PROCEEDINGS

OF THE

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TILDEN LECTURE*

Nuclear Magnetic Resonance

By R. E. Richards

An atomic nucleus of spin quantum number, I, possesses magnetic moment, μ, which arises from the circulation of electric charge associated with the spin of the particle. If a substance containing these nuclei is placed in a strong uniform magnetic field, H_0, the energy of the magnetic moment depends on its orientation with respect to the lines of force of the applied field. The quantum theory requires that this energy can have only discrete values, so that only certain orientations of the nuclear magnet in the applied field are allowed, and a nucleus of spin quantum number, I, is permitted to occupy one of $(2I + 1)$ orientations. The energy separation of adjacent levels is $\mu H_0/I$, and if suitably polarised radiation is applied to the sample, transitions of the nuclei among these energy levels can be induced, in accordance with the equation

$$h\nu_0 = \mu H_0/I = \gamma H_0/2\pi I, \quad . \quad . \quad . \quad (1)$$

where h is Planck's constant, ν_0 is the frequency of the radiation, and γ is the magnetogyric ratio. Note that for a given nucleus, there is a simple linear relation between frequency and applied field strength, H_0.

The probability that the radiation will induce an upward or a downward transition of a nucleus between the energy levels is the same. Therefore, a net absorption of energy from the radiation occurs only if there is an excess population of nuclei in the lower energy level. When energy is transferred between the nuclei and the radiation, a nuclear magnetic resonance spectrum may be observed.

When H_0 is 10^4 gauss, the frequencies of radiation required to excite the nuclei from one energy level to another lie in the region of 10 Mc./sec., so that nuclear magnetic resonance is a branch of radiofrequency spectroscopy. When a similar experiment is performed with substances containing unpaired electrons, an electron-spin resonance spectrum may be observed. Because the magnetic moment of the electron is of the order of 10^3 times those of nuclei, the frequency of radiation required for electron-spin resonance (see equation 1) is of the order of 10,000 Mc./sec., in the microwave region.

The chemical interest in nuclear resonance lies in the complex ways in which the spectra are often affected by interactions between a nucleus and its surroundings. These interactions can be considered conveniently under three headings, namely, (*a*) interactions between the extranuclear electrons and the applied magnetic field, H_0; (*b*) interactions between neighbouring magnetic moments, which can occur in a variety of ways; (*c*) interactions between nuclear electric quadrupole moments and electric field gradients at the nucleus.

The usefulness of nuclear magnetic resonance spectra is limited in practice by the line width and by the signal-to-noise ratio. If the lines are broad, information depending on fine structure may be lost. The strength of a nuclear resonance at a given field H_0 depends only on the number of nuclei causing it and their physical properties, and is measured by the area under the resonance. The broader the resonance line, the smaller will be its height for a given area,

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and thus the lower the signal-to-noise ratio. Increasing the excess population of one energy level over the other (if there are only two energy levels as for a proton) will give a stronger signal.

(*a*) *Chemical Shifts*.—When a chemical substance is placed in a strong magnetic field, H_0, orbital currents are induced in the electron clouds which set up a weak diamagnetic moment proportional to the applied field. This diamagnetic moment opposes the applied field, so that the field actually experienced by a nucleus is reduced by a factor, σ. We therefore write $H_e = H_0(1 - \sigma)$, and equation (1) becomes

$$h\nu_0 = \mu H_0(1 - \sigma)/I \quad . \quad . \quad . \quad (2)$$

where H_e is the field actually experienced by the nucleus.

The value of σ depends on the strength of the diamagnetic moments which H_0 can induce in the extranuclear electrons. This is affected by the density and spatial distribution of the electrons and therefore varies with the chemical environment of the nucleus. The factor σ is known as the chemical shift and varies over a range of as little as twenty parts per million (p.p.m.) for proton resonances and as much as 2% for cobalt resonances.

The theory of this diamagnetic shielding of the nucleus by the electrons has been given by Ramsey,[1] but unfortunately at present it can be applied rigorously only to the simplest molecules. Approximate approaches to the theory of diamagnetic moments of complex molecules have been attempted by valence-bond and molecular-orbital methods, and there is every hope that useful progress will be made along these lines soon.[2] At present, however, the uses of chemical shifts rest mainly on qualitative theories and on empirical correlations.

The electron density on the hydrogen atom is so low that the induced diamagnetic currents are very small, so that, for protons, σ is very sensitive to the influences of stronger magnetic moments induced in other parts of the molecule. A particularly striking illustration of this effect occurs in molecules with a conjugated ring system. In molecules such as benzene, the applied magnetic field can produce a very strong diamagnetic moment at right angles to the plane of the ring by inducing current circulation in the π-electron system. The local field associated with this induced moment often dominates the chemical shifts of protons in the molecule. For example, in coproporphyrin-I methyl ether a strong current circulation is induced in the porphyrin ring. The diamagnetic moment opposes the applied field, H_0, in the centre of the ring, causing the resonances of the NH protons to occur at low frequencies in a fixed field, H_0 (or at high fields at a fixed frequency); the lines of force of the induced moment, however, *assist* H_0 on the outside of the ring, causing the proton resonances of the HC$\leqslant$ groups to occur at frequencies about 14 p.p.m. higher than the NH group (or at *low* fields at fixed frequency).

The effect of electric fields,[3] of bond type,[4] and of unpaired electron spin density[5] in certain paramagnetic molecules can also be interpreted qualitatively and sometimes quantitatively, and such studies have led to a great range of useful chemical applications.

The empirical applications of chemical shifts are very extensive and of great value in chemistry. The use of the so-called high-resolution nuclear magnetic resonance spectra in organic chemistry has now reached an advanced stage of sophistication and can be applied to very complex molecules.

The chemical shifts (σ) of protons in a great range of organic compounds have been correlated with the chemical environment and functional group containing the protons. A measurement of the chemical shifts of the protons in an unknown substance may then permit many of its structural features to be identified, and from the relative intensities of the chemically shifted lines the relative number of protons in the different groups can be obtained. Recent examples have been given by Shoolery.[6] The applications to inorganic chemistry have not been so extensive but, even so, many useful results have been obtained, and are reviewed by Muetterties and Phillips.[7] For example, the tin resonance of a mixture of stannic bromide and stannic chloride has five components due to $SnBr_4$, $SnBr_3Cl$, $SnBr_2Cl_2$, $SnBrCl_3$, and $SnCl_4$. The relative intensities are consistent with a simple statistical equilibrium involving substances with equal thermodynamic stabilities.[8] The ^{17}O resonance of aqueous solutions of paramagnetic ions has two components which are associated respectively with the water molecules of the solvent and with those of the hydrated ions. A limit can be placed on the rate of exchange of water between

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[1] Ramsey, *Phys. Rev.*, 1950, **78**, 699.

[2] McGarvey, *J. Chem. Phys.*, 1957, **27**, 68; Stephen, *Proc. Roy. Soc.*, 1957, *A*, **243**, 264; Pople, *Discuss. Faraday Soc.*, in the press; Kern and Lipscomb, *J. Chem. Phys.*, 1962, **37**, 260, 267, 275, 279.

[3] Frank and Gutowsky, *Arch. Sci.*, 1958, **11**, 215; Marshall and Pople, *Mol. Phys.*, 1958, **1**, 199.

[4] Bothner-By and Naar-Colin, *Ann. New York Acad. Sci.*, 1958, **70**, 833.

[5] Benson, Eaton, Josey, and Phillips, *J. Amer. Chem. Soc.*, 1961, **83**, 3714.

[6] Shoolery, *Discuss. Faraday Soc.*, 1962, in the press.

[7] Muetterties and Phillips, "Advances in Inorganic Chemistry and Radiochemistry," Academic Press, New York, 1962, Vol. IV, p. 231.

[8] Burke and Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326.

hydrated ion and solvent and, from the relative intensities, approximate hydration numbers can be calculated.[9] The chemical shift of the ^{17}O resonance in the hydrated rare-earth ions can be shown to arise from very weak covalent bonds involving the $2s$ (or $2s$ and $2p$) orbitals of the oxygen and the $6s$ orbitals of the rare-earth ion.[9]

(*b*) *Interaction between magnetic dipoles*.—Let us now consider some of the ways in which interactions between the nuclear magnetic moments of a sample may affect the nuclear resonance spectrum.

(i) *Static dipolar interaction.* This occurs in crystals when the nuclei are rigidly fixed in space. The magnetic moment of each nucleus generates a weak magnetic field in its environment and at any point in the crystal all these "local" fields combine to produce a net resultant H_{local} directed along the lines of force of H_0. H_{local} can take on a range of values on either side of zero, depending on the instantaneous orientations of the various nuclear moments causing it, so that the nuclei at any site in the unit cell of the crystal will, between them, experience a range of fields of the order of H_{local} on either side of H_0, the applied magnetic field. The result is a broadening of the nuclear resonance by an amount of the order of H_{local}, which is proportional to μ/r^3, where r is the distance from the moment μ. For hydrogen atoms which have large nuclear magnetic moments and small radii, the broadening of the nuclear magnetic resonance lines in crystals is typically about 10 gauss or 1000 p.p.m. in a field of 10^4 gauss; on the other hand, for larger atoms such as thallium, with small nuclear moments, the broadening may be as small as 0·1 gauss or 10 p.p.m. The chemical shifts of proton resonances range over only 20 p.p.m. so it is clearly impossible to observe these effects in solids when the lines are far too broad. On the other hand, for some inorganic substances, the chemical shifts are greater and the broadening is smaller. For example, the thallium resonance of crystalline Tl_2Cl_3 shows two resolved components with intensities in the ratio of 3:1. These are chemically shifted resonances for thallous and thallichloride ions in accordance with the structure $Tl^{I}_3[Tl^{III}Cl_6]$.

In simple crystals the broadening of the nuclear resonance, which depends on $\sum_i\sum_j(\mu_1\mu_2/r_{ij}{}^3)$, can sometimes be used to obtain internuclear distances,[10] but this method has only limited applications. When molecular motion occurs in the crystal, the local fields, H_{local}, may be more or less averaged out, and a detailed study of this effect as a function of temperature can lead to information about the type of molecular motion occurring and the potential barriers which hinder it.[10]

In the liquid or gaseous state the molecular motion is so vigorous and random that no static component of the local field remains; the characteristic broadening of the nuclear resonance lines of solids is completely lost and line widths become dominated by the Heisenberg uncertainty principle and may be as small as 10^{-4} gauss or 0·01 p.p.m. at 10^4 gauss. All that remains of the local magnetic fields are components fluctuating randomly in accordance with the thermal motion of the molecules in the liquid. The important effects of these fluctuations will be considered later. The very narrow lines which may occur in the nuclear magnetic resonance spectra of liquids reveal a further mode of interaction between nuclei which can provide useful information for the chemist.

(ii) *Spin–spin coupling*. The second type of interaction between nuclear moments is transmitted only through chemical bonds. This scalar coupling arises from a weak spin polarisation of the electrons in a chemical bond by the magnetic moment of one nucleus which produces a small magnetic field at another nucleus joined to it through the chemical bond or bonds. The magnetic field produced at the nucleus depends on the orientation or orientations of the nuclei causing it, so that the nucleus experiences a variety of situations which reflect some of the properties of atoms to which it is joined. This scalar coupling is independent of molecular orientation in the magnetic field because it is transmitted through the chemical bonds, and is therefore not affected by the molecular motion in the liquid. The result of the interaction is to produce the so-called "spin multiplets" in nuclear magnetic resonance spectra. For example, acetaldehyde shows two regions of proton resonances, one at low fields due to the CHO proton, and another at higher fields, with three times the intensity, due to the protons of the methyl group. A scalar interaction is transmitted between the nuclei through the chemical bonds, and because carbon and oxygen have nuclei with zero magnetic moments, only the protons are involved. These have a spin quantum number, $I = \frac{1}{2}$, so that the proton of the CHO group is allowed two orientations in H_0. Each of these orientations transmits a slightly different effect through the chemical bonds to the protons of the methyl group, the resonance of which therefore appears as a doublet; because the two orientations of the CHO proton are more or less equally probable, the two components of the methyl doublet are of equal intensity. The separation of the two lines of the doublet is a measure of the strength of the scalar

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[9] Swift and Connick, *J. Chem. Phys.*, 1962, **37**, 307.

[10] Richards, "Determination of Organic Structures by Physical Methods," ed. Phillips and Nachod, Academic Press, New York, 1962, Vol. II, p. 537.

coupling and is equal to the spin–spin coupling constant, J. The proton of the CHO group experiences a variety of magnetic fields determined by the various combinations of the two allowed orientations for each of the three CH_3 protons. These combinations are

$$
\begin{array}{llll}
+\tfrac{1}{2}+\tfrac{1}{2}+\tfrac{1}{2}\ ; & +\tfrac{1}{2}+\tfrac{1}{2}-\tfrac{1}{2}\ ; & +\tfrac{1}{2}-\tfrac{1}{2}-\tfrac{1}{2}\ ; & -\tfrac{1}{2}-\tfrac{1}{2}-\tfrac{1}{2} \\
 & +\tfrac{1}{2}-\tfrac{1}{2}+\tfrac{1}{2} & -\tfrac{1}{2}+\tfrac{1}{2}-\tfrac{1}{2} & \\
 & -\tfrac{1}{2}+\tfrac{1}{2}+\tfrac{1}{2} & -\tfrac{1}{2}-\tfrac{1}{2}+\tfrac{1}{2} &
\end{array}
$$

The CHO resonance is therefore a quartet, the two inner components being three times as strong as the outer ones, because they correspond to arrangements of the CH_3 protons which can be achieved in three times as many ways.

In more complex molecules the spin–spin coupling leads to much more complicated fine structure. Sometimes it is easy to interpret the spectrum in terms of the molecular structure, but sometimes it is necessary to use rather complicated procedures[11] to evaluate the chemical shifts and coupling constants which characterise the spectrum. However, in many cases the fine structure of high-resolution nuclear magnetic resonance spectra can be used to deduce information about the ways in which groups are joined together in a molecule; the nature of the functional groupings and the relative numbers of nuclei in them is obtained from the chemical shifts and relative intensities of the resonances.

The values of the spin–spin coupling constants depend very sensitively on the stereochemical arrangement of the bonds joining the nuclei together. The theory of spin–spin coupling[12] can be applied rigorously only in the simplest cases, but valence-bond approximations have been used very successfully by Karplus[13] to interpret the variation with bond angle of spin–spin coupling between protons.

A powerful method of studying spin–spin coupling depends on the simultaneous excitation of two or more nuclear resonances in the same sample. For example, in a sample of $^{13}CH_3I$, the proton resonance is a doublet.[14] The proton resonance is split by scalar coupling with the carbon-13 nucleus which has a spin, $I = \frac{1}{2}$; the iodine nucleus produces no effect because of very strong quadrupole relaxation. If, whilst the proton resonance is constantly observed, the ^{13}C resonance is excited by simultaneous application of radiation of the appropriate frequency, the ^{13}C nucleus will be flipped back and forth among its two allowed orientations. If the irradiation is intense enough, the ^{13}C nuclei are reoriented so rapidly that the protons are no longer able to distinguish their two different orientations and the proton resonance collapses to a singlet. As soon as the radiation exciting the ^{13}C nuclei is removed, the protons again experience the spin–spin coupling and the proton resonance regains the doublet structure. Double irradiation involving two groups of chemically shifted protons can be used as an aid to the analysis of complex high-resolution spectra, and for the determination of relative signs of spin–spin coupling constants.[15] An elegant double-resonance method has been described by Anderson[16] which permits the determination of chemical shifts of ^{13}C resonances in some compounds where direct observation is made difficult by very weak signals.

The values of spin–spin coupling constants between protons in organic compounds are usually in the range 1—100 c./sec., *i.e.*, of the order of 1 p.p.m. at 50 Mc./sec. Spin–spin interaction between protons can therefore be observed only in liquids, where the resonances are narrow enough; the lines in solids are far too broad (~ 1000 p.p.m.). Spin–spin coupling constants among atoms of high atomic number may, however, be very much greater than for protons. For example, spin–spin coupling between nuclei of platinum and phosphorus in alkylphosphine complexes of platinum have been found[17] to be as large as 6 Kc./sec. In some solid compounds of thallium, the spin–spin coupling between the two abundant isotopes Tl^{203} and Tl^{205} is so strong that it determines the line widths of the thallium resonances in these compounds.[18]

(iii) *Relaxation times.* We now turn to the third type of interaction between magnetic moments in the sample which may be called dynamic dipolar coupling. The local magnetic fields generated by the nuclear moments produce no "static" component in a liquid as explained above, because of the random molecular motion. The fields still exist, however, as fluctuating components having a distribution of intensity, $F(\nu)$, with frequency corresponding to the molecular motion. The frequency distribution of the Brownian motion in a liquid has the form

$$F(\nu) \propto 2\tau_c/(1 + \nu^2\tau_c^2), \quad . \quad . \quad . \quad (3)$$

where τ_c is the so-called correlation time for the motion and is a measure of the time taken for the molecule to change its orientation or position signi-

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[11] Pople, Bernstein, and Schneider, "High Resolution Nuclear Magnetic Resonance," McGraw Hill, New York, 1959.
[12] Ramsey, *Phys. Rev.*, 1953, **91**, 303.
[13] Karplus, *J. Chem. Phys.*, 1959, **30**, 11.
[14] Royden, *Phys. Rev.*, 1954, **96**, 543.
[15] Maher and Evans, *Proc. Chem. Soc.*, 1961, 208; Freeman, *Mol. Phys.*, 1961, **4**, 385.
[16] Anderson, *J. Chem. Phys.*, 1962, **37**, 1373.
[17] Pidcock and Richards, *Proc. Chem. Soc.*, 1962, 184.
[18] Freeman, Gasser, and Richards, *Mol. Phys.*, 1959, **2**, 301.

ficantly. The form of the correlation function for various values of τ_c is shown in Fig. 1.

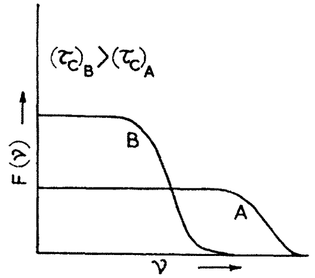

FIG. 1. *Intensity of field fluctuations as a function of frequency.*

The effect of these fluctuating magnetic fields is to modify the life-times of the nuclei in their various energy levels and hence by the uncertainty principle to change the nuclear resonance line-width. The Heisenberg uncertainty principle can be written approximately as

$$\Delta E\cdot t \approx h/2\pi \approx h\cdot\Delta\nu\cdot t \qquad \ldots \quad (4)$$
$$\text{or } \Delta\nu \approx 1/2\pi t,$$

where ΔE and $\Delta\nu$ are the uncertainty or spread of the energy and line width, and t is the lifetime of the particle in the energy level. The lifetime of a nucleus in an energy level is characterised in terms of two "relaxation times," T_1 and T_2. T_1 is the spin–lattice relaxation time; it is a measure of the time taken for a nucleus to exchange energy with the thermal motion of the molecules around it; and T_2 is the spin–spin relaxation time, and is a measure of the time taken for two nuclei to exchange a quantum of energy, one falling from an upper to a lower energy level, and the other using the quantum of energy to raise it from a lower to an upper energy level. Spin–lattice relaxation is the process by which a nuclear-spin system heats up or cools down to the temperature of the "lattice," which may be a gas, liquid, or solid. Spin–spin relaxation is an adiabatic process in which energy is passed through the spin system but not exchanged with other forms of energy. In liquids, T_1 and T_2 are usually approximately equal, so only T_1 will be considered in the discussion which follows.

For nuclear spins the probability of a spontaneous transition from one energy level to another is nearly zero, and for nuclei with $I = \frac{1}{2}$, the only agency which can bring about a change from one energy level to another is a magnetic field fluctuating at the resonance frequency, $\nu_0 = \mu H_0(1 - \sigma)/Ih$. In a liquid, such as water, the only source of such a fluctuating magnetic field is the local fields of the proton magnetic moments fluctuating with the range of frequencies corresponding to the correlation function of the molecular motion. It is the component of these fluctuating fields at the frequency ν_0 which provides a mechanism by which the nuclear spins can exchange energy with the thermal motion of the molecules and which permits spin–lattice relaxation.

For most mobile liquids, τ_c is of the order of 10^{-10}—10^{-12} seconds. The value of $F(\nu)$ (equation 3) therefore has a maximum at a frequency near 10^{11} c./sec. The significant frequency for relaxation is ν_0, which is usually about 10^7 c./sec. for nuclei; at this frequency, $\nu_0\tau_0 \ll 1$, so that $F(\nu) \propto \tau_c$, and it is therefore clear that $F(\nu_0)$ must be very weak. Spin–lattice relaxation is therefore very ineffective, and the spin–lattice relaxation time, T_1, is long (about 3 seconds in water). The line width of the nuclear resonance in the liquid is determined by the relaxation time and is therefore only a fraction of a cycle, and this is why high-resolution nuclear magnetic resonance is possible in diamagnetic liquids. In viscous liquids, the molecules move more slowly, τ_c is larger, $F(\nu_0)$ is greater, relaxation is more effective, T_1 is shorter, and the lines become broader.

The intensity of the fluctuating component at ν_0 depends, not only on τ_c, but also on the strength of magnetic moments in the liquid and on the mean approach distances to the nuclei concerned. These factors depend on molecular structure and on molecular interaction in the liquid. For example, the relaxation time of the protons in the benzene ring of toluene in dilute solution in carbon disulphide is about 60 seconds, whereas for the protons of the methyl group it is about 15 seconds.

If the liquid contains a paramagnetic solute, dramatic changes in the relaxation times may be brought about. The unpaired electron of the paramagnetic substance has a magnetic moment of the order of 10^3 times greater than those of the nuclei, so that although the correlation spectrum of field fluctuations may not be changed significantly, the total intensity of the magnetic field fluctuations is much greater. Very small concentrations of paramagnetic solute can shorten nuclear relaxation times considerably, and we can expect to observe differential effects on the nuclei in different parts of a molecule which will reflect any preferred types of collision in the liquid.

Double spin flips: The fluctuating magnetic fields can also induce more complex transitions than the simple spin–lattice relaxation described above. One interesting effect is to induce two simultaneous transitions, in which one magnetic moment falls from a higher to a lower energy level and another simultaneously jumps from a lower to a higher energy level. If the first particle is an electron and the second a nucleus, the process involves loss of energy by the spin system and can be regarded as a mode of relaxation. If, in such a solution, the electron resonance is strongly excited so as to disturb the population of the electrons ($S = \frac{1}{2}$) among their two energy levels, a continuous flow of electrons from the upper to the lower energy level will be produced (Fig. 2). The relaxation process involves the relaxation of an electron from the upper to the lower energy level, with a simultaneous jump of a nucleus from a lower to an upper energy level; the excess energy is lost as thermal motion of the molecules. The result is to pump nuclei from the lower to the upper energy level and so to disturb the relative population of the levels; this disturbance is reflected directly in a change in the intensity of the nuclear resonance signal. As the rate of excitation of the electron resonance is slowly increased, the nuclear resonance signal grows weaker and then vanishes when the populations of the two nuclear levels have become equalised. Further increase in the intensity of the irradiation of the electron resonances causes the nuclear resonance to reappear, but now inverted, as the population of the upper state becomes greater than that of the lower one. When the electron resonance is completely saturated, the inverted nuclear resonance may be as much as $\gamma_e/2\gamma_N$ times stronger than normally, where γ_e and γ_N are the magnetogyric ratios of the electron and the nucleus, respectively; the ratio is about 330 for protons and greater for most other nuclei.

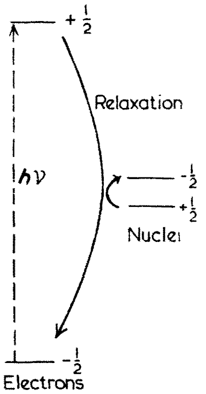

FIG. 2. *Double transitions causing upward jumps of nuclei when electrons relax.*

This so-called dynamic nuclear polarisation has hardly been exploited at the present time. There are clearly great possibilities of its use for observing nuclear resonances which are otherwise too weak, for example, ^{13}C resonances in natural abundance in organic compounds. Preliminary work shows[19] that not all nuclear resonances in a given compound are equally affected during this type of experiment. This means that we cannot expect to retain the valuable "group-counting" uses of intensities in nuclear resonance spectra obtained by dynamic polarisation. On the other hand, the variations may well lead to valuable information about molecular interactions in solution.[20]

(*c*) *Electric Quadrupole Interaction.*—The final type of interaction to be considered here is of the greatest importance in determining line widths of nuclear resonances. Nuclei with spin quantum numbers greater than ½ usually have an aspherical distribution of electric charge, which can be expressed as an electric quadrupole moment. This moment can couple strongly with any electric field gradient set up at the nucleus by the electrons distributed around it. If the molecule is tumbling over in a liquid, this electric quadrupole coupling tends to reorient the nucleus into another energy level in the applied magnetic field. The effect is to shorten the lifetime of the nucleus in a given energy level and to reduce T_1 according to an equation of the form

$$1/T_1 \propto (\text{eq Q})^2\eta/T, \qquad . \; . \; . \quad (4)$$

where (eq Q) is the product of the electric quadrupole moment and electric field gradient, η is the viscosity of the liquid, and T is the temperature. This quadrupole coupling is often very strong, so that the nuclear resonance may be characterised by very short spin–lattice relaxation times. The broadening of the nuclear resonance lines by this relaxation is a great limitation on the study of nuclei affected by it, because the broadening is often so great as to make the signal undetectable. The effect can, however, often be turned to good account. For example, when glycerol is added to dimethylformamide, $1/T_1$ for the nitrogen resonance is found to vary linearly with viscosity as expected from equation (4).[21] The slope of the straight line is a measure of the electric field gradient at the nitrogen nucleus. Protonation of the amide with a strong acid could occur at the nitrogen or at the oxygen of the amide; the former would make the electric field at the nitrogen more symmetrical and reduce the quadrupole coupling, and the latter would increase the π-bonding at the nitrogen and also the quadrupole coupling. In mixtures of dimethylformamide and trifluoroacetic acid, the slope of the plot of $1/T_1$ against viscosity is greater than in the absence of acid, showing that protonation occurs predominantly at the oxygen atom of the amide.[21]

In this survey it has been possible only to discuss some of the properties of nuclear resonances which seem to me to be of interest to chemists. I hope, nevertheless, to have been able to show that, although some aspects of nuclear magnetic resonance may have been widely exploited, there remain many other effects which may reveal still further details about the microscopic and macroscopic properties of chemical substances.

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[19] Richards and White, *Proc. Chem. Soc.*, 1962, 119.

[20] Richards and White, *Discuss. Faraday Soc.*, in press.

[21] Herbison-Evans and Richards, *Trans. Faraday Soc.*, 1962, **58**, 845.

CHEMICAL SOCIETY MEETING

The following papers were read and discussed at a Scientific Meeting which was held in the Society's rooms at Burlington House on Thursday, March 14th, 1963, at 6 p.m.

Some o-phenanthroline Complexes of Yttrium and the Lanthanides. By F. A. HART and F. P. LAMING.

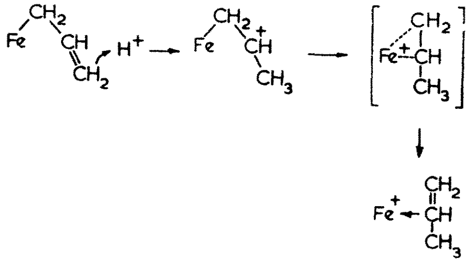
THE complex chemistry of the lanthanides has so far been limited, with rather few exceptions, to ligands containing anionic oxygen as a donor atom. There was an especial lack of information about complexes with ligands having nitrogen as the donor and because of this it has been often assumed that such compounds are relatively unstable.

We have now prepared several types of complex incorporating the uncharged nitrogen donor *o*-phenanthroline. The method of preparation is reaction in anhydrous ethanol or ethyl methyl ketone between a metal salt and a suitable molecular proportion of the ligand, when complexes having the following stoicheiometries are obtained: $MCl_3(H_2O)phen_2$, MCl_3phen_2, $M(CNS)_3phen_2$, $M(CNS)_3phen_3$, $M(NO_3)_3phen_2$, and $M(RCOO)_3phen$.

In general they are crystalline and stable in dry air. They are decomposed by water but are stable thermally, some being unchanged at 300°. Investigation of their structures is made difficult by their relative insolubility in organic solvents and the decomposition in water. However, there is evidence, particularly from infrared absorption studies, that they are mostly to be formulated as six-co-ordinate complexes of an orthodox type. Thus the thiocyanates $[Mphen_3](SCN)_3$ show a CN stretching frequency at about 2050 cm.$^{-1}$ corresponding with ionic SCN groups. An additional peak at about 2080 cm.$^{-1}$ appears in the complexes $[M(SCN)_2phen_2]SCN$, as expected if there are both ionic and co-ordinated SCN groups present. The lightest lanthanides show exceptional behaviour in that if conditions of preparation are not strictly anhydrous the hydrated complex chlorides $MCl_3(H_2O)phen_2$ are obtained. The water molecule is believed, because of the thermal stability of the hydrate, to be co-ordinated to the metal.

Stabilisation of Some Organic Systems by Complexing with Transition Metals. By J. K. P. ARIYARATNE, M. L. H. GREEN, and P. L. I. NAGY.

ORGANIC systems, not isolable in the free state, may sometimes be stabilised by bonding them to transition metals. We have shown that complexes containing a metal–allyl group, $M{\cdot}CH_2{\cdot}CH{=}CH_2$, react readily with hydrogen chloride or mineral acids and that the allyl group is protonated. The cations formed with various metals may be isolated as crystalline salts, and chemical and spectral evidence shows them to contain a propene group bonded to the metal. Studies of the cations formed from deuterium chloride show that carbon-3 is protonated and the following mechanism is suggested:

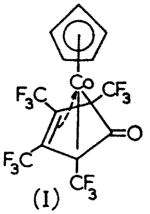


The reaction of a metal complex containing a propargyl group, $M{\cdot}CH_2{\cdot}CH{\equiv}CH_2$, with acids has also been studied. Evidence is presented for the formation of an unstable cation containing what is formally a π-allene group. The cyanoalkyl complexes, $C_5H_5Fe(CO)_2R$, where $R = CH_2{\cdot}CN$, $CH_2{\cdot}CH_2{\cdot}CN$, or $CHMe{\cdot}CN$, have been prepared and their reactions studied. The 1-cyanoalkyl complexes are quite soluble in water and readily protonate giving cationic species. On the basis of analytical and spectral evidence structures which contain a keten-imine system bonded to the metal are proposed for the cations.

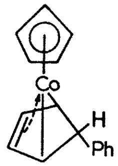
The oxoalkyl complexes, $C_5H_5Fe(CO)_2{\cdot}CH_2{\cdot}COR$, where R = H or Me, have also been prepared and their reaction with acids has been studied. Again cations are formed and the evidence indicates that they contain a vinyl alcohol system bonded to iron.

σ- and π-Bonding from Cyclic Ligands to Transition-metal Ions in Organometallic Compounds. By M. R. CHURCHILL, M. GERLOCH, and R. MASON.

THE molecular structure of π-cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonecobalt (I) and π-cyclopentadienyl-1-phenylcyclopentadienecobalt (II) have been determined by three-dimensional *X*-ray analyses. σ- and π-bonding to the cobalt ion is observed for both the cyclopentadienone and cyclopentadiene ligands as demonstrated by their conformation and the metal–carbon and carbon–carbon bond lengths which have been determined with estimated standard deviations of 0·01 Å and 0·025 Å, respectively; the stereochemistry of the cobalt ion is essentially octahedral. A comparison with π-cyclopentadienyltetramethylcyclopentadienonecobalt illustrates the dependence of the extent of σ- and π-electron donation from the ligand on the nature of the substituent, while the bonding of the cyclopentadiene is entirely similar to that reported for 2,4,6-triphenyltroponeiron tricarbonyl. A *rationale* for these structures is suggested in terms of the relative delocalisation energies of the ligands and stability of the octahedral cobalt(III) ion *vis à vis* its five-co-ordinate cobalt(I) analogue.



(I)



(II)

The nuclear magnetic resonance spectra of substituted cyclopentadiene complexes and related molecules suggest that a pseudo Diels–Alder description of these molecules may be more valid than has been previously assumed.

COMMUNICATIONS

Some Fluoroaromatic Derivatives of Tin

By J. M. HOLMES, R. D. PEACOCK, and J. C. TATLOW
(DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, BIRMINGHAM)

ALTHOUGH alkyl and aryl derivatives of tin are well known, of the corresponding fluorocarbon series only the fluoroalkyls have been isolated.[1]

We now report the preparation and characterisation (Table) of a number of fluoroaromatic derivatives of tin, including the fully substituted tetrakispentafluorophenyltin(IV). In addition the trichloro-compound has been prepared but has not been fully characterised.

TABLE

Compound	M.p.	Method	Notes
$Sn(C_6F_5)_4$	221°	1	Stable to water
$SnMe_2(C_6F_5)_2$	liq.	2	Stable to water; b.p. 94—96°/1·7 mm.
$SnPh(C_6F_5)_3$	100—102°	3	Stable to water
$Sn(C_6F_5)_3Cl$	106°	1	Stable to water
$Sn(C_6F_5)_2Cl_2$	liq.	1, 4	Reacts with water; b.p. 130°/2 mm.

Methods: 1, Grignard (C_6F_5MgBr) + $SnCl_4$. 2, Grignard + Me_2SnCl_2. 3, Grignard + $PhSnCl_3$. 4, $SnMe_2(C_6F_5)_2$ + $SnCl_4$ (Carius).

Tetrakispentafluorophenyltin(IV) is stable to its melting point. It is unreactive, probably because of steric effects, and crystallises in needles with a pseudo-cubic unit cell, as determined from a Guinier *X*-ray powder photograph, of 17·45 Å linear dimension. The chloro-compounds are more reactive; they are hydrolysed even by weak bases, and undergo a number of cleavages with the loss of the pentafluorophenyl group, *e.g.*, with oxine and with tetramethylammonium chloride—with the latter one of the products is the hexachlorostannate $[Me_4N]_2SnCl_6$.

These compounds are more easily prepared than the fluoroalkyl derivatives mainly because the Grignard reagent[2] is more accessible. However, unless reaction conditions and proportions of starting materials are carefully controlled the chief product is the tetrakis-compound.

Preliminary measurements of the recoilless emission and absorption of gamma rays (Mössbauer effect) in tetrakispentafluorophenyltin suggest that the electronegativity of the pentafluorophenyl group is approximately the same as bromine.[3]

We are grateful to the Ministry of Aviation for their support of this work.

(*Received, January* 31*st*, 1963.)

[1] Kaesz, Phillips, and Stone, *Chem. and Ind.*, 1959, 1409; Stone and Treichel, *ibid.* 1960, 837; Clark and Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 1888; Suddens, M.Sc. Thesis, Birmingham, 1960; Kaesz, Stafford, and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6228.

[2] Nield, Stephens, and Tatlow. *J.*, 1959, 166.

[3] M. Cordey-Hayes, private communication.

A Molecular Process in the Radiation-induced Oxidation of Hydrocarbons

By G. DOBSON and G. HUGHES
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ALCOHOLS and carbonyl compounds are known to be amongst the products of the radiation induced oxidation of hydrocarbons.[1,2] The following sequence of reactions has been suggested to account for their formation in oxygenated cyclohexane:

$$\text{cyclo-}C_6H_{12} \rightsquigarrow \text{cyclo-}C_6H_{11}\cdot + H\cdot \quad . \quad . \quad (1)$$

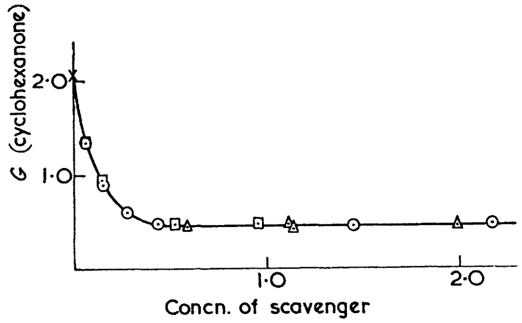
$$\text{cyclo-}C_6H_{11}\cdot + O_2 \rightarrow \text{cyclo-}C_6H_{11}O_2\cdot \quad . \quad . \quad (2)$$

$$2\ \text{cyclo-}C_6H_{11}O_2\cdot \rightarrow \text{cyclo-}C_6H_{11}\cdot OH + \text{cyclo-}C_6H_{10}O + O_2 \quad . \quad (3)$$

We have examined the effect of added scavenger on the γ-radiolysis of oxygenated cyclohexane. The concentration of oxygen was 10^{-2}M. In the presence of a suitable scavenger, it might be expected that cyclo-$C_6H_{11}O_2\cdot$ radicals would be scavenged

$$\text{cyclo-}C_6H_{11}O_2\cdot + SH \rightarrow \text{cyclo-}C_6H_{11}O_2H + S\cdot. \quad . \quad (4)$$

Addition of iodine would probably lead to scavenging of cyclo-$C_6H_{11}{}^{\circ}$ rather than cyclo-$C_6H_{11}O_2{}^{\circ}$ radicals.[3] Either process should lead to a reduction in the yields of ketone and alcohol. However, even at the highest concentrations of scavenger, we find that the yield of ketone is never decreased to zero but reaches a limiting value of *G*(cyclohexanone) = 0·46, independent of the scavenger used, as shown in the Figure. Yields are in all cases independent of dose.



Effect of scavengers on the yield of cyclohexanone in the γ-radiolysis of oxygenated cyclohexane.
Scavenger concentrations (M) *are multiplied by a normalisation factor to bring the curves into coincidence:*
○ 6[$CHPh_3$]
⊡ [CH_2Ph_2]
△ 50[I_2]
× pure cyclohexane.

Chromatographic experiments confirm that the ketone product is solely cyclohexanone and that no ketone is formed from the scavenger.

An additional process involving non-radical intermediates would then seem to be responsible for this limiting ketone yield. It is possible that an excited-molecule reaction

$$\text{cyclo-}C_6H_{12}{}^{*} + O_2 \rightarrow \text{cyclo-}C_6H_{10}O + H_2O \quad . \quad . \quad (5)$$

might be occurring, though it is not possible to distinguish between this reaction and the formation of an intermediate excited cyclo-$C_6H_{11}\cdot OOH$ which then decomposes to ketone. Reaction (5) could occur in some photo-oxidation processes though it is likely to require considerable excitation energy.

The limiting yield of cyclohexane is decreased to 0·38 in ærated solution. Thus there may be competition between reaction (5) and some other process in which cyclo-$C_6H_{12}{}^{*}$ is destroyed. Our results indicate that there is no apparent effect of iodine concentration on reaction (5). However, in deærated cyclohexane solution, iodine quenches both scavengeable and non-scavengeable processes with comparable efficiency.[4] Quenching of cyclo-$C_6H_{12}{}^{*}$ by iodine must be relatively much less efficient than reaction with oxygen.

Indirect confirmation of reaction (5) is obtained from measurements of the alcohol yields. Disproportionation of cyclo-$C_6H_{11}O_2\cdot$ radicals would lead to production of equal amounts of cyclohexanone and cyclohexanol. Our results indicate that the yield of cyclohexanol is always less than that of cyclohexanone by an amount equal to the limiting value of *G*(cyclohexanone). These results are contrary to the findings of others[2] though their results were obtained at much greater total doses.

We have found evidence for the existence of a similar molecular oxidation process in n-hexane, and experiments are in progress to investigate the possibility of such processes in other organic systems.

One of us (G.D.) thanks the Department of Scientific and Industrial Research for a maintenance allowance.

(*Received, January* 31*st*, 1963.)

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Precise Measurements with the Glass Electrode: the Time Variation of E.M.F.

By W. H. BECK, J. CAUDLE, A. K. COVINGTON, and W. F. K. WYNNE-JONES
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NEWCASTLE-UPON-TYNE, 1)

IT is now no longer disputed that the potential of a glass electrode newly placed in a solution may vary with time.[1] There is some confusion whether this is due to a slow response to proton activity, when a steady value should be taken as the correct e.m.f., or whether it is due to other reactions at the electrode surface, when an initial value should be taken. Beck and Wynne-Jones[2] concluded that the glass electrode responds instantaneously to proton activity and ascribed any time variation to asymmetry potential changes due to other potential-influencing reactions occurring at the glass–solution interface. Using this concept, Covington and Prue[3] extrapolated the linear e.m.f.–time graphs obtained when low-resistance glass electrodes were transferred rapidly with washing between dilute hydrochloric acid solutions to the time of transfer, the contribution of the asymmetry potential to each cell then being the same and on subtraction cancelling. Clever and Reeves[4] recently used high-resistance electrodes and this technique but changed the concentration of hydrochloric acid within one cell instead of using two solutions and separate reference electrodes. The e.m.f. was followed with time until the change became linear, and this linear portion was extrapolated to the time the acid concentration was changed.

Caution must be exercised in applying extrapolation techniques and a short account of our investigation of the problem of e.m.f. variation is presented for the guidance of users of glass electrodes.

We have tested various commercial electrodes, conditioned in distilled water, by transferring them between acid solutions of various concentrations each containing hydrogen reference electrodes. If a glass electrode behaves as a hydrogen electrode the e.m.f. of all cells should be identical. If a time variation occurs this can be described as a time-variable error, being the difference between the e.m.f. at a certain time in the second solution and the final e.m.f. in the first solution. Careful attention to shielding and to the prevention of electrical leakage is necessary to avoid spurious effects. Recorder traces of the output of a vibrating condenser electrometer were obtained on which the e.m.f. was measurable to 0·1 mv.

The e.m.f.–time variation may contain the following features, singly or combined: (*A*) a rapid change over the first few minutes which is largely independent of solution composition and concentration and is probably electrical rather than electrochemical in origin; (*B*) a zero, or slight and approximately linear, change; and (*C*) a rapid change, the rate of which slowly decreases, but a steady value is rarely being reached even after many hours and occasionally turning values are observed. There is evidence that other ions and probably water participate in reactions at the glass surface during (*C*).

Broadly, the characteristics of the electrodes tested fall into two classes depending upon which of the above are observed:

Class I. Electrodes recommended for use in the pH range 1—9, of resistance $< 200\ \mathrm{M}\Omega$ and believed to be made from MacInnes–Dole (soda) glass (Corning 015).

Feature (*A*) is absent. At low and intermediate acid concentrations, (*B*) is observed and extrapolation to the time of transfer shows no error (± 0·1 mv). Above a molality dependent upon the acid anion [HCl(1m), HBr(5m), sulphuric(7m), phosphoric, acetic, and perchloric acid (10m)] characteristic behaviour (*C*) is found. The error becomes more negative with time and increasing acid concentration. Reasonable extrapolation of the non-linear trace leads to smaller but apparently non-zero errors.

Class II. Electrodes usually described as "general purpose" (1—13 pH), believed to be made from lithia glass and of resistance $> 200\ \mathrm{M}\Omega$.

The characteristic e.m.f.–time curves consist of both features (*A*) and (*B*). Only at very high concentrations are (*A*) and (*C*) observed. The linear portion (*B*) when extrapolated may give an error of ± 0·3 mv, but the error at any time in (*B*) also does not exceed ± 0·3 mv.

The electrodes used by Clever and Reeves[4] apparently showed (*A*–*B*) behaviour unless the initial change had its origin in their titration technique. In either case they were correct in ignoring the initial change.

Pretreatment[5] of the glass electrode in a medium similar to that it is to be used in, reduces time variations, *i.e.*, asymmetry potential changes, and may alter the characteristic pattern of the time variation from (*C*) to (*B*), making precise measurements

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[1] Mattock, "pH Measurement and Titration," Heywood, London, 1961, pp. 104—106.
[2] Beck and Wynne-Jones, *J. Chim. phys.*, 1952, **49**, C97.
[3] Covington and Prue, *J.*, 1955, 3696; Covington, *J.*, 1960, 4441.
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possible. The success of work[3] with hydrochloric acid depended upon pretreatment of the electrodes in 0·1M-hydrochloric acid. If low-resistance electrodes are pretreated in distilled water asymmetry-potential changes are rapid and extrapolation is difficult. Accurate measurements are most likely to be possible if adequately tested glass electrodes on transfer between solutions are subjected to only small changes in pH, ionic environment, and water activity.

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Reaction of Olefin–Palladium(II) Chloride Complexes with Nucleophiles: Mechanistic Considerations

By E. W. STERN
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OLEFIN–PALLADIUM(II) chloride complexes react with a variety of nucleophiles in non-aqueous media to yield vinyl compounds.[1] The following is a discussion of recent observations which bear on the mechanism of this reaction.

The reactions of propene and [2-^{2}H]propene with acetic acid in "iso-octane" at initial pressures of 2 atmospheres and room temperature in the presence of palladium(II) chloride and disodium hydrogen phosphate gave results summarised in the Table. The apparent reaction velocity of propene is greater than that of [2-^{2}H]propene by a factor of 2·8, indicating rupture of the C–H bond at the central carbon atom of propene in the rate-determining step. The observed retention of deuterium by propenyl acetates formed from [2-^{2}H]propene rules out proton loss from the carbon undergoing nucleophilic attack[2] as a mechanistic possibility. The extent of retention supports a mechanism involving a 1,2 shift of hydride from the attacked carbon, followed by proton loss from an adjacent carbon atom. In the absence of an appreciable isotope effect in the latter step, a minimum deuterium retention of 71% would be expected.

	Propene	[2-^{2}H]propene
Total acetate yield (mole % calc. on $PdCl_2$)	15	10
Acetate (%) as isopropenyl acetate	64·0	63·6
Acetate (%) as propenyl acetate	36·0	36·4
Apparent reaction velocity (acetate yield/hr.)	0·31	0·11
Acetate (%) containing deuterium	—	75

Under similar conditions, *cis*-but-2-ene reacted with acetic acid to yield, on hydrogenation, s-butyl acetate as the sole product. It is concluded from this that methyl migration does not occur and cannot be used to rationalise the formation of propenyl acetate from propene.

Evidence for hydride migration has also been presented in the reaction of the complex $(C_2H_4PdCl_2)_2$ with deuterium oxide, which yielded acetaldehyde free from deuterium, indicating that vinyl alcohol was not a reaction intermediate.[3] The lack of exchange cited in this case is consistent with a direct 1,2 shift of hydride.[4] However, transfer involving an intermediate hydridopalladium complex cannot be rigorously excluded at this time.

The absence of diacetates from the products of reactions of olefins with an excess of acetic acid at room temperature[1] suggests strongly that formation of free carbonium-ion species after nucleophilic attack[3] is unlikely. Formation of 1,1-diacetates, when reactions were carried out at higher temperatures, or products of room temperature reactions were subjected to heat, as in distillation, can be explained by addition of acetic acid to the vinyl acetate formed initially.

The observation that the inclusion of water in reaction media leads to the production of carbonyl compounds indicates a greater intrinsic rate for the water reaction. In view of the relatively low nucleophilicity of water toward either carbon or palladium(II) complexes in replacement reactions,[5] this difference in rates may reflect the relative ease of solvation of the olefin–palladium(II) chloride complex,[6] the ease of proton loss from an O–H relative to a C–H bond in the final step, a steric phenomenon, or an effect of the nucleophilic ligand on electron distribution in the olefin complex.

The author is grateful to Mr. A. S. Logiudice for assistance with experimental work and to Dr. H. P. Leftin for discussions.

(*Received, January 19th*, 1963.)

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[3] Hafner, Jira, Sedlmeier, and Smidt, *Chem. Ber.*, 1962, **95**, 1575.
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The Stereochemistry and Conformation of π-Cyclopentadienyl-1-phenylcyclopentadienecobalt

By M. R. CHURCHILL and R. MASON
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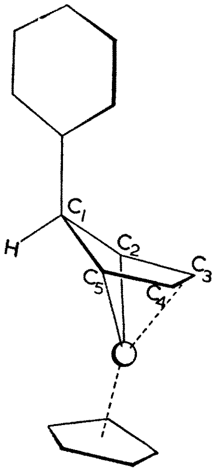
INFRARED and nuclear magnetic resonance studies of a number of transition-metal–cyclopentadiene compounds have indicated the non-equivalence of the methylene protons.[1] In the case of π-cyclopentadienylcyclopentadienecobalt, an intense band at 2781 cm.$^{-1}$ in the infrared spectrum is assigned to the 1-H_α stretch, H_α being the methylene-hydrogen atom $C_{(1)}$–H_α in the *endo*-position and assumed to lie in close proximity to, and interact with, the cobalt atom; the high-resolution nuclear magnetic resonance spectrum of this compound shows the methylene-protons as two doublets, the higher of which (τ 8·1) is assigned to the H_α resonance. The absence of a carbon–hydrogen stretching vibration in the 2780 cm.$^{-1}$ region[2] and of the H_α resonance[3] in π-cyclopentadienyl-1-phenylcyclopentadienecobalt has led to the suggestion[2] that the phenyl group occupies the *endo*-position, the cyclopentadiene ligand being assumed to be planar and bonded to the cobalt ion by two π-bonds.

We have carried out a complete single-crystal *X*-ray analysis of this compound. It has space group *Pbca* (D_{2h}^{15}; no. 61) with eight molecules in a unit cell of dimensions $a = 29{\cdot}64$, $b = 7{\cdot}70$, $c = 10{\cdot}68$ Å. The crystal structure has been determined by Patterson, Fourier, and least-squares analyses of 750 three-dimensional reflexions, the refinement analysis converging to the present discrepancy index $R = 0{\cdot}106$ after five cycles of refinement.

The Figure shows the essential geometry of the molecule.

The phenyl group occupies the *exo*-position and the "cyclopentadiene" ring is non-planar with C-1 bent away from the cobalt atom (by 36°), resulting in a cobalt–carbon distance of 2·55 Å, compared with an average cobalt–carbon distance of 2·01 Å (estimated standard deviation 0·03 Å) for the remaining four carbon atoms of this system. The plane of these four atoms and that of the π-cyclopentadienyl ring are essentially parallel ($\pm$ 4°). The average cobalt–carbon distance in the π-cyclopentadienyl ring is 2·06 $\pm$ 0·03 Å, indicating that the bonding of the cyclopentadiene to the metal is slightly stronger than that for the π-cyclopentadienyl, a feature indicated also by studies on π-cyclopentadienyl(tetramethylcyclopentadienone)cobalt[4] and its tetrakistrifluoromethyl analogue.[5]



The short bond length of 1·38 Å for the 3,4-bond in the cyclopentadiene ring, and the deviation of C-1 from the plane of the ring indicate that the cyclopentadiene is bonded to the cobalt by one π- and two σ-bonds, an unusual mode of bonding already postulated by Wilkinson *et al.*[1,6] for tricarbonyl(tetrakistrifluoromethylcyclopentadienone)iron (the structure of which will be published elsewhere[7]). In simple valence-bond terms,[8] three bonds to points in the π-cyclopentadienyl ring complete the expected octahedral co-ordination of the d^6 cobalt ion, which has a formal oxidation state of +3, as has its precursor di-π-cyclopentadienylcobalt iodide.

The cobalt–methylene-hydrogen distance (on an assumed $C_{(1)}$–H bond length of 1·1 Å) is *ca.* 3·0 Å, so that, although the hydrogen is in a formal *endo*-conformation, it is not close enough to the cobalt for interaction to occur (this would result in the characteristic $C_{(1)}$–H_α stretch at 2780 cm.$^{-1}$). It is possible that, in those cyclopentadiene derivatives for which this stretch *is* observed, C-1 will be displaced in the opposite direction, thereby allowing Co–H_α inter-

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[1] Green, Pratt, and Wilkinson, *J.*, 1959, 3753.
[2] Fischer and Herberich, *Chem. Ber.*, 1961, **94**, 1517.
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[6] Boston, Sharp, and Wilkinson, *J.*, 1962, 3488.
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action. Such a scheme has already been proposed for a number of π-cyclohexadienyl complexes of transition-metal ions.[9]

We are grateful to Professor G. Wilkinson for discussions, Drs. O. S. Mills, J. S. Rollett, and R. Sparks for computer programmes, and the Department of Scientific and Industrial Research for a Research Studentship (to M.R.C.).

(*Received, January 29th*, 1963.)

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Covalent Bonding in Fluoro-salts of the Trimethyltin Group

By H. C. CLARK and R. J. O'BRIEN

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EVIDENCE has accumulated rapidly that trimethyltin derivatives, Me$_3$SnX, have structures in which the Me$_3$Sn group interacts strongly with X, conferring five co-ordination on the tin atom. This has been observed in Me$_3$SnF,[1] Me$_3$SnClO$_4$,[2] and Me$_3$SnBF$_4$.[3] Moreover, Me$_3$SnClO$_4$ and Me$_3$SnNO$_3$ react with ammonia to form the five co-ordinate cation Me$_3$Sn(NH$_3$)$_2^+$.[4]

In extending our own studies of these compounds, we have now examined two compounds in which the Me$_3$Sn group may interact with an octahedral ion. These are trimethyltin hexafluoro-arsenate and -antimonate, prepared as white crystalline solids from trimethyltin bromide and the corresponding silver salt in liquid sulphur dioxide. The weights of silver bromide recovered and the analyses were consistent with the formulæ. If these compounds are polymers similar to the perchlorate then planar Me$_3$Sn groups are interacting with the MF$_6$ octahedra through either *cis*- or *trans*-fluorine atoms. In the former case, the symmetry of MF$_6$ becomes C_{2v} and in latter D_{4h}.

The infrared spectrum of Me$_3$SnAsF$_6$ shows the following main features. (*a*) the ν_3 vibration, observed[5] for the free AsF$_6^-$ ion at 700 cm.$^{-1}$, is split into two bonds at 710 and 675 cm.$^{-1}$, the former being about twice as intense as the latter; this is consistent with D_{4h} symmetry. (*b*) Bands associated with the Me$_3$Sn group are located at 2900—3000 (C–H stretch), and 795 cm.$^{-1}$ (CH$_3$ rocking), while there are no bands in the 500—590 region in which Sn–C vibrations are usually found. Instead, a band of moderate intensity is found at 603 cm.$^{-1}$ and is presumably a Sn–C vibration; this shift indicates considerable interaction with the AsF$_6$ group. (*c*) No bands of any intensity were present in the 400—590 cm.$^{-1}$ region. We therefore believe that the AsF$_6$ group interacts through *trans*-fluorine atoms with Me$_3$Sn to form a chain structure in which the tin atom is five co-ordinate.

For Me$_3$SnSbF$_6$, the infrared spectrum shows the following features: (*a*) the ν_3 vibration, observed[5] for the free SbF$_6^-$ ion at 660 cm.$^{-1}$, is resolved into three components at 675, 656, and 640 cm.$^{-1}$. This number of components is consistent with C_{2v} symmetry. (*b*) A new band is present at 875 cm.$^{-1}$, and a doublet at 472, 454 cm.$^{-1}$ appears. The appearance of such bands, particularly those at low frequency is also consistent with lower symmetry for the SbF$_6$ group. (*c*) The band observed at 603 cm.$^{-1}$ in the AsF$_6$ compound is found at 606 cm.$^{-1}$ in the hexafluoroantimonate and is associated with the Me$_3$Sn group.

Again, there must be strong interaction between Me$_3$Sn and SbF$_6$. The spectra provide strong evidence that, as a result of this interaction, the hexafluoroantimonate group has a *cis*-configuration while the hexafluoroarsenate group has a *trans*-configuration. This is consistent with the structure of SbF$_5$ in which *cis* fluorine atoms act as bridges between SbF$_6$ octahedra.[6] We are now attempting to confirm these configurations by nuclear magnetic resonance methods.

It has, therefore, not yet been possible to obtain an Me$_3$SnX compound in which there existed a free Me$_3$Sn$^+$ ion; in all cases strong interaction occurs and the tin atom is essentially five co-ordinate.

We are grateful for the assistance of Dr. C. Reid, and for the financial support of the National Research Council, and the award of a Canadian Industries Ltd. Fellowship to R.J.O'B.

(*Received, February 25th*, 1963.)

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[2] Okawara, Hathaway, and Webster, *Proc. Chem. Soc.*, 1963, 13.
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[4] Clark and O'Brien, *Inorg. Chem.*, 1963, in press.
[5] Peacock and Sharp, *J.*, 1959, 2762.
[6] Hoffman, Holder, and Jolly, *J. Phys. Chem.*, 1958, **62**, 364.

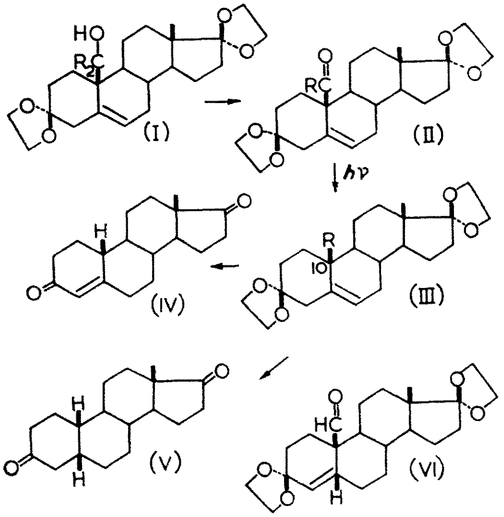
On the Photochemical Decarbonylation of a Homoallylic Conjugated Aldehyde[1]

By J. IRIARTE, J. HILL, K. SCHAFFNER, and O. JEGER
(ORGANISCH-CHEMISCHES LABORATORIUM DER EIDGENÖSSISCHEN TECHNISCHEN HOCHSCHULE, ZÜRICH)

WE report a light-induced unimolecular decarbonylation of a steroidal $\beta\gamma$-unsaturated aldehyde which shows properties of homoallylic conjugation. 3,17-Bisethylenedioxyandrost-5-en-19-al (II; R = H), m.p. 169—171° (decomp.), $[\alpha]_D$ −249° (*c* 1·44),[2] $\lambda_{max.}$ 226 and 310 mμ (ϵ 1255 and 113 in EtOH),[3] was prepared in excellent yield by oxidation of the alcohol (I; R = H)[4] with chromium trioxide in pyridine. Irradiation in ethanol at room temperature, using a high-pressure mercury lamp with Pyrex filter, caused evolution of carbon monoxide and conversion of the aldehyde (II; R = H) into compound (III; R = H), m.p. 131—132°, $[\alpha]_D$ −13° (*c* 1·41), in more than 90% yield. The reaction was not sensitive to the presence of oxygen, but when a quartz vessel and a low-pressure mercury lamp (*ca.* 90% emission at 254 mμ) was used the rate of decarbonylation was significantly slower.

The structure of the photoproduct (III; R = H) was established as follows: Acid-catalysed hydrolysis of (III; R = H) quantitatively gave œstr-4-ene-3,17-dione (IV).[5] The 10β-configuration of the photoproduct was confirmed by hydrogenation of (III; R = H) with palladium on charcoal in ethanol to a mixture of saturated 3,17-bisethylenedioxyœstranes, and acid hydrolysis of the major component to 5β-œstran-3,17-dione (V).[6] A blank experiment in the absence of hydrogen demonstrated that (III; R = H) remained unchanged under the conditions of hydrogenation.[7]

In order to trace the origin of the hydrogen atom at position 10 of compound (III), the deuterated aldehyde (II; R = D), m.p. 180—182°, $[\alpha]_D$ −241° (*c* 0·51), $\lambda_{max.}$ 226 and 310 mμ (ϵ 1380 and 113 in EtOH)[3] was irradiated. This compound was synthesised from methyl 3,17-dioxoandrost-4-en-19-oate[8] by ketalisation to methyl 3,17-bisethylenedioxyandrost-5-en-19-oate, m.p. 185—186°, $[\alpha]_D$ −113° (*c* 0·39), reduction with lithium aluminium deuteride to the alcohol (I; R = D), m.p. 196°, $[\alpha]_D$ −57° (*c* = 0·38), and oxidation with chromium trioxide in pyridine. On irradiation of the aldehyde (II; R = D) under conditions identical to those described in the first experiment, 3,17-bisethylenedioxy[10β-D]œstr-5-ene (III; R = D), m.p. 133°, $[\alpha]_D$ −11° (*c* 0·51), was formed in equally excellent yield. Mass-spectrometric comparison of the starting aldehyde (II; R = D) and the photoproduct (III: R = D) revealed no loss of deuterium during the photochemical step (deuterium content 98—99 ± 1% in both compounds).



Preliminary experiments with the saturated aldehyde (VI), m.p. 97—103°, which was obtained by oxidation with chromium trioxide in pyridine of the amorphous 3,17-bisethylenedioxy-5β-androstan-19-ol,[9] $[\alpha]_D$ + 5° (*c* 0·49), indicate that comparable irradiation conditions lead to a complex mixture of products. Decarbonylation appears to take place only to a small extent. Thus the important role of the double bond in the conversion of the aldehydes (II) into the product (III) is demonstrated.

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[1] Photochemical Reactions, Part 21; Part 20, *Helv. Chim. Acta*, 1963, **46**, 678.

[2] M.p. are uncorrected, all $[\alpha]_D$ refer to $CHCl_3$ solutions.

[3] An analogous chromophore is *e.g.*. present in dianhydrodihydrostrophanthidin; for a discussion of its ultraviolet absorption cf. Cookson and Wariyar, *J.*, 1956, 2302.

[4] Amorosa, Caglioti, Cainelli, Immer, Keller, Wehrli, Mihailović, Schaffner, Arigoni, and Jeger, *Helv. Chim. Acta*, 1962, **45**, 2674.

[5] Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5366.

[6] Rapala and Farkas, *J. Amer. Chem. Soc.*, 1958, **80**, 1008.

[7] The structure proof for the photoproduct (III; R = H) provides indirect evidence in favour of the 10α-configuration of the (different) 3,17-bisethylenedioxyœstr-5-ene, m.p. 135—137°, which had been obtained earlier *via* another route, and to which formula (III; R = H) had been provisionally assigned (cf. ref. 4, p. 2683, compound no. 52).

[8] Hagiwara, Noguchi, and Nishikawa, *Chem. Pharm. Bull.* (*Japan*), 1960, **8**, 84.

[9] The preparation of this compound will be reported elsewhere.

This photochemical decarbonylation of a $\beta\gamma$-unsaturated aldehyde represents a novel and efficient method for stereospecific labelling of an allylic position. Its mechanism and scope are currently under investigation.

From all new compounds satisfactory analyses and spectroscopic data (infrared and nuclear magnetic resonance spectra) have been obtained. We are indebted to Dr. J. Seibl for providing the mass-spectrometric data.

Generous financial support from CIBA Aktiengesellschaft, Basel, is gratefully acknowledged. Two of us thank Syntex S.A., Mexico (J.I.), and DSIR/NATO (J.H.) for fellowships.

(*Received, February 25th*, 1963.)

Generation of Tetraphenylcyclobutadiene and its Adducts from its Palladium Chloride Complex

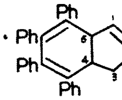
By R. C. COOKSON and D. W. JONES

(THE UNIVERSITY, SOUTHAMPTON)

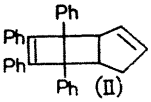
WE have used Malatesta's tetraphenylcyclobutadiene–palladium chloride complex, conveniently made from diphenylacetylene,[1] as a source of tetraphenylcyclobutadiene. Because of the publication of preliminary work on the same complex[2] we report some of our own results now.

Like Maitlis and Stone[2] we had found that treatment of the complex with triphenylphosphine in benzene gives in good yield bistriphenylphosphine-palladium dichloride, m.p. 297—298° (decomp.), and the tetraphenylcyclobutadiene dimer[3–5] of m.p. 430°. When the reaction was carried out in the presence of methyl phenylacetylenecarboxylate the intermediate cyclobutadiene was trapped[6] as methyl pentaphenylbenzoate, m.p. 355—360°, identical with a sample prepared from methyl phenylacetylenecarboxylate and tetraphenylcyclopentadienone.[7]

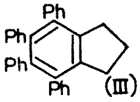
When the reaction was conducted in cyclopentadiene an adduct was formed, m.p. 184—187° (Found: C, 93·6; H, 6·2%; *M*, 400). The proton magnetic resonance spectrum, measured at 80 Mc/sec. in deuterochloroform, showed clearly that a bicyclo[2,2,1]heptene unit was absent; while the spectrum was consistent with the presence of a cyclopentene unit, having a broad doublet centred on 7·15 τ from the methylene group (C-3), a multiplet centred on 6·5 τ from the 4-proton, a broad doublet at 5·76 τ, J = 10·4 c/sec., from the 5-proton, and two multiplets centred on 4·4 and 4·09 τ from the olefinic protons. The gross structure was confirmed by synthesis of the same hydrocarbon by loss of carbon monoxide at 140° from the adduct of tetraphenylcyclopentadienone and cyclopentadiene. Neither the magnetic resonance nor the ultraviolet spectrum* ($\lambda_{\max.}$ in ethanol 312 mμ, ϵ 9450) clearly distinguishes between the valency tautomers (I) and (II), although earlier workers have always assumed, without rigorous proof, that analogous products from tetraphenylcyclopentadienone had structures corresponding to (I). The very ready aromatisation of the dihydro-derivative to the indane (III) with *N*-bromosuccinimide at room temperature does favour the cyclohexadiene structure (I). The problem is of some interest since it might give evidence on whether tetraphenylcyclobutadiene reacts in the closed (IV) or open form (V). So far we have not succeeded in isolating an adduct in which the four-membered ring is retained.



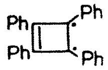
(I)



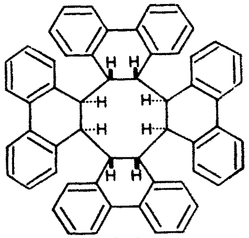
(II)



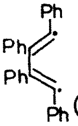
(III)



(IV)



(VI)



(V)

On the basis of the absence of C=C absorption from its Raman spectrum and the $\bar{4}$ symmetry of its unit cell, Freedman and Petersen[5] have assigned the structure "octaphenylcubane" to the dimer of tetra-

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* The spectrum of 1,2,3,4-tetraphenylcyclobutene, $\lambda_{\max.}$ 303 mμ, ϵ 19,500, which has just been recorded,[8] is sufficiently different to favour structure (II).

[1] Malatesta, Santarella, Vallarino, and Zingales, *Angew. Chem.*, 1960, **72**, 34.

[2] Blomquist and Maitlis, *J. Amer. Chem. Soc.*, 1962, **84**, 2329; Maitlis and Stone, *Proc. Chem. Soc.*, 1962, 330.

[3] Braye, Hübel, and Caplier, *J. Amer. Chem. Soc.*, 1961, **83**, 4406.

[4] Freedman, *J. Amer. Chem. Soc.*, 1961, **83**, 2195.

[5] Freedman and Petersen, *J. Amer. Chem. Soc.*, 1962, **84**, 2837.

[6] Cf. Berkoff, Cookson, Hudec, and Williams, *Proc. Chem. Soc.*, 1961, 312, and ref. 4.

[7] Dilthey, Thewalt, and Trösken, *Ber.*, 1934, **67*B***, 1959.

[8] Freedman and Frantz, *J. Amer. Chem. Soc.*, 1962, **84**, 4165.

phenylcyclobutadiene. The ultraviolet spectrum,[3] which we have confirmed ($\lambda_{max.}$ 267 mμ, ϵ 44,600, in tetrahydrofuran), would have to be explained by conjugation involving the bent bonds. Another possibility, which would be consistent with the alternating tetrad axis, with its thermal stability, and with its ultraviolet spectrum, would be the tautomeric structure (VI).

The palladium chloride complex reacts much more rapidly with ethylenebisdiphenylphosphine,[9] $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$, than with triphenylphosphine to give the diphosphine–palladium chloride complex and tetraphenylcyclobutadiene adducts or dimer. In benzene or chloroform at 20° a coloured solution is immediately formed (green or red, respectively) that gives a strong and well-resolved electron spin resonance spectrum, which is now being analysed and must be attributed to at least two radicals.

We are most grateful to Drs. R. C. Smith and T. M. Wilmshurst for the electron and Dr. S. A. Knight for the proton spin resonance spectra.

(*Received, February* 14*th*, 1963.)

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[9] Chatt and Hart, *J.*, 1960, 1378.

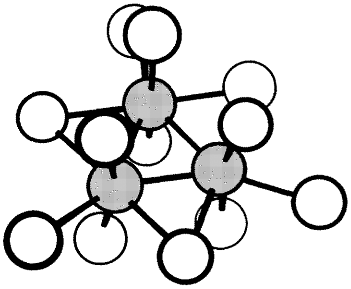
The Configuration of the Anion in $CsReCl_4$

By WARD T. ROBINSON, J. E. FERGUSSON, and BRUCE R. PENFOLD
(DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CANTERBURY, CHRISTCHURCH, NEW ZEALAND)

LIGAND field theory has been used to predict that the anion $[ReCl_4]^-$ is regular tetrahedral[1] with a d_γ^4 electron configuration for Re(III). The magnetic moment[2] of $RbReCl_4$ does not contradict this prediction. With a view to confirming the stereochemistry of rhenium in this anion we have carried out an *X*-ray analysis of the compound of empirical composition $CsReCl_4$.

The crystals are orthorhombic with the non-centrosymmetric space group *Ama*2. There are 12 $CsReCl_4$ units in a unit cell of dimensions a = 10·66, b = 14·08, and c = 14·02 Å. All atoms have been located with the aid of three-dimensional electron-density maps and, for the incompletely refined structure, the *R* factor for all observed (*hkl*) reflections is 0·21.

The $[ReCl_4]^-$ anion is not tetrahedral but is trimeric with a triangle of bonded rhenium atoms. Each of these is bonded to two bridging chlorine atoms and one terminal chlorine atom in the plane of the triangle and also to two chlorine atoms on opposite sides of this plane (see Figure). Rhenium atoms are therefore seven-co-ordinate and each is at the centre of a distorted pentagonal bipyramid which has as its apices two chlorine atoms. If there are to be sufficient bonding orbitals it is clear that a seven-co-ordinate rhenium(III) atom requires a spin-paired d^4 electron configuration.[3]



The space group requires of the ion only a plane of symmetry. This passes through one rhenium and its three attached terminal chlorines, and also the bridging chlorine to which it is not bonded. However, the ion possesses symmetry 32 (= D_3) within experimental error, the three-fold axis being normal to the triangle of rhenium atoms.

Mean values for bond lengths are: Re–Re = 2·50 Å, Re–Cl (bridging) = 2·43 Å, Re–Cl (terminal in plane of rhenium atoms) = 2·60 Å, and Re–Cl (terminal off plane of rhenium atoms) = 2·35 Å.

A detailed account of the crystal structure analysis will be presented later together with a full discussion of this most interesting, and previously unreported stereochemical arrangement.

All calculations were carried out on the University of Canterbury IBM 1620 computer using programmes written by us and by Dr. D. van der Helm of the Institute for Cancer Research, Philadelphia 11, Pa., U.S.A. The work was supported by the New Zealand Universities Research Committee by grants for equipment and a Research Fellowship (to W.T.R).

(*Received, February* 8*th*, 1963.)

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[1] Orgel, "Quelques Prob. de Chemie Minerale," 10th Solvay Conf., 1956, 289.
[2] Klemm and Frischmuth, *Z. anorg. Chem.*, 1943, **13**, 253.
[3] Nyholm, *Proc. Chem. Soc.*, 1961, 273.

Elemental Organic Compounds. Part VII.[1] A Bridged Bisbenzenechromium π-Complex*

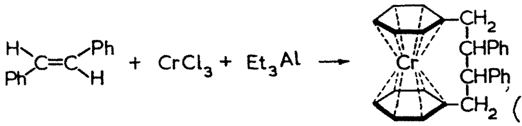
By M. TSUTSUI and M. N. LEVY

(NEW YORK UNIVERSITY, RESEARCH DIVISION, DEPARTMENTS OF CHEMICAL ENGINEERING AND CHEMISTRY, NEW YORK 53, U.S.A.)

MANY bridged metallocenes have been reported.[2] We now report preparation of the first bridged bisarene π-complex, (I) in a one-step synthesis; it results from the reduction of a transition-metal halide by triethyl aluminum in an arene environment.

The iodide or tetraphenylborate of the complex (I) was obtained on reaction of chromic chloride (1 mol.), *trans*-stilbene (1 mol.), and triethylaluminum (3 mol.) in boiling n-heptane. The iodide was precipitated and it crystallised from chloroform and n-pentane as golden-orange crystals, m.p. 145—146°, $\lambda_{max.}$ 275—285 mμ (ϵ 2·5 × 10^4) [Found: C, 60·75; H, 4·7; Cr. 9·7%; *M*, 550, 557 (thermoelectric measurement in dibromomethane). $C_{28}H_{26}CrI$ requires C, 61·0; H, 4·7; Cr, 9·4%; *M*, 541].

Pyrolysis of the iodide or its reduction[3] by lithium aluminium hydride gave 1,2,3,4-tetraphenylbutane, proving the presence of this hydrocarbon as ligand. No trace of this was detected in the original reaction, eliminating the possibility that it was a reaction coupling product. The magnetic susceptibility of the complex, kindly determined by the Gouy method by Dr. W. Cave, Monsanto Chemical Company, St. Louis, Missouri, was 1·96 B.M. The assignment of complex-formation between the 1- and the 4-phenyl group rather than between those in other positions is based on conformational feasibility from molecular models. In addition, our proposed mechanism of cyclic reductive dimerisation of *trans*-stilbene with simultaneous π-donation suggests the 1- and the 4-phenyl group as those most favourably disposed.



(I)

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society and the Arakawa Forest Chemical Company, Osaka, Japan for support of this research.

(*Received, January 21st, 1963.*)

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* Presented, in part, at the 142nd National Meeting of the American Chemical Society, September, 1962.

[1] Paper VI, Tsutsui and Chang, *Canad. J. Chem.*, in the press.

[2] Rinehart, Curby, Gustafson, Harrison, Bozak, and Budlitz. *J. Amer. Chem. Soc.*, 1962, **84**, 3263; Rosenblum, Banerjee, Danieli, and Herrich, *Tetrahedron Letters*, 1962, 423; Schlögl and Reterlik, *ibid.*, p. 573; Gustafson, *Diss. Abs.*, 1962, **23**, 71; Schlögl and Seiler, *Monatsh.*, 1960, 91, 79; *Tetrahedron Letters*, 1960, No. 7, 4.

[3] Zeiss and Tsutsui, *J. Amer. Chem. Soc.*, 1957, **79**, 3062.

NEWS AND ANNOUNCEMENTS

Chemical Society Awards.—The Council has awarded the following Medals for 1963:

Longstaff Medal to Lord Todd.
Flintoff Medal to Professor H. Raistrick.

Chemical Society Lectureships.—The Council has made the following appointments for 1963—64:

Liversidge Lectureship	Professor J. S. Anderson
Simonsen Lectureship	Professor G. Ourisson (Strasbourg)
Tilden Lectureships	Dr. V. M. Clark Professor A. F. Trotman-Dickenson
Centenary Lectureship	Professor C. Djerassi (Stanford, California)
Robert Robinson Lectureship	Professor R. B. Woodward (Harvard)

Ethel Behrens Awards.—In connection with the Anniversary Meetings held at Cardiff on March 26—29th, 1963, the Council of the Society awarded grants from the Ethel Behrens Fund to the following Fellows: R. G. S. Banks (Balliol College, Oxford), R. A. Dawe (St. Catherine's College, Oxford), J. V. Ramsbottom (Balliol College, Oxford), and R. G. Thorp (Balliol College, Oxford).

Election of New Fellows.—152 Candidates were elected to the Fellowship in March, 1963.

Deaths.—We regret to announce the deaths of *Mr. A. T. Dann* (15.12.62), of the Annual Health Research Laboratory, Parkville, Victoria; *Dr. P. Hudson* (9.2.63), of the University of Sydney, N.S.W.; and *Dr. A. D. Mitchell* (25.3.63), Ilford, Assistant Editor 1926—1962.

Library.—The Library will close for the Whitsun Holiday from 6 p.m., Friday, May 31st, until 9.30 a.m., Wednesday, June 5th, 1963.

Royal Society.—The following were included amongst those elected to the Fellowship of the Royal Society on March 21st:

Dr. Thomas Stevens Stevens, Reader in Organic Chemistry in the University of Sheffield. Distinguished for his original researches in organic chemistry, particularly for his work on the mechanism of molecular rearrangements.

Dr. Theodore Morris Sugden, Reader in Physical Chemistry in the University of Cambridge. Distinguished for his work on the detection and identification of transient species, radicals, ions, and electrons, in flames and on the reaction mechanisms involved.

Professor Arthur James Cochrane Wilson, Professor of Physics in the University of Wales, University College of South Wales and Monmouthshire, Cardiff. Distinguished for his contributions to *X*-ray analysis in the elucidation of the atomic structure of crystals.

National Chemical Laboratory—Standard Samples of Organic Compounds.—Additions have recently been made to the list of pure compounds which are available from the National Chemical Laboratory. The samples are suitable for calibration of spectrometers and for precise physicochemical measurements. Most of the 78 compounds now listed have a certified purity of greater than 99.9 per cent. Further information on the supply of these Standard Samples can be obtained from The Director, National Chemical Laboratory, Teddington, Middlesex.

The American Crystallographic Association is to publish as Monograph No. 5 the 2nd Edition of "Crystal Data (Determinative Tables)," covering the literature from 1912—1960. It is obtainable from the Polycrystal Book Service, G.P.O. Box 620, Brooklyn 1, N.Y., Price $20.00.

Personal.—*Dr. M. P. Barnett*, Associate Professor of Physics and Director of the Co-operative Computing Laboratory at the Massachusetts Institute of Technology, has been appointed to the Readership in Information Processing tenable at the Computer Unit.

Professor N. B. Chapman has been appointed Foundation Governor of Batley Grammar School until March 24th, 1964, in place of Professor D. C. Johnson, who has resigned.

Dr. G. C. Culling, formerly of the University of Chicago, is now a Research Chemist at the Jackson Laboratory of E. I. Du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.

Dr. J. F. J. Dippy has been appointed Vice-Principal of Chelsea College of Science and Technology in addition to his present appointment as Head of the Department of Chemistry.

Dr. H. E. Hallam has been given a year's leave of absence from the University College of Swansea to become Adviser in Physical Chemistry to the new University of Nigeria at Nsukka.

Dr. A. B. Hart is now Head of the High-temperature Chemistry Section, Chemistry and Biology Division, Central Electricity Generating Board.

The Title of Reader in Cytochemistry in the University of London has been conferred on *Dr. J. S. Holt*, in respect of his post at Middlesex Hospital Medical School.

Dr. P. Johnson, formerly University Research Fellow at Birmingham Medical School, has been appointed Visiting Lecturer in the Biochemistry Division of the Chemistry Department, University of Illinois, Urbana, U.S.A.

Mr. K. A. R. Julian is now Technical Sales Manager for the North, R. and J. Dempster Ltd.

Mr. B. H. Kingston, formerly of A. Boake Roberts and Company Limited, has joined the staff of Proprietary Perfumes Limited.

Dr. R. H. Ottewill has been promoted to Lecturer in Physical Chemistry within the Department of Physical and Inorganic Chemistry at the University of Bristol.

Dr. E. C. Potter is now adviser to the Chemistry and Biology Division of the Central Electricity Generating Board on scientific matters, with particular reference to electrochemistry and corrosion.

The title of Reader in the History and Philosophy of Science has been conferred upon *Dr. W. A. Smeaton* in respect of his post at University College, London.

Dr. E. S. Stern is to succeed Dr. J. Chatt as Head of the Imperial Chemical Industries Ltd. organometallic research team at the Petrochemical and Polymer Laboratory at Runcorn Heath, formerly located at the Frythe.

Mr. J. R. Whinfield, C.B.E., inventor of "Terylene" and a Director of Imperial Chemical Industries Limited (Fibres Division) has retired.

Symposia, etc.—A Conference on Prediction and Assessment of Paint Performance will be held at Scarborough, Yorks. on June 25—29th, 1963. Further enquiries should be addressed to the Secretary, Oil and Colour Chemists Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2.

The Sixth International Conference of Ionisation Phenomena in Gases sponsored by the International Union of Pure and Applied Physics, will be held at Orsay, France, on July 8—13th, 1963. Further enquiries should be addressed to P. Hubert, CENFAR, Boite Postale 6, Fontenay-aux-Roses (Seine), France.

The Third International Conference on the Physics of Electronic and Atomic Collisions will be held in London on July 22nd—26th, 1963. Further enquiries should be addressed to the Conference Secretaries, Physics Department, University College, Gower Street, W.C.1.

The Sixth Congress of the European Molecular Spectroscopy Group sponsored by I.U.P.A.C., will be held in Budapest on July 22nd—27th, 1963. Further enquiries should be addressed to the Hungarian Academy of Sciences, Budapest, Hungary.

The Sixth International Congress on Nutrition will be held in Edinburgh on August 9—15th, 1963. Further enquiries should be addressed to Dr. A. B. Meiklejohn, Department of Clinical Chemistry, Royal Infirmary, University of Edinburgh, Edinburgh.

The Eleventh International Congress of Refrigeration will be held in Munich on August 27th—September 4th, 1963. Further enquiries should be addressed to International Institute of Refrigeration, 177, Boulevard Malesherbes, Paris 17e; or REFRICONGRESS, Pfeufferstr. 2, Munich 25.

A Symposium on Oxygen in the Animal Organism, sponsored by the International Union of Biochemistry and International Union of Biological Sciences, will be held in London, on September 1st—5th, 1963. Further enquiries should be addressed to Professor F. Dickens, Courtauld Institute of Biochemistry, Middlesex Hospital Medical School, London, W.1.

An International Symposium on Nitro-compounds arranged by the Polish Academy of Sciences under the auspices of the I.U.P.A.C. will be held in Warsaw on September 18—20th, 1963. Further enquiries should be addressed to Sekretariat Miedzynarodowego Sympozjonu o Nitrozwiazkach, Palac Staszica, Warsawa, Nowy Świat 72, Poland.

The Eleventh International Conference on Spectroscopy, sponsored by the Society for Applied Spectroscopy, will be held in Belgrade, from September 30th—October 4th, 1963. Further enquiries should be addressed to Dr. V. Vukanovič, General Secretary, Prirodno-matematicki č, Fakultet, Fizičko-hemijski zavod, Studentski trg. 16, Blok C, Belgrade, Yugoslavia.

An International Conference on Beryllium Oxide, sponsored by the Australian Atomic Energy Commission, will be held in Lucas Heights (near Sydney), Australia, on October 21st—25th, 1963. Further enquiries should be addressed to the Conference Secretary, A.A.E.C. Research Establishment, Private Mail Bag, Sutherland, N.S.W., Australia.

The Thirty-seventh Congress of the Australian and New Zealand Association for the Advancement of Science will be held in Canberra, Australia, from January 20—24th, 1964. Further information may be obtained from the Joint Secretaries, Section B, A.N.Z.A.A.S., Department of Chemistry, School of General Studies, Australian National University, Box 197, P.O., Canberra City, A.C.T., Australia.

An International Symposium on the Chemistry of Natural Products, arranged by the Science Council of Japan under the auspices of the I.U.P.A.C., will be held on April 12—18th, 1964. Further enquiries should be addressed to the General Secretary of the Organising Committee, Professor Kyosuke Tsuda, University of Tokyo, Japan.

The Third International Wool Textile Research Conference, organised by the Textile Institute of France under the patronage of the International Wool Secretariat and the International Wool Textile Organisation with the support of the Central Wool Committee of France, is to be held in Paris on June 28th–July 9th, 1965. Further enquiries should be addressed to Institut Textile de France, 59 Rue de la Faisanderie, Paris (16e).

FORTHCOMING SCIENTIFIC MEETINGS

London

Thursday, May 9th, at 6 p.m.

Hugo Müller Lecture, "The Biogenesis of Phenolic Alkaloids," by Professor D. H. R. Barton, D.Sc., F.R.S., to be given in the Lecture Theatre, The Royal Institution, Albemarle Street, W.1.

Thursday, June 6th, at 6 p.m.

Meeting for the Reading of Original Papers. To be held in the Rooms of the Society, Burlington House, W.1.

Birmingham

Friday, May 10th, at 4.30 p.m.

Hugo Müller Lecture, "The Biogenesis of Phenolic Alkaloids," by Professor D. H. R. Barton, D.Sc., F.R.S. Joint Meeting with the University Chemical Society, to be held in the Chemistry Department, The University.

Liverpool

Thursday, May 9th, at 5 p.m.

Lecture, "Magnetism and Stereochemistry of First Row Transition Elements," by Professor J. Lewis, Ph.D., D.Sc. Joint Meeting with the University Chemical Society, to be held in the Donnan Laboratories, Chemistry Department, The University.

Manchester

Thursday, May 2nd, at 6.30 p.m.

Hugo Müller Lecture, "The Biogenesis of Phenolic Alkaloids," by Professor D. H. R. Barton, D.Sc., F.R.S., to be given in Room F1, Manchester College of Science and Technology.

Northern Ireland

Tuesday, May 21st, at 4.30 p.m.
Official Meeting and Lecture, "Some Recent Developments in the Chemistry of Polyenes," by Professor B. C. L. Weedon, D.Sc., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Department of Chemistry, David Keir Building, Queen's University, Belfast.

North Wales

Thursday, May 9th, at 5.45 p.m.
Lecture, "Some Problems Experienced in the Manufacture of Pure Beryllium," by J. A. Dukes. Joint Meeting with the University College of North Wales Chemical Society, to be held in the Chemistry Department, University College, Bangor.

Oxford

(Joint Meetings with the Alembic Club, to be held in the Inorganic Chemistry Laboratory.)

Monday, May 13th, at 8.30 p.m.
Lecture, "Some New Natural Products—Structural and Biosynthetic Studies," by Dr. W. D. Ollis.

Monday, May 27th, at 8.30 p.m.
Lecture, "Reactions of some Cyclobutadiene Complexes," by Professor R. C. Cookson, M.A., Ph.D.

Reading

Tuesday, May 7th, at 5.45 p.m.
Lecture, "Simple and Complex Metal Nitrates and Nitrites," by Professor C. C. Addison, D.Sc., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and University Chemical Society, to be held in the Large Chemistry Lecture Theatre, The University.

OBITUARY NOTICES

SIR IRVINE MASSON

1887—1962

SIR IRVINE MASSON, M.B.E., formerly Vice-Chancellor of the University of Sheffield, died in Edinburgh on October 22nd, 1962, at the age of seventy-five. He was a grandson of David Masson, Professor of English Literature at University College, London, 1853—65, and at Edinburgh University, 1865—95, and the only son of Sir David Orme Masson, Professor of Chemistry at the University of Melbourne during 1886—1923.

James Irvine Orme Masson was born on September 3rd, 1887, in Melbourne, where he was educated at the Grammar School and University before coming to Great Britain in 1910 as an 1851 Exhibition Scholar. After a year with Sir James Walker at Edinburgh, Masson moved to University College, London, where he worked with Sir William Ramsay, with whom his father had been associated some thirty years earlier at University College, Bristol. In 1912 Masson became assistant in chemistry at University College, London, and during the First World War he served with the R.N.V.R. and later at the Research Department of the Royal Arsenal, Woolwich. He was appointed Reader in inorganic chemistry at University College in 1920, and served the Chemical Society both as secretary (1921—24) and as an ordinary member of Council (1929—32). He became the first Professor of Chemistry and Head of the Department of Pure Science of the University of Durham (Durham Division) in 1924, and in 1938 he was appointed Vice-Chancellor of Sheffield, where he remained until retirement in 1952. At the outbreak of the Second World War he added to his duties as Vice-Chancellor the active direction of a Ministry of Supply team which was housed in the Chemistry Department and engaged in research on explosives. He was also a member and chairman of several committees of the Ministry.

Irvine Masson was a man of varied talents. His chemical work, which led to election to the Royal Society in 1939, was not voluminous, since he never had a large team of helpers and much was done with his own hands. But his work is characterised by elegance and breadth; problems were reduced to the simplest possible terms and then approached by neat, ingenious, and well-considered methods. He belonged to the group of chemists—now non-existent—who could tackle equally well problems in the inorganic, physical, and organic sections of chemistry. His first publication in the *Journal* (1910, 851) dealt with the action of calcium carbide as a dehydrating agent, and from Australia also came work, in conjunction with his father, on the decomposition of metallic cyanates by water (*Z. phys. Chem.*, 1910, **70**, 290). Subsequent publications were concerned with the theory of solutions, and with the experimental investigation of van der Waals forces by the measurement of pressure–volume–temperature relations in pure and mixed gases up to pressures of 125 atmospheres. His use of the inert gases was clearly an outcome of association with Ramsay, for whom he had unbounded admiration; but the choice was nevertheless not haphazard. One of the initial objectives was to discover whether physical or chemical forces were responsible for volume changes on mixture; and, by finding similarities between mixtures of ethylene with oxygen and with argon, Masson produced, in the first paper of the series, *prima facie* evidence in favour of the physical explanation. This investigation of gases was continued for a period of nearly 10 years (*Proc. Roy. Soc.*, 1923, *A*, **103**, 524; 1929, *A*, **122**, 283; 1930, *A*, **126**, 268) and was probably the first systematic study of Dalton's law of partial pressures.

To the organic chemist his most significant contributions were his studies of nitration and of the organic compounds of iodine. The nitration work (in particular, *J.*, 1933, 105) is a classic, in which he delimited precisely the conditions requisite for the nitration of nitrobenzene and, in a fashion typical of his liking for graphical demonstration, exhibited his results with great clarity in the form of a triangular diagram. He did not arrive at the modern mechanism of nitration, but undoubtedly paved the way for those later researches which have had an important bearing on the development of theoretical organic chemistry. The study of organic iodine compounds had been neglected since the work of Victor Meyer and Willgerodt some forty years earlier; Masson developed this work in an important series of researches (*J.*, 1935, 1669; *Nature*, 1937, **139**, 150; *J.*, 1937, 1718; *J.*, 1938, 1699, 1702, 1708), in which he demonstrated once more his remarkable ability to apply physical chemistry to problems in both organic and inorganic fields.

Masson was interested in the teaching of science, frequently serving as external examiner at other universities, and his book, "Three Centuries of Chemistry," published in 1925, shows a profound knowledge of the historical and philosophical aspects of his subject. In addition, it is enlivened and made eminently readable by unexpected touches of dry humour. For instance, in comment on the renowned misogynist, "It must have been a lasting shame to Cavendish that once on Clapham Common he was so far overtaken by irrational impulse as to rescue a female from the menaces of a cow."

As has been already indicated, Masson's work as a chemist did not cease with his appointment as Vice-Chancellor. However, the problems now under investigation, such as the viscosity of amatols, were mainly of immediate practical importance and not likely to bear fruit in the shape of post-war publications. He turned, for relaxation, to other matters; for, whilst science was his profession, classics and the arts were hobbies in which he reached professional standing. He was a great lover of books and an expert in the early history of printing. His major contribution in this field—the fruit of research during the latter years of his vice-chancellorship—is an outstanding monograph on the Mainz Psalters and Canon Missae.

Masson was tireless in his efforts on behalf of the University of Sheffield, and his flair for the lucid presentation of complex matters of finance and statistics proved invaluable. No one knew better than he what education was or what a university should and could do. As Vice-Chancellor he steered the University through its war-time problems and through the equally difficult period of development which followed. He made plans to guide the expansion from 850 students to a well-balanced and effective University of some 2500 students (a target now increased to 4750); temporary structural alterations were made and building programmes initiated; Stephenson Hall and the new Chemistry and Engineering Departments were almost completed before his retirement in 1952.

Though invariably courteous and dignified, Masson was nevertheless a determined fighter, often outspoken in formal debate. In contrast, his natural shyness in personal relationships was a handicap frequently mistaken for aloofness. Rarely at his best in large gatherings, he was an excellent host of a small party, with a turn of wit which would have surprised his detractors. Those who knew him well found him a lively companion and a true friend.

Masson became M.B.E. in 1918, was knighted in 1950, and received the honorary degree of LL.D. of the Universities of Edinburgh and Sheffield. His retirement, spent in bibliographical work in Edinburgh and in advisory posts to the Carnegie Trust and the University of St. Andrews, was saddened by the long illness of his wife Flora Lovell, daughter of Professor G. Lovell Gulland, whom he married in 1913 and who died in 1960. He leaves one son, who is sub-librarian in charge of the Brotherton Collection at the University of Leeds.

R. D. HAWORTH,
A. H. LAMBERTON.

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HAMILTON McCOMBIE

1880—1962

HAMILTON McCOMBIE was born in London on May 7th, 1880. He started his academic career as a student at Aberdeen, where he took the M.A. degree in 1900, and then moved to the Royal College of Science (now part of the Imperial College of Science and Technology), where in 1903 he qualified as A.R.C.S. and also obtained the London B.Sc. degree. He completed his student days by working at Strasbourg under Thiele and took the Ph.D. degree (*magna cum lauda*) there in 1905.

He was then appointed initially to an assistant lectureship at Mason College (now the University of Birmingham), and attended the Australia meeting of the British Association for the Advancement of Science in the summer of 1914. The First World War was declared during this meeting, which was at once abandoned. Overseas members had to find their own way home at a time of great confusion. McCombie hastened back as rapidly as possible, and in January, 1915 was commissioned in the Worcestershire Regiment. He proceeded to France and in June, 1915 was seconded to the newly-formed Special (Gas) Brigade of the Royal Engineers. The rapid development of gas warfare made the provision of expert chemical advice essential to the higher staffs of the armies, and McCombie was soon appointed Chemical Adviser to the First Army with finally the rank of Major. His work at the Headquarters of the First Army was clearly excellent and he received the M.C. and the D.S.O., and was twice mentioned in dispatches. After the Armistice he went for a short spell to Germany with the Army of Occupation, again primarily in a chemical advisory capacity.

During the war he had met J. Barcroft (later Sir Joseph Barcroft and Professor of Physiology at Cambridge) who was a member of the Chemical Warfare Committee; he had also met W. J. Pope (later Sir William Pope), the Professor of Chemistry at Cambridge, who had taken a prominent part in many chemical matters affecting the army in France. It was undoubtedly these scientists who suggested that McCombie should come to Cambridge when his army service ended.

McCombie came to Cambridge in October, 1919 as a Fellow of King's College. The number of established University teaching posts was comparatively small at that time: H. J. H. Fenton had the post of Demonstrator, F. W. Dootson that of Additional Demonstrator and therefore McCombie became Second Additional Demonstrator. The new statutes in the middle twenties considerably increased the number of University teaching posts, and enabled McCombie to shed his odd rank on election to a lectureship. During the period between the death of Sir William Pope (1940) and the election of A. R. Todd (now Lord Todd) to the Chair of Organic Chemistry (1944), McCombie was Acting Head of the Department of Organic Chemistry. He was elected to a personal Readership in Chemistry shortly before his retirement in 1945. Later he moved to Woking, where he spent the rest of his life.

McCombie's academic abilities clearly lay more strongly in administrative than in research matters. At Birmingham his first paper (with Miss E. Parry, *J.*, 1909, 584) described the preparation and reactions of cyanhydrins of aromatic aldehydes. Then, with A. E. Everest (*J.*, 1911, 1744) and subsequent students he studied the formation of imidazole compounds from aromatic α-amino-ketones. At Birmingham he also started two research projects to which he later returned in his Cambridge days. With H. A. Scarborough, who worked with him at Birmingham during the period 1912—1914 and rejoined him at Cambridge from 1920—1935, he investigated the kinetics of ester saponification and of quaternary salt formation. These measurements were of significant value in the early development of quantitative theories of "induced polarity" which ultimately led to unification by the Hammett $\rho\sigma$ equation of 1935. Thus W. Blakey, McCombie, and Scarborough (*J.*, 1926, 2867) showed that the relative rates of saponification of ethyl disubstituted benzoates were approximately the product of the relative rates of saponification of the corresponding two monosubstituted esters.

The second project started at Birmingham was the study of the stepwise chlorination of substituted phenols, and with S. A. Brazier (*J.*, 1912, 968) he found that *p*-iodophenol gave first an iododichloride which on storage underwent a rearrangement to 2-chloro-4-iodophenol. This was the first known example (and remains one of the very few known today) of the migration of a group in a side-chain to a nuclear *meta*-position. The fact that this rearrangement involved dissociation giving molecular chlorine, which then gave nuclear substitution under the influence of the phenolic group, was clearly shown in wider studies by S. Buchan and McCombie (*J.*, 1931, 137; 1932, 2857). In the meantime (1925—1929) it led McCombie and Scarborough with a succession of students (W. A. Waters, W. Blakey, W. Burns) to examine the possibility of transfer of a halogen atom from one ring to another by the rearrangement of a *N*-halogeno-amide of biphenyl or azobenzene. This work was extended to a general study of substitution in linked ring systems, and showed that in compounds such as biphenyl, benzophenone, azobenzene, and diphenyl ether the reactivities of the two benzene nuclei were independent of each other apart from the inductive influence of each aryl substituent on the other ring (see W. A. Waters, *Chem. Rev.*, 1930, 7, 407). As the current importance of these research projects decreased, McCombie apparently lost his interest in research, for after about 1925 he initiated no new research projects. It should be added that in his early Cambridge days he also directed work on the destruction of mustard gas by chlorine, and on the properties of related compounds such as divinyl sulphoxide, and he continued to act as a member of the Chemical Defence Research Committee up to the end of the Second World War. He received the Degree of Doctor of Science at Birmingham and Cambridge Universities.

His administrative activities in Cambridge were shown at King's College, where he became Assistant Tutor for Natural Sciences, and was a member of the College Council and the Estates Committee for many years, and in the University, where he was for various periods a member of the Council of the Senate, the General Board, the Buildings Syndicate, and the Faculty Board of Physics and Chemistry. In the wider sphere of activity, he was a member of the Council of the Chemical Society for the periods 1923—6 and 1938—41, of the Council of the Royal Institute of Chemistry for 1923—6, 1929—32, and 1937—8, and of the Council of the Society of Chemical Industry for 1942—5, when he became a Vice-President for the period 1945—8.

McCombie was a friendly and very hospitable man. At the time of his arrival at King's College, C. T. Heycock—who was a Fellow of the College and Goldsmiths' Reader in Metallurgy—used to invite the chemistry examiners in the Natural Sciences Tripos each year to a private dinner in the College. For many years McCombie and Dr. D. Stockdale continued this practice, and there must be very many past examiners, internal and external, who have the happiest memories of these dinner parties, both for the pleasure of the occasion itself and for the mental relaxation which it afforded during a trying period of intensive script-marking.

McCombie was deeply interested in rugby football, and it is unlikely that he ever missed attending the University match at Twickenham during his Cambridge years.

He is survived by his widow and three daughters.

I am indebted to many friends for information, and particularly to Dr. W. A. Waters, F.R.S., who kindly provided a summary of McCombie's research work.

F. G. MANN.

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