + \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + \mathsf{C} + \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + \mathsf{C} + \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + \mathsf{C} + \mathsf{C} + \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + \mathsf{C} + \mathsf{C} + \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + \mathsf{C} + \mathsf{C} + \mathsf{C} + \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + \mathsf{C}$$

Although these structural similarities are very close indeed, there is as yet no evidence to suggest that a new benzenoid-ring biosynthesis, alternative to those involving oxygenated cyclic intermediates, is operative in the Compositae.

Challenger and Holmes<sup>23</sup> suggested that it might be more than a coincidence that the first natural occurrence of a thiophen derivative (2,2':5',2"terthienyl from the Compositae, Tagetus erecta) should be from a family whose members produce polyacetylenes. It now appears<sup>24</sup> that thiophen compounds occur rather widely in the Compositae and it may be that we have here a clue to the mode of formation of the acetylenic bond rather than a manifestation of some of its later transformations.

VI) in an attempt to make Carlina oxide (IX). Preliminary studies show, however, that the cisisomer of (VI) is readily cyclised under alkaline conditions into (VII) which with acids is further transformed into the furan (VIII).26

It has been our good fortune to be able to participate in the elucidation of the structures of some of the Compositae polyacetylenes by synthetic studies, and I would like to take this opportunity of expressing our appreciation of the wholehearted cooperation of Professor and Mrs. Sörensen and their collaborators in their northerly chemical outpost. The discovery of routes to cis-pentenyne and cispentenynol made feasible syntheses of the parent lachnophyllum, matricaria, and dehydromatricaria esters:6

$$\begin{array}{c} I, Cu^{+}-H_{2}O_{2} \\ \hline 2, MnO_{2} \\ \hline 3, CrO_{3} \\ \hline 4.CH_{2}N_{2} \end{array} \end{array} \left\{ \begin{array}{c} CH_{3} \cdot CH_{2} \cdot CH_{2} C \blacksquare C \cdot C \blacksquare C \cdot CH \stackrel{\text{\tiny{des}}}{=} CH \cdot CO_{2} Me \\ CH_{3} \cdot CH \stackrel{\text{\tiny{des}}}{=} CH \cdot C \blacksquare C \cdot C \blacksquare C \cdot CH \stackrel{\text{\tiny{des}}}{=} CH \cdot CO_{2} Me \\ CH_{3} \cdot C \blacksquare C \cdot C \blacksquare C \cdot CH \stackrel{\text{\tiny{des}}}{=} CH \cdot CO_{2} Me \end{array} \right.$$

A quite unexpected bonus was forthcoming by the discovery that the synthetic cis-acids cyclised with great ease in neutral solution to lactones, one of which (X) was recognised as occurring naturally.<sup>27</sup>

Syntheses of divinyltetra-acetylene and of the cisisomer of (XII) were carried out before the identity

$$(V) \qquad HC \equiv C \cdot CH = CH \cdot CH_{2} \cdot OH \longrightarrow CH_{3} \cdot C - CH$$

$$(V) \qquad HC \equiv C \cdot CH = CH \cdot CH_{2} \cdot OH \longrightarrow CH_{3} \cdot C - CH$$

$$(VI) \qquad Ph \cdot C \equiv C \cdot C \equiv C \cdot CH = CH \cdot CH_{2} \cdot OH \xrightarrow{HO^{-}} Ph \cdot C \equiv C \cdot CH = C - CH_{2} C - CH_{2} \xrightarrow{H^{+}} Ph \cdot C \equiv C \cdot CH_{2} C - CH_{2} \xrightarrow{CH^{-}} CH$$

$$(VI) \qquad Ph \cdot C \equiv C \cdot C \equiv C \cdot CH = CH \cdot CH_{2} \cdot CH = C - CH_{2} \cdot$$

The conversion of an acetylenic alcohol, pent-2-en-4-yn-1-ol (V), into a furan derivative can be effected in the laboratory<sup>25</sup> but no similar reaction could be brought about with the trans-phenylpentenediynol of a hydrocarbon from Coreopsis species was established as the trans-compound (XII), but the synthesis<sup>28</sup> of the  $C_{13}H_6$  hydrocarbon (XI) from Helipterum, stable only for seconds in light at

- <sup>25</sup> Heilbron, Jones, and Sondheimer, J., 1947, 1586.
- <sup>26</sup> Jones, Turner, and Whiting, unpublished observation.
   <sup>27</sup> Christensen, Sörensen, Bell, Jones, and Whiting, *Festschrift Arthur Stoll*, 1957, 545.
   <sup>28</sup> Jones, Skatteböl, and Whiting, J., 1958, 1054.

<sup>\*</sup> Full accounts are given in reviews by Bu'Lock (Quart. Rev., 1956, 10, 371), Bohlmann and Mannhardt (Fortschr. Chemie organischer Naturstoffe, 1957, 14, 1), and Wailes (Rev. Pure Appl. Chem., 1956, 6, 61). <sup>28</sup> Challenger and Holmes, J., 1953, 1837.

<sup>24</sup> Sörensen and Sörensen, Acta Chem. Scand., 1958, 12, 771.

ordinary temperatures, presented the most formidable and memorable difficulties, only overcome by great patience and determination on the part of my colleagues.

Following up initial observations by Löfgren, Bohlmann and his school<sup>29</sup> have now made a survey for degradative purposes? (cf. the  $\alpha$ -glycols and oxide isolated from fungi and mentioned below).

The structures of the  $C_{17}$  hydrocarbons (XV and XVI) derived from Artemisia vulgaris and Centaurea species suggest a relationship with the  $C_{18}$  fatty acids

 $\mathsf{CH}_{=}\mathsf{CH}_{\circ}\mathsf{C}\equiv\mathsf{CH} \xrightarrow{1} \mathsf{CH}_{=}\mathsf{CH}_{\circ}\mathsf{C}\equiv\mathsf{C} \mathsf{H}_{\circ}\mathsf{C} = \mathsf{CH}_{\circ}\mathsf{C} = \mathsf{CH}_{\mathsf{C}} = \mathsf{CH}_{\mathsf{C}$ - CH,=CH·C=C·C=C·C=C·C=C·C=C·CH, (XI) 1, EtMgBr; H.CO.NMe<sub>2</sub>. 2, HC≡CMgBr. 3, EtMgBr;  $CH_{3}$ ,  $C \equiv C \cdot C \equiv C \cdot CHO$ . 4,  $SOCI_{2}$ -Py; KOEt.

of the polyacetylenes produced by more than 50 plants of the genus Centaurea, using solvent extraction rather than the earlier steam-distillation technique. The  $C_{13}H_8$  hydrocarbon (XII) is the most frequently encountered acetylenic constituent, but the greatest interest attaches to the isolation of the closely related C13 chlorohydrin (XIII) which occurs, along with its acetate and the diacetate (XIV) of the and also provide a link between the acetylenic products of the Compositae and Umbelliferae families. Lythgoe and his colleagues<sup>30</sup> have isolated the compounds responsible for the considerable toxicity of two species of the latter and in an elegant investigation have proved that they are the glycols (XVII and XVIII), clearly closely related to the Compositae hydrocarbons.

$$\begin{aligned} \mathsf{CH}_{3}^{*}\mathsf{CH} &= \mathsf{CH} \cdot \mathsf{C} \equiv \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} + = \mathsf{C} + \mathsf$$

 $\mathsf{HC} = \mathsf{C} \cdot \mathsf{C} = \mathsf{C} \cdot \mathsf{C} \mathsf{H} = \mathsf{C} = \mathsf{C} \mathsf{H} \cdot \mathsf{C} \mathsf{H} \stackrel{\text{\tiny def}}{=} \mathsf{C} \mathsf{H} \cdot \mathsf{C} \mathsf{H} \stackrel{\text{\tiny def}}{=} \mathsf{C} \mathsf{H} \cdot \mathsf{C} \mathsf{H} \stackrel{\text{\tiny def}}{=} \mathsf{C} \mathsf{H} \circ \mathsf{C} \mathsf{H} \circ \mathsf{C} \mathsf{H} \stackrel{\text{\tiny def}}{=} \mathsf{C} \mathsf{H} \circ \mathsf{C} \mathsf{H} \stackrel{\text{\scriptstyle def}}{=} \mathsf{C} \mathsf{H} \stackrel{\text{\scriptstyle def}}{=} \mathsf{C} \mathsf{H} \circ \mathsf{C} \mathsf{H} \stackrel{\text{\scriptstyle def}}{=} \mathsf{C} \mathsf{H} \circ \mathsf{C} \mathsf{H} \stackrel{\text{\scriptstyle def}}{=} \mathsf{C} \mathsf{H} \circ \mathsf{C} \mathsf{H} \stackrel{\text{\scriptstyle def}}{=} \mathsf{C} \mathsf{H} \stackrel{\text{\scriptstyle def}}{=} \mathsf{C} \mathsf{H} \circ \mathsf{C} \mathsf{H} \stackrel{\text{\scriptstyle def}}{=} \mathsf{C} \mathsf{H}$ 

corresponding a-glycol, in the roots of Centaurea ruthenica. In this instance, none of the C<sub>13</sub>H<sub>8</sub> hydrocarbon is present and these compounds must be of significance in connection with the biogenesis or metabolism of the hydrocarbon. Have we here an example of a blocked enzyme system, or are the classical olefin addition reactions used by the plant

It was pointed out by Anchel<sup>31</sup> in 1952 that certain antibiotics which had been studied in the New York Botanical Garden and elsewhere exhibited ultraviolet absorption spectra similar to those of the synthetic and Compositae polyacetylenes. These tentative conclusions were confirmed by syntheses of, e.g., agrocybin (XIX) and diatretyne I (XX), and

<sup>&</sup>lt;sup>29</sup> Bohlmann, Postulka, and Ruhnke, Chem. Ber., 1958, 91, 1642.

<sup>&</sup>lt;sup>30</sup> Anet, Lythgoe, Silk, and Trippett, J., 1953, 309; Hill, Lythgoe, Merrish, and Trippett, J., 1955, 1770. <sup>31</sup> Anchel, J. Amer. Chem. Soc., 1952, 74, 1588.

during the last six years more than 40 compounds of this class have been isolated from the metabolic products of micro-organisms, especially the wood-

(XXII) HC=C·C=C·CH=C=CH·CH(OH)·CH,·CH,·CO,H O-IN-NoOH  $HC = C \cdot C = C \cdot C = C \cdot CH_{2} \cdot CH_{2} \cdot CH_{2} \cdot CO_{2}H$ (XXIV)

 $HC \equiv C \cdot C \equiv C \cdot CH = C = CH \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO$ (XXIII)-0 O·IN-NaOH 20°  $HC = C \cdot C = C \cdot C = C \cdot CH = CH \cdot CH_{2} \cdot CH_{2} \cdot CO_{2}H$ (XXV)

extraordinary and exasperating difficulties arising from the instability of these uncrystallisable materials, and their peculiar structures were eventually elucidated.<sup>34</sup> Light-absorption measurements played a vital rôle in these investigations, as much in isolation and purification as in structure determination; indeed it is inconceivable that the work could have been done otherwise. The infrared spectrum of nemotin reveals the presence of H-C $\equiv$ C- (3280),  $-C \equiv C - C \equiv C - (2130)$ , and -HC = C = CH - (1960)groups and the carbonyl of a  $\gamma$ -lactone (1790 cm.<sup>-1</sup>), and these data, together with ultraviolet absorption spectra and studies of the hydrogenation products, sufficed to determine the structure (XXIII). Noteworthy is the dual asymmetry, i.e., nemotin is a diastereoisomer of the asymmetric carbon and allenic centres, and also the production by the same organism of both the  $C_{11}$  compounds and their  $C_{12}$ homologues, the significance of which will be discussed below.

rotting fungi. Of outstanding interest is the crystalline but very labile mycomycin (XXI), the first naturally occurring compound containing an allenic group, encountered by Celmer and Solomons<sup>32</sup> in 1952 in a search for new antibiotics. Microbiological synthesis soon became a necessary counterpart to our normal studies and at Manchester in 1952 we began to grow B.841, a member of the Basidiomycete group and probably a Poria species, which had already yielded promising results in the hands of Anchel and her colleagues.<sup>33</sup> In addition to the two unstable antibiotics, nemotinic acid (XXII) and nemotin (XXIII), which they had encountered, we were able to isolate two rather less unstable homologues, odyssic acid (XXVI) and odyssin (XXVII), separation being achieved by countercurrent distribution. (Polyacetylene production by this organism is at a high level and some 160 mg. of the mixture of the four components can be obtained per litre of broth.) Drs. Bu'Lock and Leeming nobly contended with the

In the mycomycin, nemotin, and other structural investigations the isomerisations which could be effected under alkaline conditions proved most helpful; not only were much more stable compounds produced but the light-absorption and opticalrotation changes [isomycomycin (XXIX) is optically inactive] gave valuable clues to the parent structures. Favorski in the 1880's was the first to investigate acetylene isomerisations, recording many examples of the conversion of alk-1-ynes into their 2-isomers, and also of 1,2-allenes into the more stable alk-2ynes, by alkali at 180°. In 1951 Jacobs et al.35 put these studies on a quantitative basis by showing with the pentynes that an equilibrium (see p. 206) was involved which was largely in favour of the 2-isomer. These and later investigations<sup>36</sup> have revealed the importance of hyperconjugation contributions to the stabilisation of acetylenic systems; that isomer usually predominates in which the unsaturated system is flanked by the greater number of methyl or

<sup>&</sup>lt;sup>32</sup> Celmer and Solomons, J. Amer. Chem. Soc., 1952, 74, 1870, 2245, 3838; 1953, 75, 1372, 3430.

<sup>&</sup>lt;sup>33</sup> Anchel, Polatnick, and Kavanagh, Arch. Biochem., 1950, **25**, 208; Kavanagh, Hervey, and Robbins, Proc. Nat. Acad. Sci., U.S.A., 1950, **36**, 1, 102.

<sup>&</sup>lt;sup>34</sup> Bu'Lock, Jones, and Leeming, J., 1955, 4270; Bu'Lock, Jones, Leeming, and Thompson, J., 1956, 3767; Bu'Lock, Jones, and Leeming, J., 1957, 1097.

<sup>&</sup>lt;sup>35</sup> Jacobs, Akawie, and Cooper, *J. Amer. Chem. Soc.*, 1951, **73**, 1273. <sup>36</sup> Jones, Whitham, and Whiting, *J.*, 1954, 3201.

methylene groups. The isomerisation of mycomycin (XXVIII) to isomycomycin (XXIX), which separates as a sparingly soluble alkali-metal salt, of nemotinic

be obtained from the adsorption and distribution properties. The chain lengths of monofunctional constituents can be very conveniently determined<sup>37</sup> by

$$HC \equiv C \cdot CH_{2}Et \xrightarrow{4N-KOH-EtOH} H_{2}C = C = CHEt \xrightarrow{175^{\circ}} CH_{3} \cdot C \equiv C \cdot Et$$

$$(1 \cdot 5^{\circ}) \xrightarrow{(1 \cdot 5^{\circ})} (3 \cdot 5^{\circ}) \xrightarrow{(2 \cdot 5^{\circ})} (95^{\circ})$$

$$-C \equiv C \xrightarrow{f_{1}} C \xrightarrow{f_{1}} C \xrightarrow{f_{2}} C \xrightarrow{f_{2}} C \xrightarrow{f_{1}} C \xrightarrow{f_{2}} C \xrightarrow{f_{2}} C \xrightarrow{f_{1}} C \xrightarrow{f_{2}} C \xrightarrow{f_{1}} C \xrightarrow{f_{2}} C \xrightarrow{f_{2}$$

acid to its isomer (XXIV), and of nemotin to nemotin A (XXV), together with the most recently elucidated example in the drosophilin series (see below), all represent variants on the fundamental allene-acetylene-isomerisation, initiated by proton abstraction by a strong base.

In some cases, these changes are accompanied by large decreases in optical rotation due to the elimination of the considerable asymmetry caused by the allenic group; thus  $[\alpha]_{\rm D}$  falls from  $+320^{\circ}$  to  $-3^{\circ}$  when (XXII) goes into (XXIV), and the activity of mycomycin ( $[\alpha]_{\rm D} - 130^{\circ}$ ) completely disappears. At the same time ultraviolet absorption alters; with both nemotin  $\rightarrow$  (XXV) and mycomycin  $\rightarrow$  (XXIX) large bathochromic shifts and intensity increases are observed whereas the transformation (XXII)  $\rightarrow$ (XXIV) is accompanied by the disappearance of intense absorption above 2200 Å.

We have now screened some 300 species from the Basidiomycete group for polyacetylene production by examining the light absorption of extracts and fractionated extracts, for which purpose a recording ultraviolet spectrophotometer has been invaluable. The extracts from both mycelium and culture fluid are split into acidic and neutral portions, provided that alkali-treatment does not bring about any appreciable alteration in spectrographic properties (see above). The neutral portion of the esterified acids

$$A = - \equiv - \equiv - \operatorname{co}_2 H$$
$$B \equiv - \equiv - \equiv - \operatorname{co}_2 H$$

can be fractionated further by chromatography on alumina. From the spectra of the fractions so obtained it is possible to decide whether the organism in question produces polyacetylenes in appreciable amounts and what chromophoric systems are present. Thus, owing to the fine structure and the high intensity of the absorption of the polyacetylenes, distinction can be drawn between such closely related systems as (A)–(B) and (C)–(D), and some indication of the functional groups present can often hydrogenation and reduction by lithium aluminium hydride, followed by vapour-phase chromatography of the saturated alcohols; as little as 3 mg. of the acetylenic compound will suffice to yield this important information. A comparable method based on the preparation of saturated dimethyl ethers has been developed<sup>38</sup> for bifunctional constituents. By these screening methods the re-isolation of known compounds can largely be avoided.

Polyporus anthracophilus, which produces also the interesting  $C_{31}$  triterpene eburicoic acid, gives rise to some 17 acetylenic compounds of which 12 have been isolated, largely by chromatography of esters, and their structures have been elucidated.<sup>39</sup> They are mainly  $C_{10}$  acids, occurring free or as methyl esters, but also esterified in two instances with corresponding  $C_{10}$  alcohols, *e.g.*, (IV). The latter, isolated from the roots of the common daisy (*Bellis perennis*), provided the first link between the fungal and the Compositae polyacetylenes. Although all the acetylenicethylenic compounds from *P. anthracophilus* have the double bond in the *trans*-configuration, many *cis*-compounds have now been isolated from cultures of other fungi.

We have recently completed<sup>40</sup> an investigation of *Coprinus quadrifidus*, the  $C_9$  triacetylenic triol (XXXIII) being the major product (*ca.* 50 mg./litre),

$$\begin{array}{c} c = - \equiv - \equiv - \equiv \\ p \equiv - \equiv - \equiv - \equiv \end{array}$$

accompanied by closely related  $C_9$  compounds (*e.g.*, XXX and XXXI) and the  $C_{10}$ -diol (XXXII). The triol, isolated by counter-current distribution, is a nicely crystalline substance (stable at  $-30^{\circ}$  in the dark) which explodes at  $80^{\circ}$  and rapidly blackens in light. Its structure was proved as indicated below, and advantage was taken of its isomerisation with alkali to determine its absolute configuration, L-erythronolactone (XXXIV) being obtained on ozonolysis.

<sup>&</sup>lt;sup>87</sup> Stephenson, D.Phil. Thesis, Oxford, 1959.

<sup>&</sup>lt;sup>38</sup> Gardner, D.Phil. Thesis, Oxford, 1959.

<sup>&</sup>lt;sup>39</sup> Bu'Lock, Jones, and Turner, J., 1957, 1607.

<sup>40</sup> Jones and Stephenson, J., 1959, 2197.

fact that one of the functional groups is almost in-(XXX) HC≡C·C≡C·C≡C·CH≝CH·CH;OH HC=C·C=C·C=C·CH\_CH·CH.OH (XXXI) (XXXII) HO-CH, C=C-C=C-C=C-CH= CH-CH, OH  $\begin{array}{c} (XXXIII) \quad \mathsf{HC} = \mathbb{C} \cdot \mathbb{C} = \mathbb{C} \cdot \mathbb{C} = \mathbb{C} \cdot \mathbb{C} + \mathbb{C} \cdot \mathbb{C} + \mathbb{C} \cdot \mathbb{C} + \mathbb{C} \cdot \mathbb{C} + \mathbb{C} + \mathbb{C} \cdot \mathbb{C} + \mathbb{C}$ CH, CH, CH, CH, CH, CHO (XXXIV)

 $(C_9 - C_{13})$  of polyacetylenic metabolites of intriguing complexity. Separation is extraordinarily difficult, but so far the  $C_{11}$  acids (XXXV) and (XXXVI) have been obtained pure and fully identified.<sup>41</sup> The interrupted polyacetylene chain and the terminal allenic grouping are new features which emphasise that acetylene-allene rearrangements have to be reckoned with in biogenetic schemes. The preservation of the cis-configuration in a  $\beta\gamma$ -ethylenic acid during two alkali-treatments is noteworthy, indeed attempts to convert the acid (XXXVII) into the known synthetic trans-acid have been unproductive.

variably acidic or readily derived from a carboxylic acid, is suggestive of biogenesis from acetate units comparable with that of the fatty acids. At the other end of the chain in those compounds with an even number of carbon atoms, we find methyl groups or their oxidation products, i.e., alcohols, aldehydes, and acids and their derivatives, which may be taken to indicate ready  $\omega$ -oxidation. Most noticeable is the ubiquitous presence of the free enthynyl group in all those compounds containing an odd number of carbon atoms, from which we infer that decarboxyla-

the plant polyacetylenes) and this, together with the

$$HC \equiv C \cdot CH_{2} \cdot C \equiv C \cdot C \equiv C \cdot CH \stackrel{\text{\tiny eff}}{=} CH \cdot CH_{2} \cdot CO_{2}H \qquad (XXXV)$$

$$\downarrow^{N_{0}HCO_{3}}$$

$$H_{2}C = C = CH \cdot C \equiv C \cdot C \equiv C \cdot CH \stackrel{\text{\tiny eff}}{=} CH \cdot CH_{2} \cdot CO_{2}H \qquad (XXXVI)$$

$$\downarrow^{N_{0}_{2}CO_{3}}$$

$$CH_{3} \cdot C \equiv C \cdot C \equiv C \cdot C = C \cdot CH \stackrel{\text{\tiny eff}}{=} CH \cdot CH_{3} \cdot CO_{3}H \qquad (XXXVII)$$

The structures of the acetylenic compounds so far isolated from micro-organisms are indicated diagrammatically in the accompanying Tables where tion of  $\alpha\beta$ -acetylenic acids (or, perhaps less likely, elimination of formaldehyde, i.e., reversal of laboratory method for primary acetylenic alcohols) can be

they are grouped according to their chain lengths, with the most unsaturated members of the group at the head. It will be noted that no branched-chain compounds have yet been encountered (also true of

brought about by enzyme systems present in many fungi. Evidence of a preliminary nature has been obtained<sup>38</sup> of the ability of cell-free extracts of the mycelium of Coprinus quadrifidus to bring about the decarboxylation of the dicarboxylic acid:

$$HO_2C \cdot [C \equiv C]_3 \cdot CH_2 \cdot CO_2H \longrightarrow HC \equiv C \cdot [C \equiv C]_2 \cdot CH_2 \cdot CO_2H$$

<sup>41</sup> Jones, Leeming, and Remers, J., in the press.

Acetylenic compounds from micro-organisms

C<sub>a</sub> Compounds

$$\begin{array}{rcl} HO \cdot CH_2 &\equiv \equiv \equiv & CO \cdot NH_2 & (I) \\ HO_2C &= \equiv \equiv & CO \cdot NH_2 & (2) \\ HO_2C & & CN & (2) \\ HO_2C &= \equiv & CO_2H & (3) \\ CH_3 &\equiv & = & CHO & (4) \end{array}$$

(1) Agrocybe dura. (2) Clitocybe diatreta. (3) Polyporus anthracophilus. (4) Daedalea juniperina.

Compounds  

$$H \equiv \equiv \equiv \stackrel{\bullet}{=} CO_2H \qquad (1)$$

$$H \qquad CHO \qquad (2)$$

$$H \qquad CH_2OH \qquad (2)$$

$$H \equiv \equiv \equiv \stackrel{\bullet}{\frown} CH_2OH \qquad (2) (3?)$$

$$H \qquad OH OH \qquad CH_2OH \qquad (2)$$

$$H \equiv \equiv \stackrel{\bullet}{=} - CO_2H \qquad (4)$$

Psilocybe sarcocephala. (2) Coprinus quadrifidus.
 Polyporus biformis. (4) Drosophila subatrata.

CIO Compounds

Pleurotus ulmarius. (2) Tricholoma paneolum.
 (3) Coprinus quadrifidus. (4) Polyporus anthracophilus.
 (5) Polyporus guttulatus. (6) Bellis perennis (Compositae). (7) Merulius lachrymans (dry rot).

CII Compounds

$$H = CH_2 = = \stackrel{\scriptscriptstyle \leftarrow}{=} CH_2 \cdot CO_2 H \qquad (I)$$

$$= \equiv \equiv \leq CH_2 \cdot CO_2 H \qquad (I)$$

$$H \equiv = = - \frac{HO}{-} CH_2 \cdot CO_2 H \qquad (2)$$

$$H = \begin{bmatrix} -CH_2 \cdot CO & (2) \\ 0 \end{bmatrix}$$

Drosophila subatrata.
 B.841, Poria corticola, Poria tenuis.

$$\begin{array}{ccc} C_{12} & \text{Compounds} & OH \\ CH_3 \equiv \equiv = & CH \cdot CH_2 \cdot CO_2 H & (I) \end{array}$$

C13 Compounds

$$H \equiv = = \stackrel{\circ}{=} \stackrel{t}{=} CH_2 CO_2 H \qquad (1)$$

(1) Nocardia acidophilus (Actinomycetes).

C14 Compounds

$$HO_2C \equiv \equiv \equiv CH_2 \stackrel{l}{\leftarrow} CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H \quad (1)$$
(1) Poria sinuosa.

Bu'Lock and Gregory<sup>42</sup> at Manchester have found that [1-<sup>14</sup>C]acetate is incorporated well by B.841 and that the nemotinic acid (XXII) produced has the alternating labelling indicated arising from six acetate units linked head to tail. Here is independent

and rather direct evidence of the elimination of the terminal (unlabelled) methyl group, presumably by oxidation and then C-C fission; the accompanying odyssic acid (XXVI), or its precursor, apparently manages to avoid such degradation.

In addition to the  $C_{13}$  and  $C_{17}$  Compositae compounds already mentioned, two  $C_{15}$  representatives (XXXVIII and a dehydro-derivative) have recently been isolated. On the basis of the structures of these

c,

natural polyacetylenes containing an odd number of carbon atoms, in particular the absence of carboxyl groups, Bohlmann and his colleagues<sup>29</sup> suggest that not from the methyl group, as with the fungal metabolites, but from the carboxyl group of acetate. The known odd-numbered aromatic and heterocyclic

$$CH_{3} \cdot CH = CH \cdot C = C \cdot C = CH \cdot CH = CH \cdot CH_{2} \cdot CH_{2} \cdot CH_{2} \cdot CH_{2} \cdot CH_{2} \cdot OA_{2} \quad (XXXVIII)$$



they arise by loss of a carboxyl group from the evennumbered members. It is instructive to look more closely into these structures, including those of the five compounds so far isolated from the Umbelliferae: it can be seen that the terminal groupings present in the 18 or so compounds now known are either methyl or hydroxymethyl at the one end and

#### Terminal groupings in aliphatic $C_{13}$ , $C_{15}$ , and $C_{17}$ polyacetylenes from higher plants

No. of examples

$$CH_{3} - - CH_{10} - - CH = CH_{2} \qquad 5$$

$$- CHCI \cdot CH_{2} \cdot OH \qquad 1$$

$$- CHCI \cdot CH_{2} \cdot OAc \qquad 1$$

$$- CH(OH) \cdot CH_{2} \cdot OH \qquad 1$$

$$HOCH_{2} - - CH = CH_{2} \qquad 1$$

$$CH_{3} - - CH_{12} - - CH_{2} \cdot CH_{2} \cdot OAc \qquad 2$$

$$CH_{3} - - CH_{12} - - CH_{2} - CH_{2} - CH_{2} = CH_{2} \qquad 2$$

$$\begin{array}{ccccccc} -CH_2 \cdot CH_3 & I \\ HO \cdot CH_2 & -CH_2 \cdot CH_3 & I \\ \end{array}$$

vinyl or derived groups at the other. No compounds with free ethynyl groups have been detected and, drawing a parallel between the fungal and plant polyacetylenes, it can be suggested that decarboxyla-

$$-C_6H_5 \leftarrow -C_4 - C \equiv C - CO_2H \rightarrow -C_4 - CH = CH_2$$
, etc.

tion is accompanied or preceded by  $\alpha\beta$ -reduction. The eliminated carbon atom would thus be derived, (O and S) compounds have been excluded from consideration, but even these fall into the same pattern if it be assumed that decarboxylation occurs from a carbon atom which eventually constitutes the benzenoid ring. It will doubtless be possible eventually to test speculations such as these by metabolic studies with labelled materials; it will be especially interesting to discover whether the aromatic ring in compounds such as  $CH_3 \cdot [C \equiv C_1_3 \cdot C_6 H_5]$  is derived as readily from acetate as the side chain.

Although oxygen-containing groups are commonly present at the extremities of natural polyacetylene molecules, they are encountered only infrequently as substituents on the chains, where they most probably originate by oxidation, hydration, and other processes subsequent to the synthesis of the unsaturated carbon chain. Thus the results of Bu'Lock and Gregory<sup>42</sup> show that the oxygen atom in the hydroxy-acid, nemotinic acid (XXII), and the related metabolites of B.841 is attached to a carbon atom derived from the methyl group of an acetate unit. The triol (XXXIX) is almost certainly formed by trans-hydroxylation (via the epoxide) of the corresponding trans-ethylenic alcohols, both of which accompany the triol amongst the metabolic products of Coprinus quadrifidus.<sup>40</sup> Attention has already been drawn to possible modes of formation of the oxygencontaining ring of "Carlina oxide" (XL) and the lactone (XLI).

A number of examples can be cited of the production of allenic systems by 1,4-additions to vinyl-

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<sup>42</sup> Bu'Lock and Gregory, Biochem. J., 1959, 72, 322.

acetylenes, e.g., the three annexed reactions:

$$HC = C \cdot CH = CH_{2} \xrightarrow{HCl} H_{2}C = C = CH \cdot CH_{2} Cl$$

$$\xrightarrow{NHMe_{3}} H_{2}C = C = CH \cdot CH_{2} \cdot NMe_{2}$$

$$HC = C \cdot CH = CH \cdot CH_{2} \cdot OH \xrightarrow{LiAIH_{4}} H_{2}C = C = CH \cdot CH_{2} \cdot CH_{2} \cdot OH$$

$$HC = C \cdot CH = CH \cdot CH(NHMe) \cdot CH_{3} \xrightarrow{CS_{2}} H_{2}C = C = CH - CH - CH \cdot CH_{3}$$

and a process of this type could explain the simultaneous formation of the allenic bond and the lactone ring in nemotin (XLII) and odyssin. If reversal of the alkali-isomerisation of nemotin is too unfavourable energetically, then cyclisation of the *cis*-acid (XLIII), (cf. *cis*-matricaria acid), followed by reduction of the isolated ethylenic linkage, will provide an easier pathway. terns will undoubtedly be revealed by further investigation of other plant families and fungal groups but, as I have indicated, some order is beginning to be apparent. It is possible that further knowledge of their biosynthesis and the transformations they undergo may throw light on the way in which the much more common, but less easily studied, un-

The polyacetylenes, virtually unknown a decade ago, seem to occur rather widely in nature and, although often remarkably unstable, this distressing property is amply compensated for by the comparative ease with which they can be identified and estimated. Their distribution may be of some help in botanical classification. Many more structural patsaturated fatty acids are built up. Some day we may hope better to appreciate how and why these unstable energy-rich molecules are produced. Baeyer speculated about the properties of compounds with chains composed only of carbon atoms; perhaps nature is also experimenting with "explosive diamonds."

#### LETTER TO THE EDITOR

#### The Place of Butlerov in the History of Structural Theory

#### Dear Sir,

IN a recent article W. V. Farrer and K. R. Farrer assert that "Kekulé and Couper . . . are responsible almost entirely for the genesis of the structural theory. The claims of Butlerov, advanced by Russian writers, depend more on repetition than on documentary evidence." They only admit that Butlerov "Later made his own brilliant contribution to the structural theory with his concept of tautomerism." This assumption, often met in literature, is probably based upon a misunderstanding due to insufficient knowledge of Soviet scientific works in the field of history of structural theory.

In this case the question of the contents of classical structural theory resulted in the question of priority.

If one considers that structural theory includes only the thesis of 4-valency of carbon and the ability of carbon atoms and atoms of other elements to effect chain combinations between themselves, then it is evident that Kekulé and Couper are "responsible almost entirely for genesis" of the theory of chemical structure.

But if one considers that the statement of dependence of the chemical properties of an organic molecule on its chemical structure, together with all consequences derived therefrom, is the basis of classical structural theory, then the rise of this theory is connected with Butlerov's name who in 1861<sup>1</sup> formulated the statement<sup>2</sup> that "Die chemische Natur eines zusammengesetzten Molecüls wird durch die Natur und die Ouantität seiner elementaren Bestandtheile und durch seine chemische Structur bedingt." In this case the conceptions of the valency of elements and of atomic bonds are only the premises for formulation of chemical structure.

We cannot here detail the arguments in favour of the second point of view (this has been discussed in detail in author's book<sup>3</sup>), but there are analogous statements in contemporary literature also. L. Pauling, for example, in his Nobel prize speech, after mentioning Frankland's, Kekulé's, and Couper's works, said: "In 1861 Butlerov, making use for the first time of the term chemical structure, stated clearly that the properties of a compound are determined by

its molecular structure and reflect the way in which atoms are bonded to one another in the molecules of the compounds. The development of the structural theory of organic chemistry then progressed rapidly ... "<sup>4</sup> To these words we can only add that term chemical structure was used in a different sense<sup>5</sup> before Butlerov's times.

> Yours sincerely, G. V. Bykov.

> > April, 1960.

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Institute of History of Natural Science and Technics of the U.S.S.R. Academy of Sciences.

Reply from W. V. Farrar and K. R. Farrar:

We thank Academician Bykov for his courteous letter. His claim that "the rise of [the Structure Theory] is connected with Butlerov's name" is a modest one, with which we are in complete agreement. Here we would only add that it is connected with other names as well.

May 17th, 1960.

<sup>2</sup> Butlerov, Z. Chem. Pharm., 1861, 4, 553. <sup>3</sup> Bykov, "History of the Classical Theory of Chemical Structure," U.S.S.R. Acad. Sci. Publn., Moscow, 1960.

<sup>4</sup> Pauling, Science, 1956, 123, 255.

<sup>b</sup> Hess in 1845; Khodnev in 1847; Sokolov in 1858; see Bykov, "The Problems of History of Natural Science and Technics," Moscow, 1957, N 4, 179.

#### COMMUNICATIONS

#### Pentafluoropyridine

#### By R. E. BANKS, A. E. GINSBERG, and R. N. HASZELDINE

(FACULTY OF TECHNOLOGY, UNIVERSITY OF MANCHESTER)

THE first perfluoro-aromatic heterocyclic compound, perfluoropyridine, has now been obtained by defluorination of perfluoropiperidine:



Iron wire; 580-610° at <1 mm. pressure; contact time about 1 sec.

These relatively mild conditions, quite different from those needed for defluorination of an alicyclic compound, show that the N-F bond facilitates defluorination. Thus, in our equipment, designed for defluorination experiments at low pressure and with short contact time, perfluoromethylcyclohexane is recovered quantitatively at 700°. With different equipment, others<sup>1</sup> have shown that defluorination

of perfluoromethylcyclohexane to perfluorotoluene requires long contact times (10--30 min.) at 760 mm.

Pentafluoropyridine, separated in >20% yield from unchanged perfluoropiperidine and intermediate unsaturated perfluoro-heterocyclic compounds by gas chromatography, has m.p.  $-42^{\circ}$ , b.p.  $83 \cdot 5^{\circ}$ (isoteniscope),  $n^{20}_{D}$  1.3856. Its aromatic character is immediately revealed by the characteristic ring absorption of its vapour at 1497 cm.<sup>-1</sup>, close to that (1536 cm.<sup>-1</sup>) in hexafluorobenzene (b.p.  $81^\circ$ );<sup>2</sup> as noted earlier,<sup>3</sup> replacement of = CF- by = N- in fluoro-compounds has but little effect on boiling point. It should clearly be possible to prepare such compounds as perfluoro-quinolines, -pyrimidines, or -pyrazines, by a similar approach.

One of the authors (A.E.G.) is indebted to the Carl Duisberg Stiftung (Leverkusen, Germany) for a maintenance grant.

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<sup>&</sup>lt;sup>1</sup> Proc. Chem. Soc., 1959, 285.

<sup>&</sup>lt;sup>1</sup> Gething, Patrick, Stacey, and Tatlow, Nature, 1959, 183, 588.

<sup>&</sup>lt;sup>2</sup> Birchall and Haszeldine, J., 1959, 13.

<sup>&</sup>lt;sup>3</sup> Haszeldine, J., 1951, 102.

#### The Use of Phosphorohydrazidates as Phosphorylating Agents

By D. M. BROWN and N. K. HAMER

(UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE)

THE facts that acylhydrazides are oxidised by iodine to symmetrical diacylhydrazides1 and that, under suitable conditions, they may be oxidised to acid chlorides by chlorine<sup>2</sup> suggest that the intermediate in such oxidations is a powerful acylating agent. It seemed possible that the phosphorohydrazidates might act as phosphorylating agents under oxidative conditions.

Some phenyl phosphorohydrazidates have been shown to be oxidised by ammoniacal silver nitrate and Fehling's solution.<sup>3</sup> Iodine in presence of a tertiary base is a more convenient oxidising agent and it converted diphenyl and dibenzyl phosphorohydrazidate into the corresponding acids in aqueous solution containing pyridine at room temperature in 10 minutes according to the equation:

$$(RO)_2 PO \cdot NH \cdot NH_2 + 2I_2 + H_2O \rightarrow (RO)_2 PO \cdot OH + N_2 + 4HI$$

Under anhydrous conditions ethanol was phosphorylated in pyridine solution by these reagents to give the corresponding triesters. The dibenzyl ethyl phosphate formed underwent further reaction with

- <sup>1</sup> Curtius, J. prakt. Chem., 1894, **50**, 281. <sup>2</sup> Carpino, J. Amer. Chem. Soc., 1957, **79**, 96; Davies, Storrie and Tucker, J., 1931, 624. <sup>3</sup> Ephraim and Sackheim, Ber., 1911, **44**, 3416.

the iodide ion generated, to yield benzyl ethyl hydrogen phosphate and benzyl iodide.

More interest lies in the oxidation of sodium phenyl phosphorohydrazidate,<sup>3</sup> which crystallised and was used as its hemihydrate. Reaction with the calculated quantity of iodine in dry pyridine at room temperature was rapid and gave  $P^1P^2$ -diphenyl dihydrogen pyrophosphate in quantitative yield. With 2-benzyloxyethyl cyclohexylammonium hydrogen phosphate in pyridine, P1-2-benzyloxyethyl P2-phenyl dihydrogen pyrophosphate was the major product, the appearance of small amounts of diphenyl dihydrogen pyrophosphate and phenyl dihydrogen phosphate being ascribed to the presence of water since the hemihydrate was used in this experiment.

1-Ethylpiperidinium phenyl phosphorohydrazidate reacted with the stoicheiometric amount of ethanol in dry pyridine when oxidised with iodine, giving ethyl phenyl hydrogen phosphate in good yield. Thus this type of reagent is potentially of value both for the synthesis of unsymmetrically substituted pyrophosphates and for the phosphorylation of alcohols.

(Received, April 8th, 1960.)

# The Structure of a Monophosphoinositide By D. M. BROWN, B. F. C. CLARK, G. E. HALL, and R. LETTERS (UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE)

A MONOPHOSPHOINOSITIDE from soya bean is the only member of the class for which the position of attachment of the phosphate to the myoinositol residue has been elucidated.<sup>1</sup> Alkaline hydrolysis of the lipid yielded myoinositol 1- and 2-phosphate, derived from the intermediate cyclic 1,2-phosphate. Since the myoinositol 1-phosphate was optically active and was shown<sup>2</sup> to have the absolute configuration depicted in (I), the original lipid must have been (II;  $\mathbf{R}$  = fatty acyl residues). We find, by a method which avoids any ambiguity due to phosphate migration, that a monophosphoinositide from horse liver has the same structure.

The purified<sup>3</sup> lipid, almost certainly a di-O-acyl-

- <sup>1</sup> Pizer and Ballou, J. Amer. Chem. Soc., 1959, **81**, 915. <sup>2</sup> Pizer and Ballou, J. Amer. Chem. Soc., 1959, **81**, 4745.

- <sup>4</sup> Folch, Ascoli, Lees, Heath, and LeBaron, J. Biol. Chem., 1951, 191, 833; Hanahan and Olley, *ibid.*, 1958, 231, 813.
  <sup>4</sup> McKibbin, J. Biol. Chem., 1956, 220, 537.
  <sup>5</sup> Hall and Shaefer, "Organic Analysis," Vol. II, Interscience Publ. Inc., London, 1954, p. 55.

glycerol myoinositol phosphate from earlier work,<sup>4</sup> gave myoinositol 1- and 2-phosphate on alkaline hydrolysis, showing that one or other of these positions was the linkage point. Removal of the fatty



acids from the lipid by hydroxylamine<sup>5</sup> yielded glycerol inositol phosphate (II; R = H) isolated as the cyclohexylamine salt,  $[\alpha]_{\rm p} - 13.2^{\circ}$  in H<sub>2</sub>O. The salt was chromatographically identical with synthetic glycerol 1-[myoinositol 1(3)-phosphate] but differed from the corresponding myoinositol-2 compound.<sup>6</sup> When the salt was treated with periodate followed by phenylhydrazine formate at pH 6,6 the glycerol residue was destroyed, showing the  $\alpha$ -linkage of the latter, and inositol 1-phosphate was isolated as the biscyclohexylammonium salt,  $[\alpha]_{D} + 2\cdot 2^{\circ}$  at pH 7, increasing positively towards lower wavelengths in a plain optical rotatory dispersion curve, and  $[\alpha]_{p} - 8.5^{\circ}$  at pH 2. These values correspond to those of the L-enantiomorph of myoinositol 1-phosphate (I) isolated from the soya lipid.<sup>8</sup> The form of the dispersion curve is at variance with that described by Hawthorne, Kemp, and Ellis<sup>9</sup> for an inositol phosphate from soya lipid but it is not clear how they isolated the compound and we are unable to account for the discrepancy.

The observations establish the structure of the lipid apart from the position of the fatty acids, which is the subject of work in progress, but much evidence

The advantage of the present degradative method lies in the fact that all steps can be carried out on a microscale, suitable for structural determination of less readily accessible lipids. In this situation, suitably controlled enzymic experiments can normally replace optical rotation measurements for establishing absolute configuration.

in the literature, both biosynthetic and degradative,

leads to the view that these are invariably esterified

The rotation of the isolated glycerol inositol

phosphate (II; R = H) is the same as that of the

corresponding compound from beef liver,<sup>7</sup> so that

the structure of the lipid from that source is now

absolute configuration of the myoinositol phosphate

to the glycerol residue.

residue is still in doubt.<sup>10</sup>

(Received, April 8th, 1960.)

- <sup>6</sup> Brown, Hall, and Letters, J., 1959, 3547. <sup>7</sup> Brockerhoff and Hanahan, J. Amer. Chem. Soc., 1959, **81**, 2591.
- <sup>8</sup> Ref. 2 and personal communication from Dr. C. E. Ballou.
- <sup>9</sup> Hawthorne, Kemp, and Ellis, *Nature*, 1960, **185**, 37. <sup>10</sup> Lecocq, Coulon-Morelec, and Faure, *Compt. rend.*, 1960, **250**, 940.

#### A Radiation-induced Chain Reaction in the Decomposition of Nitrous Oxide

By G. R. A. JOHNSON

(DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DURHAM, KING'S COLLEGE, NEWCASTLE UPON TYNE, 1)

THE decomposition of nitrous oxide by ionising radiations has been reported1 to proceed with an overall yield of  $G(-N_2O) = 12$  (molecules decomposed per 100 ev); the products formed were in the ratio,  $N_2:O_2:NO_2 = 1:0.14:0.48$ . The decomposition was independent of the nitrous oxide pressure from 1 atmosphere to almost the critical pressure and independent of the type of radiation and of the temperature between room temperature and 150°c.

It has now been found that the radiation-induced decomposition of nitrous oxide occurs with a very greatly increased yield, corresponding to  $G(-N_2O)$  $= 9.4 \times 10^4$ , when the gas pressure is reduced to 70 mm. Hg.

In the experiments under consideration, a "Pyrex" vessel (380 ml.) containing pure nitrous oxide was irradiated with X-rays from a Victor Maximar X-ray set operating at 200 kv and 15 mA. The dose rate was  $3.9 \times 10^{14}$  ev min.<sup>-1</sup> ml.<sup>-1</sup> in the gas at N.T.P.; this was calculated from the measured initial yield of nitrogen formed from nitrous oxide irradiated at 765 mm. and 20°c, by assuming that  $G(N_2) = 9.7.1$ The dose rate at the lower pressures used was calculated from the value at N.T.P., the dose absorbed in the gas being assumed proportional to the gas pressure.

At pressures of 68-73 mm. at 20°, and with total doses between 0.39 and 1.65  $\times$  10<sup>14</sup> ev ml.<sup>-1</sup> the yields of nitrogen and oxygen were found to be directly proportional to the total radiation dose and corresponded to  $G(N_2) = 6.2 \times 10^4$  and  $G(O_2) =$  $1.55 \times 10^4$ . Nitric oxide was also formed as an initial product and measurements of the nitric oxide yields, while less accurate than the measurements of the nitrogen and oxygen yields, gave values which agreed, within experimental error, with the stoicheiometric value,  $G(NO) = 2G(N_2) - 4G(O_2) = 6.2 \times 10^4$ . At greater total doses (~ 3 × 10<sup>15</sup> ev ml.<sup>-1</sup>), brown fumes of nitrogen peroxide were observed in the irradiated gas; this is presumably a secondary product.

The mechanism of the radiation-induced decom-

established with some certainty. It appears, too, that the phosphoinositides from wheat germ and cardiac muscle also have the same structure although the

<sup>&</sup>lt;sup>1</sup> Harteck and Dondes, Nucleonics, 1956, 14, 66.

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position of nitrous oxide at atmospheric pressure and of the chain-decomposition at lower pressures reported here has not yet been elucidated. Probably, however, ionic, rather than free-radical, intermediates are responsible for the chain-reaction since photochemical decomposition of nitrous oxide with

A New Method for the 17*α*-Hydroxylation of Steroids By (Miss) E. J. BAILEY and J. ELKS (GLAXO LABORATORIES LTD., GREENFORD, MIDDLESEX) and D. H. R. BARTON (IMPERIAL COLLEGE, LONDON, S.W.7)

WE have found a new method for the introduction of a  $17\alpha$ -hydroxyl group into steroidal 20-ketones. Recently<sup>1</sup> it was shown that ketones such as limonin are smoothly converted into diosphenols on being shaken with oxygen in the presence of potassium t-butoxide in t-butyl alcohol. This reaction, which involves the attack of oxygen on the anion of a ketone, is not without precedent. In general, however, the initial hydroperoxidation is followed by fission of one of the carbonyl-carbon bonds and has no practical value.<sup>2</sup> The contrasting results secured with limonin and its congeners<sup>1</sup> suggested that the reaction might be useful in steroid chemistry.

When any of several steroidal 20-ketones, without a substituent at position 17 or 21, was treated under the conditions specified above it took up 1 mol. of

#### Starting ketone

oxygen and gave a reasonable yield of a  $17\alpha$ -hydroperoxide. Reduction of these hydroperoxides catalytically or, better, with zinc dust and acetic acid

wavelengths of 1849, 1470, and 1236 Å at nitrous

oxide pressures in the same region as those used

here does not proceed by a chain-mechanism.<sup>2,3,4</sup>

I thank Professor J. Weiss for his interest.



Starting ketone	Derived $17\alpha$ -hydroperoxide	Yield (%)
(I; $R = \beta$ - OAc, $R' = \alpha$ - H, $X = H_2$ )	(II; $R = \beta$ - OH, $R' = \alpha$ - H, $X = H_2$ ),	35
(I; $R = \beta$ - OH, $R' = \alpha$ - H, $X = H_2$ )	m.p. $169-172^{\circ}$ (decomp.), $[\alpha]_{\rm D} + 54^{\circ} (c \ 0.50)^{a}$	23
(I; $R = \beta$ - OAc, $R' = \alpha$ - H, $X = O$ )	(II; $\mathbf{R} = \boldsymbol{\beta} \cdot \mathbf{OH}, \mathbf{R}' = \boldsymbol{\alpha} \cdot \mathbf{H}, \mathbf{X} = \mathbf{O}$ ),	57
(I; $R = \beta$ - OH, $R' = \alpha$ - H, $X = O$ )	$[\alpha]_{\rm D} + 71^{\circ} (c \ 1.0)$	51
(I; R = $\alpha$ - OH, R' = $\beta$ - H, X = H <sub>2</sub> )	(II; $R = \alpha$ - OH, $R' = \beta$ - H, $X = H_2$ ), m.p. 162—163° (decomp.), $[\alpha]_p + 64° (c \ 1.0)$	46
(I; $\mathbf{R} = \alpha \cdot \mathbf{OAc}, \mathbf{R}' = \beta \cdot \mathbf{H}, \mathbf{X} = \mathbf{O}$ )	(II; $R = \alpha - OH$ , $R' = \beta - H$ , $X = O$ ), m p. 158-160° (decomp.)	57
(I; $\mathbf{R} = \alpha - \mathbf{OH}, \mathbf{R}' = \beta - \mathbf{H}, \mathbf{X} = \mathbf{O}$ )	$[\alpha]_{\rm p} + 85^{\circ} (c \ 1.0)$	33
(III; $R = OAc$ ) or	(IV; $R = OH$ ), m.p. 163—165° (decomp.),	55 <sup>b</sup>
(III; $\mathbf{R} = \mathbf{OH}$ )	$[\alpha]_{\rm D} + 67^{\circ} (c \ 1.0)$	50

<sup>a</sup> All rotations for MeOH solutions. <sup>b</sup> With sodium t-butoxide and sodium t-pentyloxide the yields were 59% and 49% respectively.

<sup>1</sup> Barton and Templeton, unpublished experiments: see Arigoni, Barton, Corey, and Jeger, *Experientia*, 1960, 16, 41. <sup>2</sup> Doering and Chanley, J. Amer. Chem. Soc., 1946, 68, 586; Doering and Haines, *ibid.*, 1954, 76, 482; Elkik, Bull.

Soc. chim. France, 1959, 933; and references there cited.

(I; (I; (II (II

<sup>&</sup>lt;sup>2</sup> MacDonald, J., 1928, 1. <sup>3</sup> Noyes, J. Chem. Phys., 1937, 5, 807.

<sup>&</sup>lt;sup>4</sup> Zelikoff and Aschenbrand, J. Chem. Phys., 1957, 27, 123.

gave the corresponding  $17\alpha$ -alcohols in high yield. The method may have advantages over prior procedures3 in some instances.

The Table summarises a number of examples. The yields (not necessarily optimal) refer to pure isolated hydroperoxides. The total hydroperoxide content after oxygenation was 60-80%. In general the best yields of hydroperoxide were secured by using  $\sim$ N-potassium t-butoxide containing an excess of the base. The figures in the Table refer to reactions induced by potassium t-butoxide unless specified to the contrary. A  $3\beta$ -acetoxy-group, when present, was normally hydrolysed by the base during the reaction. (Received, April 5th, 1960.)

<sup>3</sup> Fieser and Fieser, "Steroids," Reinhold Publ. Corp., New York, 1959, pp. 652-659.

#### Akuamma alkaloids, Part III. $\psi$ -Akuammicine

By P. N. EDWARDS and G. F. SMITH

micine.

#### (DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, MANCHESTER, 13)

The alkaloid  $\psi$ -akuammicine,  $C_{20}H_{22}O_2N_2$ , first isolated by Henry<sup>1</sup> from the seeds of Picralima klaineana, was reported by Robinson and Thomas<sup>2</sup> to have infrared and ultraviolet spectra very similar to those of akuammicine, isolated from the same source.

Akuammicine, for which we have now conclusively proved structure (I) by conversion into a base identical with base (II) synthesised from Wieland-Gumlich aldehyde,<sup>3</sup> is strongly lævorotatory,  $[\alpha]^{20}$  $-727^{\circ} \pm 10^{\circ}$  (in MeOH, c 0.15). We have found  $\psi$ -akuammicine to be optically inactive; its 2,16- and



19,20-dihydro-derivatives (m.p. 142-143° and 166-168° respectively; infrared spectra identical with those of the corresponding akuammicine derivatives3) are likewise optically inactive. The conclusion that  $\psi$ -akuammicine is the racemate of akuammicine was confirmed by resolution of the former by fractional crystallisation of the (+)tartrate from methanol, the more soluble salt affording akuammicine; the base isolated from the less soluble tartrate had m.p. 181–182.5°,  $[\alpha]^{23}_{p}$ +720°  $\pm$  10° (in MeOH, c 0.24), and infrared and ultraviolet spectra identical with those of akuammicine. On being mixed with an equal weight of akuam-

- <sup>3</sup> Edwards and Smith, J., in the press.
- <sup>4</sup> Robinson, "The Structural Relations of Natural Products," Oxford Univ. Press, 1955, p. 113.
- <sup>5</sup> Wenkert, J. Amer. Chem. Soc., 1959, 81, 1474.

micine, the dextrorotatory base yielded  $\psi$ -akuam-

This is the first racemic alkaloid in the strychninevohimbine group.

The possibility of racemisation of akuammicine during the isolation was considered. The isolation involved percolation with hot methanol, separation into basic and non-basic fractions, and chromatography on neutral alumina. Prolonged exposure to hot methanol appeared to present the only possibility for racemisation. Akuammicine is, in fact, slowly decomposed in boiling methanol or benzene (this decomposition is being investigated) but no  $\psi$ akuammicine could be detected.

There does not appear to be a simple pathway by which racemisation of akuammicine could occur in vivo. Racemisation would have to involve at least fission of both the 7,3- and the 15,16-bond, followed by an optically non-specific resynthesis. We therefore suggest that at a very early stage of the biosynthesis of akuammicine and  $\psi$ -akuammicine, e.g., when the carbon skeleton is still as shown in (III),  $C_{(15)}$  is trigonal (asterisk in III) and is reduced to the tetrahedral state, before quaternisation of the indole  $\beta$ -position, in two ways: one way is optically specific and leads to the configuration common to all the other known indole alkaloids and thus to akuammicine; the other is non-specific and leads to racemic  $C_{(15)}$  and hence to  $\psi$ -akuammicine. This would accord with the view<sup>4</sup> that a phenylalanine is the precursor in the biosynthesis of indole alkaloids, but not with Wenkert's postulate<sup>5</sup> of an optically pure prephenic acid derivative as precursor.

We thank the D.S.I.R. for a maintenance grant (to P.N.E.).

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<sup>&</sup>lt;sup>1</sup> Henry, J., 1932, **135**, 2759. <sup>2</sup> Robinson and Thomas, J., 1955, 2049.

#### Kinetics and Mechanisms of Reversible Elimination, Deuterium and Radiochlorine Exchange, and Rearrangement of Camphene Hydrochloride in Nitrobenzene

By Y. POCKER

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THE mechanism of the deuterium exchange between camphene hydrochloride and deuterium chloride in non-hydroxylic solvents1 is still one of the main unsolved problems<sup>2</sup> connected with the rearrangement of camphene hydrochloride to isobornyl chloride. In a detailed kinetic investigation in nitrobenzene at  $25.0^{\circ}$ , we now find that addition of hydrogen chloride to camphene (X) is of the first order in olefin but of the second order in acid:

$$v (addn.) = -d[X]/dt = -d[H^+]/dt$$
  
=  $-d[Cl^-]/dt = k_3[X][HCl]^2$ 

where  $k_3 = 2.56 \text{ sec.}^{-1} \text{ l.}^2 \text{ mole}^{-2}$ . This is in accord with a two-step process,<sup>3</sup> the first stage of which is the formation of a hydrocamphene-isobornyl cation,<sup>1,2,4</sup> XH<sup>+</sup>, and a hydrogen dichloride anion,<sup>3,5</sup>  $HCl_2^-$ . The second step is reaction of the cation with one of the chlorine atoms of the anion. Isotopic dilution experiments indicate that the intermediate is initially partitioned to give camphene hydrochloride and isobornyl chloride in the ratio of ca. 40:1. Starting with camphene hydrochloride (XHCl) and hydrogen radiochloride (H<sup>36</sup>Cl) we find that the radiochlorine exchange is well expressed by the linear equation: v (<sup>36</sup>Cl-exchange) =  $k_1^*$ [XHCl] +  $k_2^*$ [XHCl][HCl] with  $k_1^* = 0.5 \times 10^{-5}$  sec.<sup>-1</sup> and  $k_2^* = 4 \times 10^{-2}$  sec.<sup>-1</sup> l. mole<sup>-1</sup>, while the rearrangement to isobornyl chloride follows the equation: v (rearrangement) =  $k_{\rm R}$ [XHCl][HCl] with  $k_{\rm R}$ = 0.95 × 10<sup>-3</sup> sec.<sup>-1</sup> l. mole<sup>-1</sup>. The catalytic coefficient of radiochlorine exchange is thus ca. 42 times larger than that for rearrangement, and this accords with the principle of microscopic reversibility. A similar ratio has been obtained with deuterium chloride as catalyst.

The first-order rate coefficients of elimination of hydrogen chloride from camphene hydrochloride are independent of the concentration of 2,6-lutidine, tribenzylamine, or tetrabutylammonium chloride when the latter is low; v (elimination) =  $k_1^{E}$ [XHCl] with  $k_1^{E} = 0.5 \times 10^{-5}$  sec.<sup>-1</sup>. At higher concentrations of the ammonium chloride a mild linear catalysis sets in, v (elimination) =  $k_1^{E}$  [XHCl] +  $k_2^{E}$ [XHCl][Bu<sub>4</sub>NCl] with  $k_2 \approx 2 \times 10^{-4}$  sec.<sup>-1</sup> l. mole<sup>-1</sup>, similar to that observed in other E1 eliminations in non-hydroxylic solvents.<sup>6</sup> By using tetrabutylammonium radiochloride, we showed that, when its concentration is sufficient to form an HCl<sub>2</sub>complex with all the hydrogen chloride produced in the elimination, little or no radiochlorine is introduced into the camphene hydrochloride, and that the dilution of tracer is almost entirely due to the production of hydrogen chloride of normal isotopic abundance. Protio- and deutero-chloride strongly catalyse the elimination, and the initial rates fit the following linear equation fairly well: v (elimination)  $= +d[X]/dt = +d[H^+]/dt = +d[Cl^-]/dt =$  $k_1^{\text{E}}$ [XHCl] +  $k_2^{\text{E}}$ [XHCl][HCl]. For protiochloride and  $k_{1^{E}} = 0.5 \times 10^{-5}$  sec.<sup>-1</sup> and  $k_{2^{E}} =$  $2.3 \times 10^{-3}$  sec.<sup>-1</sup> l. mole.<sup>-1</sup> For deuterochloride  $k_{1^{\rm E}} = 0.5 \times 10^{-5}$  sec.<sup>-1</sup> and  $k_{2^{\rm E}} = 2.1 \times 10^{-3}$  sec.<sup>-1</sup> 1. mole<sup>-1</sup>. But the elimination in the presence of free acid comes to an early equilibrium because of the reverse reaction. When the latter becomes dominant we find that deuterium exchange takes place between camphene hydrochloride and deuterium chloride. The rate of exchange under such conditions is well represented by: v (D-exchange) =  $k_1^{\text{D}}$ [XHCl] +  $k_{2^{D}}$ [XHCl][DCl] with  $k_{1^{D}} \approx k_{1^{E}}$  and  $k_{2^{D}} \approx k_{2^{E}}$ . It thus appears that deuterium exchange is a direct consequence of elimination and back-addition.

All the above-mentioned hydrogen chloridecatalysed components of reaction have the same stoicheiometric composition, XHCl,HCl  $\equiv$  XH<sup>+</sup>HCl<sub>2</sub><sup>-</sup>  $\equiv$  X,2HCl, but some of them differ in the structure of their respective activated complexes. Thus the transition state for radiochlorine exchange involves the transfer of a chloride ion from (ClH<sup>36</sup>Cl)<sup>-</sup> to the tertiary centre of the cation XH+ to produce HCl and XH<sup>36</sup>Cl and is lower in terms of free energy than that involving the transfer of a hydrogen ion from XH<sup>+</sup> to HCl<sub>2</sub>, leading to elimination or deuterium ex-

 <sup>1</sup> Nevell, de Salas, and Wilson, J., 1939, 1188.
 <sup>2</sup> Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons Inc., New York, 1953, Vol. III, Chapter 1, by Bartlett, p. 67.

<sup>3</sup> Pocker, J., 1960, 1292.

76, 4046. <sup>6</sup> de la Mare, Hughes, Ingold, and Pocker, J., 1954, 2930; Pocker, J., 1960, in the press; Trans. Faraday Soc., 1959, 10, 16, 24 55, 1266; Winstein, Smith, and Darwish, Tetrahedron Letters, 1959, No. 16, 24.

<sup>Bateman, Cooper, Hughes, and Ingold, J., 1940, 930; Ingold, cited by H. B. Watson in Ann. Reports, 1939, 36, 197;
Brown, Hughes, Ingold, and Smith, Nature, 1951, 168, 65; Ingold, "Structure and Mechanism in Organic Chemistry,"
G. Bell and Sons, London, 1953, pp. 490, 517; Dewar, "The Electronic Theory of Organic Chemistry," Clarendon
Press, Oxford, 1949, p. 212; Winstein and Trifan, J. Amer. Chem. Soc., 1949, 71, 2953; 1952, 74, 1147, 1154.
<sup>6</sup> Bartlett and Pöckel, J. Amer. Chem. Soc., 1938, 60, 1585; Hebrandson, Dickenson, jun., and Weinstein,</sup> *ibid.*, 1954,

change; and this in turn is lower than that involving the transfer of a chloride ion from  $HCl_2^-$  to the secondary centre of the cation to produce isobornyl chloride (rearrangement). The principle of microscopic reversibility requires that the transfer of a hydrogen ion from HCl to camphene to produce the XH<sup>+</sup>HCl<sub>2</sub><sup>-</sup> ion pair be rate-determining in the addition which produces camphene hydrochloride, while the chloride-ion transfer to the secondary centre of the cation must be rate-determining in the addition which produces isobornyl chloride. In the absence of free hydrogen chloride the uncatalysed reaction of camphene hydrochloride leads predominantly to elimination with little or no radiochlorine exchange or rearrangement. This change in the free-energy diagram for the partitioning of the intermediate is understandable in terms of the greater capacity of Cl<sup>-</sup> to abstract a proton from XH<sup>+</sup> in the XH<sup>+</sup>Cl<sup>-</sup> ion-pair than that of HCl<sub>2</sub><sup>-</sup> from XH<sup>+</sup> in the XH<sup>+</sup>HCl<sub>2</sub><sup>-</sup> ion pair.

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# Photo-induced Fries Rearrangements By J. C. Anderson and C. B. Reese (UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE)

BARTON and QUINKERT<sup>1</sup> showed recently that alkylated acetoxycyclohexadienones of type (I) usually underwent photochemical transformations in nucleophilic solvents, the bond joining the two oxygen-bearing carbon atoms being cleaved. The products were unsaturated carboxylic acids, esters, or amides depending on the nature of the solvent.



Catechol monoacetate (II) is the simplest aromatic analogue of (I); its hypothetical tautomeric ketoform may be represented by (I; R = H). When an absolute-alcoholic solution of catechol monoacetate was exposed in a stoppered quartz vessel at 30° to ultraviolet light, the infrared absorption spectrum of the products being examined at intervals, the intensity of the original ester-carbonyl band ( $\nu_{max}$ , in CHCl<sub>3</sub> at 1756 cm.<sup>-1</sup>) was found to decrease gradually whilst two new bands (1672, 1645 cm.-1) appeared. When the ester-carbonyl band had disappeared, the products were chromatographed on silica gel and identified, by comparison with authentic specimens, as catechol (46%), and 2,3- (III) (m.p. 98°; 22%) and 3,4-dihydroxyacetophenone (IV) (m.p. 122°; 18%).

The normal acid-catalysed Fries rearrangement of catechol acetates yields predominantly 3,4-dihydroxyacetophenone<sup>2</sup> (IV), whereas the photochemical rearrangement apparently favours the isomer (III). This could be of preparative value. That the isomer (III) might be an intermediate in the formation of (IV) is disproved by the observation that both isomers are stable under the experimental conditions.

This photo-induced Fries rearrangement may be general. Irradiation of ethanolic phenyl acetate, the simplest example possible, caused rearrangement at a rate comparable with that of catechol monoacetate, giving phenol, o- and p-hydroxyacetophenone, and certainly not more than a trace of the *meta*-isomer. Barton and Quinkert<sup>1</sup> obtained 3-hydroxy-2,4,6-trimethylphenyl acetate from the dienone (I; R = Me). That the former was photo-stable was possibly because only a *meta*-position was available for acetyl migration.

The mechanism of this rearrangement remains unestablished. Irradiation of phenol in ethanol containing ethyl acetate yielded no hydroxyacetophenones; thus ethyl acetate, formed by ester exchange, was apparently not the acylating agent. When an alcoholic solution of phenyl acetate and catechol was irradiated, only monohydroxyacetophenones were obtained. A similar experiment with phenol and catechol monoacetate yielded only dihydroxyacetophenones. Thus the rearrangement appears to be intramolecular.

We thank Professor Sir Alexander Todd, F.R.S., for his interest and encouragement. One of us (J.C.A.) is indebted to the D.S.I.R. for a maintenance grant.

(Received, March 26th, 1960.)

<sup>&</sup>lt;sup>1</sup> Barton and Quinkert, J., 1960, 1; Proc. Chem. Soc., 1958, 197.

<sup>&</sup>lt;sup>2</sup> Miller, Hartung, Rock, and Crossley, J. Amer. Chem. Soc., 1938, 60, 7.

#### The Effect of Oxygen and Hydrogen Peroxide on the Oxidising Action of Nitrous Acid

A. JOHNSON and A. P. LOCKETT

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WE report here a new mechanism of oxidation with nitrous acid in the presence of small amounts of peroxy-compounds. The substrate is attacked by hydroxyl radicals produced from nitrous acid *via* pernitrous acid by means of a chain reaction.

Oxidation reactions with nitrous acid have attracted attention from time to time, and recently Singer *et al.*<sup>1</sup> have shown that in mineral acid solutions below *ca.* 2.5N the oxidising entity is molecular nitrous acid. These workers used solutions which had been flushed with nitrogen in order to remove dissolved oxygen as far as possible, and they stated that the trace of oxygen which remained had no effect. On the other hand, Ainsworth and Johnson<sup>2</sup> observed that, in the oxidation of the disulphuric esters of quinols and of leuco-indigos by means of nitrous acid under conditions almost identical with those used by Singer *et al.*, the presence of residual oxygen led to a marked increase in the rate of consumption of both ester and nitrous acid.

We have repeated some of these experiments with formic acid and have shown that here too, the presence of even small traces of oxygen does lead to an increased rate of oxidation. Once the oxygen has been consumed the reaction slows down and the mechanism suggested by Singer *et al.* operates.

An extension of Ainsworth and Johnson's work, in which the ester (I) was oxidised with nitrous acid



in hydrochloric acid in the presence of varying amounts of oxygen, has revealed that the effect of oxygen is due to its reduction to either  $HO_2$  or hydrogen peroxide.<sup>3</sup> These peroxy-species react with the nitrous acid to produce pernitrous acid, and this then exists in the presence of a large excess of nitrous acid. Under these conditions a chain reaction is initiated in which the substrate (sulphuric ester, formic acid, etc.) is oxidised by hydroxyl radicals, and the chain is propagated by the reaction of nitrous acid with nitrogen dioxide to produce more pernitrous acid. Chain termination occurs by the combination of hydroxyl radical with nitrogen dioxide to produce nitric acid.

HO <sub>2</sub> • or H <sub>2</sub> O <sub>2</sub>			(1)
$HOONO + H_2O$			(2)
HO O NO + HO			(2a)
HO + ONO .			(3)
Oxidation products			(4)
HOONO + NO			(5)
•NO <sub>2</sub>			(6)
HNO3			(7)
	$\begin{array}{c} HO_{2} \cdot \text{ or } H_{2}O_{2} \\ HO \cdot O \cdot NO + H_{2}O \\ HO \cdot O \cdot NO + HO \cdot \\ HO \cdot + \cdot ONO \\ Oxidation products \\ HO \cdot O \cdot NO + NO \\ \cdot NO_{2} \\ HNO_{3} \\ \end{array}$	$\begin{array}{cccc} HO_{2} & \text{or} & H_{2}O_{2} & & . \\ HO & O & NO & + & H_{2}O & \\ HO & O & NO & + & HO & . \\ HO & + & ONO & . & . \\ Oxidation products & \\ HO & O & NO & + & NO & . \\ NO_{2} & . & . & . & . \\ HNO_{3} & . & . & . & . \end{array}$	$\begin{array}{cccc} HO_2 \cdot \text{ or } H_2O_2 & & & \\ HO \cdot O \cdot NO + H_2O & & \\ HO \cdot O \cdot NO + HO \cdot & & \\ HO \cdot + \cdot ONO & & \\ Oxidation products & \\ HO \cdot O \cdot NO + NO & & \\ HO O \cdot NO_2 & & & \\ HNO_3 & & & \\ \end{array}$

Reactions 2, 3, and 7 have been reported by Halfpenny and Robinson,<sup>4</sup> but since they used approximately equimolar quantities of hydrogen peroxide and nitrous acid they were not able to observe the propagation reaction (4).

In the oxidation of (I),  $HO_2$  and  $H_2O_2$  arise from reaction of oxygen with the quinol which is produced slowly from (I) by hydrolysis. With formic acid,  $HO_2$  could arise via the formate radical which Singer et al.<sup>1</sup> have shown to be an intermediate.

$$\begin{array}{l} H \cdot CO_2 H + HO \cdot NO \rightarrow H \cdot CO_2 \cdot + H_2O + NO \\ H \cdot CO_2 \cdot + O_2 \rightarrow CO_2 + HO_3 \cdot \end{array}$$

Clearly, with any substrate which is oxidised by a two-electron charge, peroxy-species capable of producing pernitrous acid from nitrous acid could arise *via* reaction of the intermediate free radical with oxygen, and thus lead to an enhanced rate of oxidation by the mechanism here proposed. Naturally, the same mechanism can be set in operation by the addition to nitrous acid-substrate solutions of hydrogen peroxide, instead of relying on its production from adventitious oxygen. Thus, the addition of hydrogen peroxide to solutions of nitrous acid and acrylonitrile (which do not otherwise interact) causes the rapid consumption of both compounds to an extent which far exceeds the amount of peroxide added.

One of us (A.P.L.) is indebted to Courtaulds' Educational and Scientific Trust Fund and to the Salters' Institute of Industrial Chemistry for scholarships. Some experiments with acrylonitrile were carried out by Mr. E. J. W. Smallridge.

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- <sup>1</sup> Longstaff and Singer, J., 1954, 2604; Singer and Vamplew, J., 1956, 3971.
- <sup>2</sup> Ainsworth and Johnson, J. Soc. Dyers and Colourists, 1955, 71, 592.
- <sup>3</sup> Johnson and Lockett, J. Soc. Dyers and Colourists, in the press.
- <sup>4</sup> Halfpenny and Robinson, J., 1952, 928, 939.

# The Role of Peroxides in Slow Combustion of Hydrocarbons

By J. CARTLIDGE and C. F. H. TIPPER

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KIRK and KNOX<sup>1</sup> presented evidence to show that the lifetime of ethyl and isopropyl hydroperoxides is too short ( $\sim$  few sec.) above 300°c for them to be the intermediates (lifetime  $\sim 1-2$  min.) responsible for degenerate branching during the slow combustion of ethane and propane. They conclude that these hydroperoxides are never formed under these conditions. We have oxidised propane in a flow system<sup>2</sup> at 327°C (ratio C<sub>3</sub>H<sub>8</sub>:O<sub>2</sub>, 2:1; residence time, 6 min.). Although about 1 ml. of product was condensed at - 78°c during 150 min., paper-chromatographic analysis<sup>3</sup> showed that peroxides were not present apart from very small amounts of hydrogen peroxide, addition compounds of hydrogen peroxide with aldehydes [i.e. RCH(OH)·O·OH and R·CH(OH)·O·O·CHR·OH], and peracetic acid, supporting the above conclusion.

However, the products from n-butane between 315° and 345° contained an appreciable amount (5-10%, which was approximately half the total peroxidic material present) of butyl hydroperoxide and various of its aldehyde addition compounds (e.g.  $C_4H_9$ ·O·O·CHR·OH). The rest of the peroxides consisted of hydrogen peroxide, free and combined with aldehyde, and traces of perpropionic acid. The oxidation of cyclohexane between 300° and 316° also gave appreciable yields of the monohydroperoxide

<sup>1</sup> Kirk and Knox, Proc. Chem. Soc., 1959, 384.

<sup>2</sup> Cartlidge and Tipper, Proc. Chem. Soc., 1959, 190.

- <sup>3</sup> Cartlidge and Tipper, Analyt. Chim. Acta, 1960, 22, 106.
- <sup>4</sup> Long and Todd, Proc. Chem. Soc., 1959, 328.

and its compounds with aldehydes, together with much smaller amounts of hydrogen peroxide, whereas from n-heptane at about 310° the main peroxidic product was a dihydroperoxyheptane (free and combined with aldehyde), as was indeed the case at lower temperatures also (cf. ref. 2). The amount of hydrogen peroxide formed above 300° was appreciable, in general agreement with the results of Long and Todd.<sup>4</sup>

It appears very probable from Kirk and Knox's results<sup>1</sup> that if hydroperoxides are formed during slow combustion they will cause chain-branching, since at least a proportion will decompose homogeneously giving radicals. It also seems likely that some homogeneous decomposition of hydroxyalkyl peroxides (i.e. R·O·O·CHR'·OH) will occur. Thus our results suggest that degenerate branching due to peroxides may well be important in many hydrocarbon-oxygen systems up to 350°. Of course, the reaction of oxygen with the free aldehyde present must also lead to branching, and the relative importance of the two types of intermediate in such systems will obviously depend on the hydrocarbon, the temperature, the condition of the vessel surface, and the fuel:oxygen ratio.

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in vacuo then yielded about 70% of bisperfluoro-

 $(CF_3)_2PCI + LiN_3 \rightarrow (CF_3)_2PN_3 + LiCI$ 

65.1; N, 19.7%; M, 211. C<sub>2</sub>F<sub>6</sub>N<sub>3</sub>P requires P, 14.7;

 $CF_3$ , 65.4; N, 19.9%; M, 211.0) solidifies in liquid

nitrogen to a glass. Vapour pressures of about 1 mm.

at  $-60^{\circ}$  and 57 mm. at 0° have been observed. The

infrared absorption spectrum has a strong sharp peak

at 4.7  $\mu$  typical of the azide group.<sup>3</sup> Absorption in

This azide (Found: P, 14.5; CF<sub>3</sub> as fluoroform,

methylphosphinic azide:

# The Preparation of a Polymeric Bisperfluoromethylphosphonitrile By G. TESI, C. P. HABER, and C. M. DOUGLAS

(U.S. NAVAL ORDNANCE LABORATORY, CORONA, CALIFORNIA)

THE capability of phosphonitrilic halides to polymerise to elastomeric materials led to replacement of the chlorine atoms by groups which might improve the thermal stability of the polymer. We have studied the synthesis of a material having the structure  $[(CF_3)_2 PN]_x.$ 

It is known that the reaction of halogenophosphines with alkali-metal azides affords polymeric phosphonitriles.1 When chlorobistrifluoromethylphosphine<sup>2</sup> was treated with lithium azide at 0° for 24 hours, a smooth reaction took place and distillation

 <sup>&</sup>lt;sup>1</sup> Herring, Chem. and Ind., in the press.
 <sup>2</sup> Bennett, Emeléus, and Haszeldine, J., 1953, 1565.
 <sup>3</sup> Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., Ltd., 1958, p. 274.

the region  $8.0-9.0 \mu$  is typical of the C-F stretching vibration for the compounds (CF<sub>3</sub>)<sub>2</sub>PX.<sup>2</sup> Acidtreatment of the residue from alkaline hydrolysis of the azide liberated hydrazoic acid which was identified by its infrared spectrum<sup>4</sup> in CCl<sub>4</sub>. Although reasonably stable at 0°, it decomposes slowly at room temperature. However, on several occasions and without apparent reasons, violent explosions occurred, even at liquid-nitrogen temperature.

Slow decomposition of the azide at 50-60°/37 mm. yielded the calculated amount of nitrogen:

$$n(CF_3)_2 PN_3 \xrightarrow{d} [(CF_3)_2 PN]_n + nN_2$$

The white, waxy material obtained had m.p. 90-94°

(Found: C, 12.7; N, 7.5; P, 16.1; F, 60.0. C<sub>2</sub>F<sub>6</sub>NP requires C, 13.1; N, 7.6; P, 16.9; F, 62.3%) was insoluble in all the usual organic solvents. X-Ray analysis by diffractometer showed a completely amorphous pattern. Refluxing this material with sulphuric, nitric, or perchloric acid did not appear to affect the composition. Treatment with 10% sodium hydroxide solution resulted in partial hydrolysis, with liberation of one mole of fluoroform per (CF<sub>3</sub>)<sub>2</sub>PN unit.

This work was supported by the Bureau of Weapons, Department of the Navy, through the Foundational Research Programme.

(Received, April 20th, 1960.)

<sup>4</sup> Buswell, McMillan, Rodebush, and Wall, J. Amer. Chem. Soc., 1939, 61, 2809.

# The Microwave Spectrum and Structure of Silyl Isothiocyanate

# By D. R. JENKINS, R. KEWLEY, and T. M. SUGDEN (DEPARTMENT OF PHYSICAL CHEMISTRY, THE UNIVERSITY, CAMBRIDGE)

THE microwave spectra of silvl isothiocyanate and its fully deuterated form have been investigated in the regions 18,000-26,000 and 35,000-37,000 Mc./sec. Examination of the rotational transitions  $J = 6 \leftarrow 5$ ,  $7 \leftarrow 6, 8 \leftarrow 7$ , and  $12 \leftarrow 11$  for SiH<sub>3</sub>·NCS, and J = $8 \leftarrow 7$  and  $9 \leftarrow 8$  for SiD<sub>3</sub> NCS shows that the spectra derive from symmetric top molecules, in agreement with the infrared data.<sup>1,2</sup>

For SiH<sub>3</sub>·NCS, lines due to the most abundant molecule <sup>28</sup>SiH<sub>3</sub>.<sup>14</sup>N<sup>12</sup>C<sup>32</sup>S and those containing <sup>29</sup>Si, <sup>30</sup>Si, and <sup>34</sup>S were observed, and for the deuterated compound, those due to the two isotopic forms, <sup>28</sup>SiD<sub>3</sub>.<sup>14</sup>N<sup>12</sup>C<sup>32</sup>S and <sup>30</sup>SiD<sub>3</sub>.<sup>14</sup>N<sup>12</sup>C<sup>32</sup>S. The results, in conjunction with the Si-H distance and H-Si-H angle estimated from the infrared spectrum of  $SiH_3$  NCS,<sup>2</sup> give the following structure:

 $Si-H = 1.48 \pm 0.01 \text{ Å}$  $Si-S = 4.485 \pm 0.003 \text{ Å}$  $\angle$  H-Si-N = 108° 30′ ±1°  $Si-N = 1.729 \pm 0.020 \text{ Å}$ C-S = 1.56 Å (assumed)  $N-C = 1.196 \pm 0.020 \text{ Å}$ (Si-N-C-S linear)

The observed  $B_o$  for  ${}^{28}\text{SiH}_3.{}^{14}\text{N}{}^{12}\text{C}{}^{32}\text{S}$  of 1515.98 Mc./sec. excludes the possibility of this compound's having the structure SiH<sub>3</sub> SCN since the reasonable parameters, Si–S = 2.21 Å, S–C = 1.61 Å, C–N = 1.21 Å, Si-H = 1.48 Å,  $\angle$  H-Si-H =  $110^{\circ}$  30', give  $B_e = 1671$  Mc./sec. for a molecule with linear Si-S-C-N and an even larger value for a molecule bent at the sulphur atom.

A group of lines in the  $J = 8 \leftarrow 7$  transition, based on  $B_v = 1526.34$  Mc./sec. (normal SiH<sub>3</sub>·NCS) showed a pattern which is due to an excited degenerate bending vibration. Its intensity at  $-80^{\circ}$  was slightly greater than that of the ground vibrational state transition, thus indicating a bending frequency of well below 100 cm.<sup>-1</sup>. This agrees with the fact that only one of the two expected skeletal bending frequencies has been observed in the Raman spectrum.<sup>3</sup>

It is very interesting to contrast the structure of SiH<sub>3</sub>·NCS with that of CH<sub>3</sub>·NCS (in which  $\angle$  CNC'  $= 142^{\circ 4}$ ) and also to note the difference between the planar Si<sub>3</sub>N skeleton<sup>5</sup> in (SiH<sub>3</sub>)<sub>3</sub>N and the pyramidal arrangement in (CH<sub>3</sub>)<sub>3</sub>N. These facts indicate interaction of the lone-pair electrons of the nitrogen with the silicon 3*d*-orbitals.

The samples used, made by treating SiH<sub>3</sub>I or SiD<sub>3</sub>I with silver thiocyanate,<sup>6</sup> were kindly supplied by Dr. E. A. V. Ebsworth of the Department of Organic and Inorganic Chemistry, University of Cambridge. This method produces the iso-compound, whereas the reaction between iodosilane and silver cyanide gives the normal cyanide SiH<sub>3</sub>·CN.<sup>7</sup>

(Received, April 5th, 1960.)

<sup>&</sup>lt;sup>1</sup> MacDiarmid and Maddock, J. Inorg. Nuclear Chem., 1955, 1, 411.

Mould and Wilkinson, unpublished work.

Woodward and Taylor, unpublished work

<sup>4</sup> Beard and Dailey, J. Amer. Chem. Soc., 1949, 71, 929.

<sup>&</sup>lt;sup>5</sup> Hedberg, J. Amer. Chem. Soc., 1955, 77, 6491.

 <sup>&</sup>lt;sup>6</sup> MacDiarmid, J. Inorg. Nuclear Chem., 1956, 2, 88.
 <sup>7</sup> Sheridan and Turner, Proc. Chem. Soc., 1960, 21.

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#### Synthesis of $(\pm)$ -Vernolic, Linoleic, and $\gamma$ -Linolenic Acid

By J. M. OSBOND

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VERNOLIC ACID (cis-12,13-epoxy-cis-octadec-9-enoic acid) (X), the principal seed-oil acid from Vernonia anthelmintica1,2 has been synthesised. cis-Oct-2-en-1ol (I), prepared by partial reduction of oct-2-yn-1-ol\* was brominated by phosphorus tribromide in ether under conditions controlled to avoid stereomutation, giving the cis-bromide (II) containing a trace of *trans*-CH=CH ( $\nu_{max}$ , 965 cm.<sup>-1</sup>).



12,13-dihydroxystearic acid<sup>7,8</sup> (m.p. 96–97°), and  
(b) treatment with peracetic acid to give the di-  
epoxide<sup>†</sup> (XIV) [
$$\nu_{max}$$
. 775, 815, 830 cm.<sup>-1</sup> (epoxide<sup>4</sup>)]  
identical (mixed m.p.; infrared spectrum) with an  
authentic specimen<sup>6</sup> (m.p. 78°) obtained from  
linoleic acid (XII). In a similar way the C<sub>19</sub> analogue  
(XI) was prepared by using undec-10-ynoic acid  
(II  $\rightarrow$  VI  $\rightarrow$  IX  $\rightarrow$  XI). Reduction (PtO<sub>2</sub>) of the

CH<sub>3</sub> [CH<sub>2</sub>]<sub>4</sub>·[CH<sup>2</sup>-CH·CH<sub>2</sub>]<sub>x</sub> C=C·[CH<sub>2</sub>]<sub>3</sub>·CO<sub>2</sub>H  
V; 
$$x = 1$$
;  $y = 7$ ; m.p. 14—16°  
VI;  $x = 1$ ;  $y = 8$ ; m.p. 8—9°  
VII;  $x = 2$ ;  $y = 4$ ; b.p. 162°/0.02 mm.

$$CH_{3} \cdot [CH_{2}]_{4} \cdot CH - CH \cdot CH_{2} \cdot CH = CH \cdot [CH_{2}]_{3} \cdot CO_{2}H$$
  
X; y = 7; m.p. 35-36°  
XI; y = 8; m.p. 40-41°

$$CH_{3} \cdot [CH_{2}]_{4} \cdot [CH = CH \cdot CH_{2}]_{x} \cdot [CH_{2}]_{y} \cdot CO_{2}H$$

$$XII; x = 2; y = 6$$

$$XIII; x = 3; y = 3$$

$$CH_{3} \cdot [CH_{2}]_{4} \cdot$$

The di-Grignard reagent from dec-9-ynoic acid and the bromide (II) were condensed at 20° in tetrahydrofuran by means of a cuprous salt,<sup>3</sup> to give an acid (V) which was converted into the cis-epoxide<sup>†</sup> (VIII) by peracetic acid [ $\nu_{max}$ . (in CS<sub>2</sub>) 775, 810 cm.<sup>-1</sup> (cis-epoxide<sup>4</sup>), 1707 cm.<sup>-1</sup> (C=O, acid)]. Partial reduction\* readily gave  $(\pm)$ -vernolic acid<sup>†</sup> (X), m.p.  $35-36^{\circ}$  [ $\nu_{max}$ . 775, 820 (*cis*-epoxide<sup>4</sup>), 1650, 3040 (CH=CH), no *trans*-CH=CH at 965, 1707 cm.<sup>-1</sup> (C=O), acid)]. Since the natural isomer<sup>2</sup> has m.p. 25–28° and the  $(\pm)$ -form, m.p. 18–19° (partial synthesis from linoleic acid<sup>5,6</sup>) we proved the structure of the product (X) by (a) conversion<sup>7</sup> into  $(\pm)$ -threo-12,13-dihydroxyoctadec-9-enoic acid1,7 (m.p. 52–53°), followed by reduction to  $(\pm)$ -threo-

– ĊH·CH₂]₂·[CH₂]₀·CO₂H XIV; m.p. 76·5—77·5° enynoic acid (V) gave stearic acid (m.p. 69.5-70°;

0

90% yield) and partial reduction\* gave linoleic acid (XII). Similarly, partial reduction\* of undeca-2,5diyn-1-ol gave the alcohol (III) and thence the bromide (IV) (some trans-isomer formed). Condensation with hept-6-ynoic acid afforded a product (VII) which on partial reduction\* gave  $\gamma$ -linolenic acid<sup>3</sup> (XIII); the acids (XII) and (XIII) were characterised by formation of the 9,10,12,13-tetra- and 6,7,9,10,12,13-hexa-bromostearic acids (m.p. 114-115.5 and 201.5-202° respectively) identical with those obtained previously.3

I thank Dr. A. Wagland for the infrared spectra. (Received, April 13th, 1960.)

- \* Lindlar's catalyst (Lindlar, Helv. Chim. Acta, 1952, 35, 446) in light petroleum-quinoline was used.
- † Oxiran-oxygen estimated by method of Durbetaki (Analyt. Chem., 1956, 28, 200).
- <sup>1</sup> Gunstone, J., 1954, 1611. <sup>2</sup> Smith, Koch, and Wolff, J. Amer. Oil Chemists' Soc., 1959, **36**, 219. <sup>3</sup> Cf, Osbond and Wickens, Chem. and Ind., 1959, 1288.
- <sup>4</sup> Shreve, Heether, Knight, and Swern, Analyt. Chem., 1951, 23, 277; Patterson, ibid., 1954, 26, 823.
   <sup>5</sup> Pigulevskii and Naidenova, J. Gen. Chem. (U.S.S.R.), 1958, 28, 234.
- <sup>6</sup> Swern and Dickel, J. Amer. Chem. Soc., 1954, 76, 1957. <sup>7</sup> Bharucha and Gunstone, J., 1956, 1611.
- <sup>8</sup> Huber, J. Amer. Chem. Soc., 1951, 73, 2730.

#### The Solvent Extraction of Solvated Ion-Pairs: A Theoretical Approach

By H. IRVING and D. C. LEWIS

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THE partition of metal halide acido-complexes between aqueous halogen acids and binary mixtures of organic solvents is receiving considerable attention. When the two organic solvents are very similar in character (e.g., two higher aliphatic ketones) the distribution ratio, q, may be a simple linear function of their mole fractions in the mixture.<sup>1</sup> With dissimilar solvents the problem is less straightforward and attempts to correlate the distribution ratio with the dielectric constant,  $\epsilon$ , and with the donor power of the solvents (as measured by Gordy and Stanford's index<sup>2</sup>) are not particularly successful. This is illustrated in Fig. 1, for some new data<sup>3</sup> for the

energy of an ion is regarded as made up of three terms: (i) the electrostatic energy of the ion considered as a charge in a medium of dielectric constant  $\epsilon$ ; (ii) the energy of its interaction with its solvation sheaths; and (iii) the work done against cohesive forces in forming a cavity in the solvent to accommodate the ion. We next consider the energy change due to the formation of an ion-pair from two solvated univalent ions of opposite charge with particular reference to the situation where the anion is relatively little solvated. Finally, we relate the partition coefficient of the solvated ion-pair to the difference between its solvation energies in the aqueous



FIG. 1. The distribution ratio of indium (8  $\times$  10<sup>-5</sup>M) between 4N-HCl and 1:1 molar mixtures of hexone with various diluents as a function of  $1/\epsilon$  and of  $\Delta \mu$ . Determined with <sup>114</sup>In.

Diluents: I, cyclohexane; II, dibutyl phthalate; III, chlorobenzene; IV, o-dichlorobenzene; V, methyl benzoate; VI, o-nitrotoluene; VII, nitrobenzene; VIII, benzonitrile; IX, benzaldehyde; X, butyraldehyde; XI, acetophenone; XII, chloroform.

partition of indium between 4N-hydrochloric acid and 1:1 molar % mixtures of hexone (isobutyl methyl ketone) with a variety of other organic solvents termed diluents below.

In a theoretical approach to this problem we consider a model system in which the total solvation

- <sup>1</sup> Irving and Rossotti, *J.*, 1956, 2475. <sup>2</sup> Gordy and Stanford, *J. Chem. Phys.*, 1941, **9**, 204.
- <sup>3</sup> Irving and Lewis, unpublished results.

medium and in the mixture of organic solvents.

To evaluate these solvation energies we assume that the Born charging equation can be used in calculating the electrostatic contribution (i), that the basicity of the organic solvent can be measured in terms of the shift,  $\Delta \mu$ , which it produces in the infra-

red absorption band of  $CH_3$ ·OD (cf. Gordy and Stanford<sup>2</sup>), and that the internal pressure (P) of a solvent can be evaluated from its latent heat of vapourisation and its molar volume.

When applied to the partition of solvated metal halide acido-complexes between an aqueous phase of given composition and mixtures, m, of one particular organic solvent, h, with a variety of organic diluents, d, these considerations lead to an equation of the form (1), where  $k_1$  and  $k_2$  are constants for a given temperature,  $N_d$  is the mole fraction of diluent in the mixture, A is a constant for the organic solvent h, and for a given partitionable solute E, B, and V are fixed parameters which can be evaluated from their expressions as functions of, *e.g.*, dielectric constant and the radii of solvated cation and anion. The values of  $\epsilon$ ,  $\Delta \mu$ , and P for the pure organic solvent (hexone in the case below), for pure diluents, or for

$$\log q = k_1 - k_2 \{ A + (E/\epsilon_m) + N_d [B(\Delta \mu_h - \Delta \mu_d) + V(P_d - P_h)] \} \quad . \quad . \quad . \quad (1)$$



FIG. 2. The data for the distribution of indium employed for Fig. 1, plotted against, as abscissa:  $\{8.45 + (95.4/\epsilon_m) + 0.5[91.7(\Delta \mu_h - \Delta \mu_d) + 293(P_d - P_b)]\}$ 



FIG. 3. The distribution ratio of indium (8 × 10<sup>-5</sup>M) between 4N-HCl and mixtures of hexone and diluents of composition ranging from 0 to 100 mole %, plotted against:  $\{8.45 + (95.4/\epsilon_m) + N_d[91.7(\Delta\mu_h - \Delta\mu_d) + 293(P_d - P_h)]\}$ 

mixtures of solvent and diluent are distinguished by the subscripts h, d, and m.

Fig. 2 shows the distribution data already used in Fig. 1, replotted against the variable term on the right-hand side of equation (1) in which reasonable calculated values for E, B, and V have been inserted. The fit is now unexpectedly good. That the validity of equation (1) is not limited to the rather arbitrarily chosen equimolar mixtures of hexone and diluents referred to in Figs. 1 and 2 is shown in Fig. 3, which presents typical data for mixed solvents for which the

<sup>4</sup> Goble and Maddock, Trans. Faraday Soc., 1959, 55, 591.

<sup>5</sup> Irving and Edgington, Proc. Chem. Soc., 1959, 360.

composition was varied over the whole range  $0.0 \leq N_{\rm d} \leq 1.0$ .

In certain systems the value of q for an intermediate composition of the mixture exceeds the value for either pure component.4,5 Such synergic effects, which have a variety of causes, are not covered by the above treatment which includes the simplifying assumption that the dielectric constant,  $\epsilon_{\rm m}$ , of the mixed solvent is a linear function of the mole fractions and dielectric constants of the pure components. (Received, April 12th, 1960.)

# Transfer of a Diazo-group By D. G. FARNUM and P. YATES (DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY)

DURING studies of there action of diazo-ketones with bases,<sup>1</sup> we have obtained evidence of transfer of the diazo-group.

An ethereal solution of  $\alpha$ -diazoacetophenone (I) was added to a suspension of methyl sodiophenylacetate<sup>2</sup> (II) in boiling ether and the mixture was boiled under reflux for two hours. The portion of the product insoluble in aqueous 2% potassium hydroxide was resolved into an oil and crystalline 3-benzoyl-4-phenylpyrazole<sup>1</sup> (IV) and dimethyl  $(\pm)$ - $\alpha,\beta$ -diphenylsuccinate<sup>3\*</sup> (V): the oil was shown to contain methyl  $\alpha$ -diazo- $\alpha$ -phenylacetate (III) in the

to the characteristic bands of an authentic sample<sup>4</sup> of the ester (III) [but not with those of the starting material (I) which are at 4.78 and 6.17  $\mu$ ]. Further, treatment of the oil with p-nitrobenzoic acid and copper powder in boiling chloroform gave methyl  $\alpha$ -p-nitrobenzoyloxy- $\alpha$ -phenylacetate.<sup>5</sup>

From the base-soluble fraction were isolated a further quantity of the pyrazole (IV) as well as 3-benzoyl-4-hydroxy-5-phenylpyrazole<sup>1</sup> (VI).

The formation of the several products can readily be rationalised in terms of reversible terminal attack<sup>1</sup> on the diazo-ketone, as shown in the chart.

$$\begin{array}{cccc} \mathsf{Ph} \cdot \mathsf{CO} \cdot \mathsf{CHN}_2 &+& \mathsf{Ph} \cdot \bar{\mathsf{CH}} \cdot \mathsf{CO}_2 \mathsf{Me} \rightleftharpoons \mathsf{Ph} \cdot \mathsf{CO} \cdot \bar{\mathsf{CH}} \cdot \mathsf{N} = \mathsf{N} \cdot \mathsf{CHPh} \cdot \mathsf{CO}_2 \mathsf{Me} \\ (I) & (II) & (II) & // & \\ (I) & (II) & // & \\ \end{array}$$

$$\begin{array}{cccc} \mathsf{Ph} \cdot \mathsf{CO}_2 \mathsf{CO}_2 \mathsf{Me} &+& \mathsf{Ph} \cdot \mathsf{CO} \cdot \mathsf{CH}_2^- \rightleftharpoons \mathsf{Ph} \cdot \mathsf{CO} \cdot \mathsf{CH}_2 \cdot \mathsf{N} = \mathsf{N} \cdot \bar{\mathsf{CPh}} \cdot \mathsf{CO}_2 \mathsf{Me} & & \mathsf{HO}_{\begin{array}{c} \mathsf{Ph}} & \mathsf{Ph}_{\begin{array}{c} \mathsf$$

following manner. Its infrared spectrum (in  $CH_2Cl_2$ ) possessed, in addition to bands attributable to methyl phenylacetate, a sharp band at 4.82  $\mu$  and a shoulder at 5.9  $\mu$ ; these bands correspond in position

This work was carried out during the tenure of a United States Public Health Predoctoral Fellowship by D.G.F.

(Received, April 4th, 1960.)

<sup>3</sup> Brook, Cohen, and Wright, J. Org. Chem., 1953, 18, 447.
 <sup>4</sup> Curtius and Müller, Ber., 1904, 37, 1261.
 <sup>5</sup> Meiser, U.S.P. 2,426,276/1947; cf. Chem. Abs., 1948, 42, 222.

<sup>\*</sup> We are indebted to Professor George F. Wright for a sample of  $(\pm)$ - $\alpha$ ,  $\beta$ -diphenylsuccinic acid.

<sup>&</sup>lt;sup>1</sup> Yates and Shapiro, J. Amer. Chem. Soc., 1959, **81**, 212; Yates and Farnum, unpublished work. <sup>2</sup> Shivers, Dillon, and Hauser, J. Amer. Chem. Soc., 1947, **69**, 119.

# Isotactic Copolymers of Styrene and 4-Methylpent-1-ene By I. H. ANDERSON, G. M. BURNETT, and P. J. T. TAIT (CHEMISTRY DEPARTMENT, UNIVERSITY OF ABERDEEN, OLD ABERDEEN)

THE stereospecific polymerisation of styrene by means of Ziegler-Natta catalysts has been reported by several workers. Polystyrene produced by the catalytic system  $\alpha$ -TiCl<sub>3</sub>-AlEt<sub>3</sub> is more than 90% isotactic.14-Methylpent-1-ene can also be polymerised by the same catalyst system to give predominantly crystalline polymer.<sup>2</sup> This catalyst system has now been used to polymerise a mixture of styrene and 4-methylpent-1-ene.

The monomers and solvent were carefully purified, outgassed, and distilled into a vessel where they were mixed with the catalyst system. The polymerisation course was then followed dilatometrically at 50°. The resulting polymer was isolated by precipitation with a mixture of methanol and hydrochloric acid.

The solvent used has a pronounced effect on the rate of polymerisation. In n-heptane the rate of polymerisation is extremely small, whereas with toluene as solvent the rate increases five-fold.

The Table compares the solubilities of the polymerisation product with those of the homopolymers prepared with the same catalyst system. Since it is



- A, Crystalline isotactic polystyrene.
- B, Crystalline isotactic poly-(4-methylpent-1-ene).
- C, Physical mixture of A and B.

- D, Poly-(4-methylpent-1-ene), ether-soluble fraction.
- E, Crude copolymerisation product.
- F, Copolymerisation product, ether-soluble fraction.
- <sup>1</sup> Burnett and Tait, Polymer, in the press.
- <sup>2</sup> Natta et al., Atti Accad. Naz Lincei, Rend. Sci., fis. mat. nat., 1955, 29, 397.

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well known that both atactic and isotactic polystyrene of relatively low molecular weight are insoluble in cold hexane, it is significant that polymer containing some 30% of styrene dissolves in this solvent. This seems to indicate that the ether-soluble fraction contains some copolymer. same values of  $2\theta$ , and for this reason it is impossible to determine whether or not the polystyrene present in the copolymer shows its normal diffraction pattern, since masking would occur because of the greater crystallinity of the poly-(4-methylpent-1-ene). There is, however, some slight evidence that the crystalline

	Extract with cold ether		Extract with hot heptane		Extract with cold hexane	
	% soluble	% styrene	% soluble	% styrene	% soluble	% styrene
Polystyrene			10		0	
Poly-(4-methylpent-1-ene)	30		100		100	
Crude product	79	39	89	32		
Ether-soluble					95	30

The X-ray diffraction patterns of these polymers are shown in the Figure. The most important feature of these patterns is the partial crystallinity exhibited by the ether-soluble fraction (F) of the copolymerisation as opposed to the amorphous character shown by a similar ether-soluble fraction (D) of poly-(4-methylpent-1-ene).

The main peaks in the diffraction patterns of crystalline isotactic polystyrene and crystalline isotactic poly-(4-methylpent-1-ene) occur at about the isotactic polystyrene peak at  $2\theta = 8.10^{\circ}$  may be present.

Since the repeating distances of crystalline polystyrene (6.65 Å) and crystalline poly-(4-methylpent-1-ene) (13.85 Å) are very different it is unlikely that more than 30% of styrene could be incorporated in the polyolefin chain in a random manner without markedly reducing the ultimate crystallinity of the product. A more probable explanation is that the polymer consists of blocks of styrene and olefin units. (*Received, April 4th*, 1960.)

## **NEWS AND ANNOUNCEMENTS**

Editorial Office: Change of Address.—The Editorial Office of the Chemical Society has moved to 38 York Terrace, Regent's Park, London, N.W.1 (Telephone: WELbeck 1707). Correspondence for the Editors will be forwarded if sent to Burlington House or 9/10 Savile Row, but telephone calls must be to the new number.

Library.—From July 16th until September 30th, 1960, the Library will close at 5 p.m. instead of at 7.30 p.m. The Library will not be open on August 1st and 2nd.

**Election of New Fellows.**—428 Candidates, whose names were published in *Proceedings* for March and April, have been elected to the Fellowship.

**British Association.**—The preliminary programme for the Annual Meeting of the British Association, to be held at Cardiff on August 31st—September 7th, 1960, is now available. Copies can be obtained from the Secretary, British Association for the Advancement of Science, 18 Adam Street, Adelphi, London, W.C.2. The full programme, giving detailed arrangements for the meeting, will be published early in August, and will be sent only to those who have intimated their intention to attend the meeting. The preliminary programme includes details of travel arrangements and accommodation, and early application is advised.

International Symposium on Inorganic Polymers.— A meeting sponsored by The Chemical Society will be held at the University of Nottingham on July 18th—21st, 1961. A fuller announcement, indicating the scope of the symposium, and giving details of the principal speakers, etc., will be issued in October next. This will be published in *Proceedings of The Chemical Society*, and copies will also be sent to those who apply before October 1st, 1960 to the General Secretary, The Chemical Society, Burlington House, London, W.1.

The Royal Society.—To mark the Tercentenary Celebrations of The Royal Society, the University of Oxford is to confer the Honorary Degree of Doctor of Science on July 21st on five scientists of international repute. These include two Honorary Fellows of The Chemical Society:

*Professor Nikolai Semenov*, Director of the Institute of Chemical Physics of the U.S.S.R. Academy of Sciences, who is distinguished for his work on chemical kinetics and the mechanisms of chain reactions.

Dr. E. W. R. Steacie, F.R.S., President of the

National Research Council, Ottawa, distinguished for his work in the mechanism of chemical reactions and the function of free radicals.

New Chair of Biochemistry in Dublin.—A decree establishing a Chair of Biochemistry at Trinity College, Dublin has been approved, and the University Council will proceed to a nomination. In 1934 the late Dr. W. R. Fearon was appointed to a Chair of Biochemistry created "for the present holder only". The new Chair will be subject to the usual conditions of tenure governing Class A professorships.

Awards of the Meldola Medal for 1959.—The Meldola Medal, which is the gift of the Society of Maccabaeans, is normally awarded annually, the award for a particular year being made to the chemist who, being a British subject and under 30 years of age on December 31st in that year, shows the most promise as indicated by his or her published work. Awards are made by the Council of the Royal Institute of Chemistry, with the concurrence of the Society of Maccabaeans, on the recommendation of a specially appointed advisory committee.

Since the Medal was first instituted in 1921 awards have been made every year, except for the war years 1942—1945, inclusive, when they were suspended, and for 1934 and 1958, when it was concluded that no candidate had produced evidence of original work of the exceptional quality required. On the other hand, two awards were made for each of the years 1936, 1946, 1951, and 1952, when there were two candidates adjudged to be of equal merit in diverse fields of work. For the same reason it has been decided to make two awards of the Meldola Medal for 1959. The recipients will be:

John Ivan George Cadogan, for his work in the field of organic chemistry, with special reference to reactions of free radicals in solution and to reactions of organophosphorus compounds.

Thomas Cudworth Waddington, for his work in the fields of physical and inorganic chemistry, with special reference to thermochemistry and reactivity of azides; photoconductivity of anthracene; lattice energies and infrared spectra of inorganic salts; and liquid hydrogen chloride as an ionising solvent.

**Ciba Fellowships.**—The Ciba Fellowship Trust has awarded Fellowships for the academic year 1960—61 to:

Dr. V. P. Arya, Banaras University, London University and the Polytechnic, Zurich, to study in Stockholm (Natural Products Chemistry).

Dr. K. Jones, Sheffield University, to study at Heidelberg University (Organic Chemistry).

Miss P. M. Bryant, Oxford University, to study at Basle (Organic Chemistry).

*Mr. J. R. Miller*, Cambridge University, to study at Munich (Inorganic Chemistry).

Van 't Hoff Fund.—The Committee of the Van 't Hoff Fund for the endowment of investigations in the field of pure and applied chemistry invites applications for grants from the fund.

The amount available for next year is about 1,500 Dutch guilders. Applications should be sent by registered post to Het Bestuur der Kon. Ned. Akademie van Wetenschappen, bestemd voor de Commissie van het "Van 't Hoff Fonds," Trippenhuis, Kloveniersburgwal 29, Amsterdam, before December 1st, 1960. The purpose for which the grant is required, the reasons for the application, and the amount desired must be stated.

Grants from the Fund for 1960 were awarded to *Professor H. O. Huisman* (Amsterdam), *Dr. M. Sy* (Maisons-Alfort, France), and *Dr. K. Kovacs* and *Dr. T. Vajda* (Budapest).

**Deaths.**—We regret to announce the deaths of the following: Mr. J. Allen (14.5.60), of Southwold, and Mr. E. J. Boake (17.3.60), of Messrs. A. Boake, Roberts & Co. Ltd.

**Personal.**—*Dr. C. C. Addison*, at present Reader in the Department of Chemistry, the University of Nottingham, has been elected Professor of Inorganic Chemistry as from October 1st, 1960.

Dr. Barbara Auret has been appointed Superintendent of Laboratories in the Department of Chemistry in the Queen's University of Belfast.

Professor G. M. Badger has been elected Dean of the Faculty of Science for 1960 in the University of Adelaide, Australia.

Dr. J. Bell, Manager of the I.C.I. Nobel Division Silicones Department for the last three years, has been appointed to the Board of the Division in succession to Mr. F. B. Wrightson, Engineering and Technical Director, who retired on April 30th.

The posthumous award of the Diploma of Appreciation of the Society of Dyers and Colourists has been made to the late *Dr. Abraham Burawoy* in recognition of the valuable contributions made by him in those branches of fundamental and synthetic chemistry which affect specially the chemistry of colouring matters.

Mr. S. H. Cakebread has taken up an appointment as Chief Research Chemist with Rolls Confectionery Ltd., a division of J. Lyons & Co. Ltd.

Dr. R. D. Chambers has been appointed Lecturer in Chemistry in the Durham Colleges.

Mr. C. G. Childs, Technical Manager of Bowmans Chemicals Ltd., has been appointed a Director.

Dr. C. J. T. Cronshaw has been awarded the Perkin Medal of the Society of Dyers and Colourists.

Dr. H. J. T. Ellingham, Secretary and Registrar of The Royal Institute of Chemistry, was admitted to Honorary Associateship of the Birmingham College of Advanced Technology on April 30th. Mr. D. R. Fellows has returned to the Standard Telecommunications Laboratories, Harlow, after spending a year with the sister company in Germany.

*Mr. V. Gallafent* has been elected a Vice-President of the Royal Photographic Society of Great Britain.

Dr. A. Goosen and Mr. P. Jeffs (formerly of Imperial Chemical Industries Limited, Akers Laboratory) have been appointed to Lectureships in Organic Chemistry in the University of Natal, Pietermaritzburg, South Africa.

Dr. M. L. H. Green has been appointed a University Demonstrator in the Department of Organic and Inorganic Chemistry in the University of Cambridge, with a tenure of three years from October 1st next.

Mr. N. Hamer and Mr. J. W. Reidy have been awarded Silver Medals of the Society of Dyers and Colourists.

Dr. D. M. Hirst has been appointed Lecturer in Geochemistry in the Durham Colleges.

Mr. N. A. Iliff has succeeded Mr. L. H. Williams as Managing Director of Shell Chemical Co. Ltd.

Mr. F. A. Jackman has been elected President of the National Benzole and Allied Products Association.

Dr. Leonard Keay, Visiting Lecturer in Biochemistry at the Massachusetts Institute of Technology, and former Research Fellow of the Salters' Institute of Industrial Chemistry, has been appointed research biochemist with the Research and Engineering Division, Monsanto Chemical Company, Dayton, 7, Ohio, U.S.A.

The University of Sheffield has appointed Dr. S. F. A. Kettle as a lecturer in Chemistry and Dr. K. R. Jennings as an assistant lecturer. Dr. P. G. Perkins has been appointed a lecturer in Inorganic Chemistry.

Dr. W. Klyne, Reader of Biochemistry at the Postgraduate Medical School of London, has been appointed to the University Chair of Chemistry tenable at Westfield College.

*Professor L. le Roux*, of the Department of Physical Chemistry, Pretoria University, has been appointed Chief Chemist, South African Atomic Energy Board, Pretoria, and will spend the next eighteen months in the U.S.A. and Canada, and then six months in England.

Dr. P. R. Lewis has been elected to a Fellowship of Corpus Christi College, Cambridge.

Dame Kathleen Lonsdale, Professor of Chemistry and Head of the Department of Crystallography, University College, London, is among those who are to be admitted to the Honorary Degree of D.Sc. of the University of Wales at Cardiff on September 5th, during meetings of the British Association.

Mr. A. W. Marsden, until recently organising secretary at the secretariat offices of the XV International Dairy Congress in London, has left the dairy industry after more than ten years' service to international dairying. He has been appointed organising secretary of the Second World Congress of Man-Made Fibres, which will take place in London in 1962.

Dr. S. M. Nelson has been appointed to a Lectureship in Organic Chemistry in the Queen's University of Belfast.

Miss Mamie Olliver, lately Chief Chemist of Chivers & Sons Ltd., has been appointed Chief Research Chemist of the Connaught Food Products Ltd. (comprising Chivers & Sons Ltd., Wm. P. Hartley Ltd., and Wm. Moorhouse & Sons Ltd.) Section of the Schweppes Research Laboratories, Hendon.

Dr. M. W. Partridge, at present Lord Trent Reader in Pharmaceutical Chemistry, the University of Nottingham, has been elected to the Lord Trent Chair in the same subject as from October 1st, 1960.

*Mr. S. J. Pentecost* has been awarded a Long Service Diploma of the Society of Dyers and Colourists.

*Professor V. Pretorius*, Senior Lecturer, has been appointed to the Chair in Physical Chemistry, University of Pretoria.

Mr. Ralph S. Robinson has resigned from his position with Bate Chemical Corporation, Toronto, to take over full responsibility as Technical Director over all Canadian operations of Reichhold Chemicals Ltd. and its associates.

Dr. Mario Scalera, assistant to the General Manager of Cyanamid's Central Research Division, has been elected a Vice-President of the Cyanamid European Research Institute in Geneva.

Dr. M. H. B. Stiddard has been appointed Lecturer in Chemistry in the University of Hull, this appointment to take effect from October 1st.

Dr. James Taylor has been appointed Chairman of Almin Ltd., the parent company of the Associated Light Metal Industries Group, recently acquired by ICI and ALCOA.

Mr. B. Topley, who has been a Director of Albright & Wilson Ltd. since 1944, has been elected Deputy Chairman of the Board.

The Research Medal of the Royal Agricultural Society of England has been awarded to *Professor R. L. Wain*, of Wye College (University of London).

Professor F. L. Warren, University of Natal, will visit London during July, before proceeding to the I.U.P.A.C. Congress in Australia in August.

Dr. T. S. West of the University of Birmingham has been awarded an Austrian State Fellowship, and will be on study leave in Vienna for about four months.

Dr. W. E. Willmott of Damancy & Co. Ltd., Ware, has been appointed to the Board as Director of Research.

## APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the publication of this issue of Proceedings. Such objections will be treated as confidential. The forms of application are available in the Rooms of the Society for inspection by Fellows.)

- Akers, Richard John. 129 Breamore Road, Goodmayes, Essex.
- Ashton, Herbert Martin, Ph.D. Esso Research Ltd., 50 Stratton Street, London, W.1.
- Barash, Louis, M.S. Bell Telephone Laboratories, 1A-240 Murray Hill, New Jersey, U.S.A. Batterbee, John Edward, B.Sc. 397 Melton Road,
- Leicester.
- Beddard, John, B.Sc. 70 Dene Road, Didsbury, Manchester, 20.
- Breen, Geoffrey John Waudby. 47 Cameron Street, Rockdale, Sydney, New South Wales, Australia.
- Brown, Keith Spalding, Jr., B.Sc. 413 Merrill Crest Drive, Madison, Wisconsin, U.S.A. Browning, Holford, B.Sc. Woodside, Wood Road, Codsall, nr. Wolverhampton.
- Bull, James Ronald, B.Sc. 14 Bullbrand Road, Sarnia, Natal, South Africa.
- Byers Brown, William, M.Sc. Chemistry Department,
- University of Manchester, Manchester, 13. Carnam, Daryl Ann, B.A. Department of Chemistry, Mount Holyoke College, South Hadley, Massachusetts, U.S.A.
- Chalkley, George Roger. Pembroke College, Oxford. Clarke, Dennis Edward William. 39 The Ridgeway, St. Albans, Herts.
- Clement, Gerald Edwin, B.A. Department of Chemistry, Purdue University, West Lafayette, Indiana, U.S.A.
- D'Andrea, Carl Louis, B.A. New York University, Chem-istry Department, Washington Square, New York, 3, U.Ś.A.
- Davis, Geoffrey Thomas, B.A. 13 The Meads, Northchurch, Berkhamsted.
- Dickens, Brian, M.S., A.R.I.C. 308 Gibbs Laboratories, Department of Chemistry, Harvard University,
- Cambridge, 38, Massachusetts, U.S.A. Dock, Alan Walter. Manfred Hudson Hall, University College, P. Bag 167H, Salisbury, Southern Rhodesia.
- Ehrlich, Hans Werner Walter, Ph.D. Chemistry Department, Kings Buildings, West Mains Road, Edinburgh, 9.
- Fairbourn, Alan, B.Sc. Kenyon House, Alexander Street, London, W.2.
- Fraser, George William. 9 James Street, Kip Hill, Stanley, Co. Durham.
- Gasser, Robert Paul Holland, M.A., D.Phil. Corpus Christi College, Oxford. Green, Michael, Ph.D. Cyanamid European Research
- Institute, 91 Route de la Capite, Cologny, Geneva, Switzerland.
- Griffiths, James Edward, M.Sc., Ph.D. Department of Chemistry, University of Southern California, Los Angeles, 7, California, U.S.A.
- Hall, Francis Michael, M.Sc. 24 Toorak Avenue, West Wollongong, New South Wales, Australia.
- Hariharan, Alleppey Venkiteswaran, M.Sc. Radiochemdistry Division, Atomic Energy Establishment, Trombay, Bombay, 38, India.
- Harrison, Douglas Grimley, B.Sc. 2 Butterfield Lane. St. Albans, Herts.
- Hedger, Joy West, B.Sc. St. Ann's College, 187 Brougham Place, North Adelaide, South Australia.
- Inman, Colin Hugh. Crescent House, Steyning, Sussex.
- Ivimey, Judith Greta. 15 Dunkirk Avenue, Kingsgrove, Sydney, New South Wales, Australia.

- Jones, Brian Francis. 160 Bolton Road, Pendleton, Salford, 6, Manchester.
- Kalnins, Andrejs, B.Sc. 9 Elm Grove, Oaklands, South Australia.
- Kemmitt, Raymond David Walter, B.Sc., A.R.C.S. 129 Shardeloes Road, New Cross, London, S.E.14.
- Kirby, Gerald Francis. 169 Clarence Crescent, Clapham Park, London, S.W.4.
- Kitching, William, B.Sc. Department of Chemistry, University of Queensland, St. Lucia, Brisbane, Queensland, Australia.
- Kostiner, Edward. 84-47 Chevy Chase Road, Jamaica, 32, New York, U.S.A.
- Laslett, Robert Lacy. 77 Welland Avenue, Welland, South Adelaide, South Australia.
- Lüttke, Wolfgang, Dr.rer.nat. Schlüsselstrasse 35. Freiburg i Br., Germany.
- McCormack, Cathal Gabriel. 105 Upper Leeson Street, Dublin.
- MacDonald, John Mackillop, B.Sc. Chemistry Depart-ment, University of Western Ontario, London, Ontario, Canada.
- Magin, Ralph Walter, B.S. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, 39, Massachusetts, U.S.A.
- Mains, Harold Eugene, B.Sc. Ohio University, College of Arts and Sciences, Department of Chemistry, Athens, Ohio, U.S.A.
- Marchant, Keith. 96 Lower Hill Street, Blaenavon, Mon.
- Maxey, Cornelius Richard, B.Sc. Meadow Dyke, Claylake, Spalding, Lincs.
- Metzger, Norman, B.Sc. 2086 Anthony Avenue, Bronx, 57, New York, U.S.A. Mortimer, Peter Inkster, M.Sc. Department of Chem-
- istry, University of California, 405 Hilgard Avenue,
- Kity, University of Camorina, 405 Lingue Linne, Los Angeles, 24, California, U.S.A. Motz, Kaye L., Ph.D. Department of Chemistry, Uni-versity of Michigan, Ann Arbor, Michigan, U.S.A. Murdoch, Henry Drummond, B.Sc., A.R.C.S.T. 420
- Carntynehall Road, Glasgow, E.2.
- Nakagawa, Yasushi, B.S. P.O. Box No. 2424, Boulevard Station, Norman, Oklahoma, U.S.A.
- Ortega, Manuel Valerio, Ph.D. Av. Country Club 208,
- Mexico, 21, D.F., Mexico. Parsons, Robert W., Jr., Ph.D. 44 Lenox Road, Summit, New Jersey, U.S.A.
- Perkins, Peter Graham, Ph.D. British Cotton Industry Research Association, Shirley Institute, Didsbury, Manchester, 20.
- Phillip, Arpad Tibor, B.Sc. 203 Headland Road, Dee Why, Sydney, New South Wales, Australia.
- Pierens, Raymond Kent, B.Sc. 17 Henry Street, Ryde, New South Wales, Australia. Pieth, George, Dr.Sc.Tech. Acta Cherina, Highgate Road,
- Boden-Altrincham, Cheshire. Raggatt, Peter Rufus. St. Peter's Hall, Oxford. Rakhit, Sumanas, Ph.D., M.Pharm. Department of

- Chemistry, University Laval, Quebec, Canada. Redpath, James, B.Sc., A.R.C.S.T. 22 Mingulay Crescent, Glasgow, N.2.
- Rigby, Maurice. 106 Hardhorn Road, Poulton-le-Fylde, nr. Blackpool.
- Rochester, Colin Herbert, B.Sc. 66 Granville Park, Lewisham, London, S.E.13.

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#### PROCEEDINGS

- Roff-Jarrett, Alan Thomas. 12 Durleigh Road, Bridgwater, Somerset.
- Saraswat, Ishwari Prasad, M.S. Radio Chemistry Division, Atomic Energy Establishment, Trombay, Bombay, 73, India.
- Sarwar, Sheikh Mohammed, B.Sc. 24 Aspland Grove, London, E.8.
- Scott, Thomas Arthur, B.Sc. University College of Wales, Department of Biochemistry, School of Rural Science, Penglais, Aberystwyth.
- Searle, Robert John Griffith, B.Sc. 14A Lower Park Road, Tenby, Pembs.
- Self, Margaret Mary, B.Sc. 111 Burgh Road, Gorlestonon-Sea, Great Yarmouth, Norfolk.
- Shadbolt, Roy Stanley. 69 Ludwick Way, Welwyn Garden City, Herts. Siegel, Samuel, Ph.D., M.S. Department of Chemistry,
- Siegel, Samuel, Ph.D., M.S. Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, U.S.A. Sinha, Shyama Prasad, B.Sc. Department of Chemistry,
- Bucknell University, Lewisburg, Pennsylvania, U.S.A. Smith, Thomas Daniel, M.Sc. Chemistry Department,
- The Royal College of Science and Technology, Glasgow, C.1.
- Stead, James Brian, Ph.D. Chapel Road, Hayfield, via Stockport, Cheshire.

- Stevens, Roger James. 142 Worple Road, Staines, Middlesex.
- Szentpeteri, Istvan, Ph.D., M.Sc. Vaci utca 40, Budapest V, Hungary.
- Tada, Masao, B.Sc. Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan.
- Trozzolo, Anthony Marion, Ph.D., M.S. Bell Telephone Laboratories, Murray Hill, New Jersey, U.S.A.
- Van Heiningen, Jan Jacob, B.S. Department of Chemistry, University of California, Los Angeles, 24, California, U.S.A.
- Verge, John Pomfret. "Mataroa," Dawlish Avenue, Shirley, Southampton.
- Warren, Brian Thomas. 51 Barnfield Road, Belvedere, Kent.
- Westaway, Donald Lawrence. 11 Clarence Place, Double Bay, New South Wales, Australia.
- Whitfield, Frank Brierley, M.Sc. 6 Gregory Avenue, Croydon, Sydney, New South Wales, Australia.
- Wiltshire, Winthrop Wilbert Wilberforce. Chancellor Hall, University College of the West Indies, Mona, St. Andrew, Jamaica, West Indies.
- Zabicy, Jacob, Ph.D. Shikoun Hamoumhim 33/2, Kiriat Hayovel, Jerusalem, Israel.

# OBITUARY NOTICE WILLIAM EDWARD GARNER 1889—1960

**PROFESSOR W. E. GARNER** died on March 4th, 1960, at his home at Westbury-on-Trym, Bristol, where he had lived for over thirty years.

Garner was born at Hugglescote, Leicestershire, in 1889, the eldest son in a family of three sons and a daughter. His younger brothers also attained distinction in the scientific world: Sir Harry Garner, after notable achievements in the field of aircraft research and development became Chief Scientist to the Ministry of Supply, and F. H. Garner was for many years until his retirement in 1959 Professor of Chemical Engineering in the University of Birmingham.

After attending Market Bosworth Grammar School (1902-7) Garner went to Birmingham University (1908-13). He was awarded an 1851 Exhibition in 1913 and proceeded to the University of Göttingen to work with Professor Gustav Tammann. Garner's research at Göttingen was curtailed by the outbreak of the first World War and he only managed to get out of Germany in time. In the University of Birmingham he carried out research under Professor P. F. Frankland and it is interesting to recall that he began his scientific life as an organic chemist-his first publication being on the preparation of oximes, amines, and the reactions of thionyl chloride with lactic acid and ethyl lactate. It was undoubtedly his year at Göttingen which influenced much of his subsequent research. Tammann-who held the Chair of Inorganic Chemistry—was then surging ahead with his fundamental investigations of the internal pressure of solutions, equilibria between crystalline and liquid states, particularly melting and nucleation, and crystallisation of inorganic and organic liquids and metals, and he had gathered around him some twenty to thirty research workers from all parts of the world. In this atmosphere Garner met many distinguished European physical chemists and was in close contact with the development of the new and growing branch of chemistry—known as physical chemistry.

On his return to England in 1914 he joined the scientific staff of Woolwich Arsenal where he carried out some outstanding research work with Sir Robert Robertson on the calorimetry of high explosives. Garner's experience at Woolwich was later to be invaluable to him when he became an adviser to the Ordnance Factories, and later Superintendent of Chemical and Explosive Research in the Ministry of Supply during the second World War.

On leaving Woolwich Arsenal he was appointed Assistant Lecturer in the University of Birmingham (January, 1919) and later Assistant Lecturer at University College, London (October, 1919). From that time dated his close and happy association with Professor F. G. Donnan and a fruitful period of research which was to have a significant influence on developments in physical chemistry. Garner had a wide interest in, and deep knowledge of, many branches of physical chemistry and was only happy when following several developing lines. It was during his University College period that he began his studies on heterogeneous catalysis and heats of adsorption, the kinetics of reaction in gases and in solution and in particular the study of explosive reaction in gases, and the ionisation and radiation from flames. Notable among these researches was the discovery of the effect of small amounts of hydrogen on the radiation from the carbon monoxide flames and the heats of adsorption of gases in charcoal.

In 1927 Garner was appointed to the Leverhulme Chair of Physical and Inorganic Chemistry in the University of Bristol, and until his retirement at the age limit in 1955—except for the war period—he carried out there a series of experimental studies of far reaching practical and theoretical importance. He began a wide and systematic study of the kinetics of solid reactions. These investigations fell naturally into two groups: (a) endothermic solid reactions such as the dissociation of hydrates and carbonates; (b) exothermic solid reactions—in particular metallic azides and fulminates. He developed a number of fruitful experimental methods including pressuretime measurements, loss of weight using a microbalance, and microscopy examination of surfaces of decomposing crystals-especially useful in studying nucleation. These investigations, which established the mechanism of interface reactions and nucleation processes, show Garner's wide grasp of the disciplines of physics and chemistry. As with much of his other work on the solid state he was fully cognisant with the fundamental physical approach and the flexibility of his mind made it easy for him to apply the new ideas, such as dislocation theory, lattice defect, and energy levels in solids, to chemical reactions in solids and at surfaces. Parallel with these studies he continued his interests in catalysis and the chemisorption on oxide surfaces.

Garner's work was interrupted by the second World War and immediately on its outbreak he established an extra-mural research team in the University of Bristol to assist the Government Ordnance Factories in explosives and munitions research. This large team continued for the duration of the war and was of invaluable help to the production factories and in developing new explosives and other essential war materials. Although never losing contact with the work of this group, Garner moved to Fort Halstead in Kent in 1943 to become Superintendent of Chemical and Explosives Research for the Ministry of Supply. He later became Deputy Chief of Armament Research and then later Chief Superintendent Armament Research. His enthusiasm, wise guidance, and inspiration were of paramount importance to the war effort. He served on very many high-level committees and was associated with many notable developments in new armaments and munitions. His services were recognised in 1946 by the award of the C.B.E. During the whole of the period

that he was at Fort Halstead, Garner would return to Bristol on the Friday evening, gave his lectures on Saturday morning and attend to departmental matters before returning to London on the Sunday afternoon.

On the cessation of hostilities Garner returned to his University work, although until his retirement he was actively engaged in the work of the Scientific Advisory Council of the Ministry of Supply and other Government committees. During the post-war period he built around him in Bristol one of the strongest research groups in the country. He continued with increasing vigour his studies of heterogeneous catalysis and in particular the heats of adsorption of hydrogen, carbon monoxide, oxygen, and carbon dioxide on zinc, manganese, chromium, and copper oxides and elucidated the mechanism of the reversible and irreversible chemisorption of gases on these oxides and the interpretation of the experimental results in terms of modern theories of the defect lattice. After his retirement in 1955 he organised a symposium on Chemisorption at Keele, Staffordshire, which was published by the Chemical Society, and edited a large volume on the Chemistry of the Solid State. Most of the contributors to the latter volume were former students or colleagues at Bristol -others were close scientific friends-and this work, which presents the broad basis of progress in solid state chemistry, is very much a tribute to Garner's work and inspiration.

Garner was a man of charm and kindness who won the affection and admiration of all who came into contact with him. His unselfishness and sincerity made him the most likeable of men and he was always ready with encouragement, advice and assistance to his students and colleagues. He was a quiet, unobtrusive man, entirely devoid of personal ambition; devoted to his work whether in the laboratory or the councils of the University. But these qualities did not obscure the greatness of the man. He was an enthusiastic and inspiring leader of research, conscientious in the discharge of his duties and an adherent of the best traditions of science. His interests were wide; he was a collector of paintings and china and had a critical appreciation of art. He was knowledgeable on many subjects-he had a good library of books on the history of chemistry; he was very interested in period furniture and he always enjoyed an hour or so in the sale-room. But above all, he was an enthusiastic gardener and it was a great thrill to him to raise a rare seedling or to produce some unusual fruit. These hobbies were a great comfort to him in his retirement and in recent years he extended his greenhouses and took up the growing of orchids. The care of his plants was a major concern to him during his illness.

He was a man of great tenacity and courage. This

characterised his scientific work and everything else he tackled; no problem ever daunted him. When I visited him last summer in hospital he was busy studying catalogues of wheel-chairs since it was thought that he would be able to walk only with difficulty. But despite the doctors' fears Garner, with his indomitable courage, was soon on his feet again and for a short time before his final illness he visited the Staff House of the University for lunch—a pleasure he enjoyed during the five years of his retirement.

He had a wide circle of friends and those who had the pleasure of knowing him valued a friendship which will endure as a cherished memory of a lovable character.

Garner was a well-known figure at scientific gatherings and although not outstanding as a lecturer he was at his best in presenting his own experimental discoveries or introducing some new idea which he was then developing. Scientific

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#### ARS LONGA VITA BREVIS

FROM a thesis (contributed by Dr. H. Irving):

After being exposed to an intense beam of neutrons for several months we proposed to examine the chemical changes in a sample of X. societies and Government committees made great calls upon his time. He was President of the Faraday Society (1945—47) and served as a member of the Council of the Royal Society and of the Faraday Society. He was a member of the Scientific Advisory Council of the Ministry of Supply for almost the whole of the period 1942—60 and had been associated with that body since its inception. He was also Senior Scientific Adviser for Civil Defence in the South West Region.

He received many honours: he was elected to the Fellowship of the Royal Society in 1937; was a Fellow of University College, London, and was made a Commander of the British Empire in 1947. He was well-known abroad and was an honorary member of the Polish Chemical Society, a correspondent councillor of the Patronato "Alfonso el Sabio", Madrid, 1959. He was a member of the Joint Services Mission to the U.S.A. and Canada, 1948.

C. E. H. BAWN.

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#### "CONCENSUS OF OPINION"

VARIOUS kind letters and conversations make me concsious that this phrase, which I wrote on p. 161 of *Proceedings*, errs in spelling and sence. The Consice Oxford English Dictionary and indeed the consensus of authority have convinsed me that this is so. I apologise and offer no defence (*pace* my American friends). THE EDITOR.