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The I.U.P.A.C. Journal "Pure and Applied Chemistry" By W. A. Noyes (PRESIDENT, THE UNION OF PURE AND APPLIED CHEMISTRY)

THE new journal *Pure and Applied Chemistry* is not yet as well known as it should be. This is a pity, for it is issued by the International Union of Pure and Applied Chemistry (I.U.P.A.C.) and chemists should know what is being done by their international union. Also, it is a somewhat novel type of publication. New journals are not always welcome these days, and it may therefore be useful to explain why this one was established, and how it functions.

The main activities of I.U.P.A.C. are to organise and sponsor Symposia, and through its Commissions to issue nomenclature rules, lists of symbols, tables of data, analytical methods, etc., on which international agreement is desirable. Before 1957 the reports of Symposia, nomenclature rules, etc., were published either in the Comptes rendus of the Union -which had a very restricted circulation-or were scattered in a wide variety of scientific journals and books. The Union had to bear the heavy cost of its Comptes rendus, with no compensating return from the more popular features; and it was impossible to obtain anywhere a comprehensive survey, or even a fleeting impression, of the Union's total activities. Nor had the Union any machinery whereby it could bring its work to the notice of chemists in general.

In an attempt to improve this situation, the Union in 1957 appointed Butterworths Scientific Publications as its official publisher. A I.U.P.A.C. Publications Committee was set up, with Dr. H. W. Thompson as Chairman, and Dr. R. S. Cahn as Secretary, and each of the Union's publications was sold as a separate book under its standard crest. Much success was achieved, as judged by the large sale of a number of the items running into thousands, and the Union's activities became more widely known. However, full success was hampered by the fact that so much-and not the least important or interesting-of the Union's work consists in Commission recommendations covering only a few pages. and the difficulties of advertising and obtaining a reasonable price for such small publications are notorious. Some copyright arrangements also raised difficulties, but the Union purchased, at considerable cost to itself, for the benefit of scientific organisations everywhere, the translation and reproduction rights of all the main nomenclature reports. Also, it was still difficult to get an overall picture of the Union's activities, covering as they do such a very wide field.

Accordingly, in 1960, Pure and Applied Chemistry was started as a new journal, published by Butterworths Scientific Publications.* This contains all Symposia reports selected for publication from those held under the Union's sponsorship, as well as the Commission reports (nomenclature, symbols, tables of data, etc.), thus providing the comprehensive survey for those who need to know the full scope and detail of the scientific work of the Union. The financial and administrative business of the Union, composition of Commissions, etc., will continue to be published in its Comptes rendus and Bulletin, the former being put out after each main Conference and the latter at more frequent intervals. It is likely that the Bulletin may also be used for the preliminary dis-

^{*} All enquiries should be addressed to Butterworths Scientific Publications, 4-5 Bell Yard, London, W.C.2, England. The subscription rate is £6.0.0 or 18 U.S. dollars per volume of about 600 pages. Two volumes per year are planned, with supplements if necessary, and a system for annual subscriptions is being arranged.

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semination of *tentative* nomenclature rules and standard procedures before they are finally agreed for printing in the Journal itself.

A novel feature of *Pure and Applied Chemistry* is the recognition from the start that, while reference libraries and large laboratories will wish to have the complete journal, its miscellaneous content may not be required by most individual chemists. A regular magnified "off-print" service was therefore arranged, whereby each item of each issue is available for purchase separately, the Symposia reports and large sets of nomenclature reports as bound books, and the shorter items in the format of normal reprints. Contents of past and future issues, with prices for separate purchase, are given in the Journal and through the normal advertising media of the publishing trade.

To supervise the Journal, the Union has set up an Editorial Board of international authority, with Dr. H. W. Thompson (St. John's College, Oxford, England) as Chairman and Professor B. C. L. Weedon (Queen Mary College, Mile End Road, London, E.1), as Scientific Editor, to whom reference can be made on the scientific aspects of the Journal and about any publications which are contemplated in it from Commissions or the organisers of Symposia sponsored by the Union. The new venture seems to provide advantages to all parties. It provides a better dissemination of the Union's work. individual chemists can obtain the complete journal or separate items as they wish, reprints of their Symposia papers can be obtained by authors at discount rates, the Union is freed from much financial liability, and the publishers have only one journal to make instead of a varied miscellany.

With a journal of this unusual kind it is not

surprising that a number of problems of detailed policy should arise in the early stages, but they seem so far to have been overcome. For example, arrangements have now been made with the publishers to allow reproduction of basic scientific data such as the atomic weight tables, nomenclature rules, etc., in recognised scientific journals in all countries. However, they must first be printed in Pure and Applied Chemistry, permission to reproduce must be obtained from the Union and publishers, and appropriate acknowledgement must be made to the source of the data. Normally, publication in the Journal is only in one of the usual European languages, and as a general policy only the main lectures at Symposia will be printed. While the Union reserves the right to publish in its Journal all or part of the proceedings of all Symposia which it sponsors or organises, it does not always exercise this right, and this aspect must be clarified by the organisers with the Secretary General of the Union when the meeting is being planned. Delegates to such Symposia will be allowed a substantial discount on the printed proceedings.

At the time of writing of this article, three volumes of *Pure and Applied Chemistry* have appeared, and the fourth will shortly be completed. They include reports on standard nomenclature and presentation of data in chromatography, dissociation constants of acids, procedures for microchemical analysis, and the calibration of spectrometers in the ultraviolet and infrared. Topics of Symposia include radioactivation analysis, the organic chemistry of natural products, macromolecules, enzymes, thermochemistry and thermodynamics, molecular spectroscopy, the determination of toxic substances, and wood chemistry. Commitments for other volumes already extend to 1964.

TILDEN LECTURE*

Hydrido- and Related Organo-complexes of Transition Metals

By J. CHATT

IF this Lecture had been given ten years ago I could have discussed in considerable detail the whole of the chemistry of complex compounds containing either a hydrogen atom or the carbon atom of an organic radical bound by means of a σ -bond to a transition metal. This is no longer true; a great number of hydrido-, alkyl, and aryl complexes of transition metals has been discovered during the last decade. Nevertheless, even now very few simple molecular hydrides or organometallic compounds of the general formula $[MR_x]_n$ or $[MR_xX_y]_n$ (where M is a transition metal and R is hydrogen, an alkyl or an aryl group) have been made.

The most exciting recent development has been the discovery that, when ligands of high ligand-field strength are attached to a transition metal, the metal acquires some of the properties of a metalloid element in so far as its covalent σ -bonding properties are concerned. Thus it becomes capable of forming stable metal-metal bonds, as in manganese carbonyl,

^{*} Delivered before the Chemical Society on January 24th, 1962, at the University, Reading; on February 1st at Imperial College, London, S.W.7; on March 8th at the University, Leicester; and on March 19th at the University, Swansea.

[(CO)₅Mn–Mn(CO)₅], and stable σ -bonds to hydrogen and to hydrocarbon radicals. It is not possible in the course of an hour to survey all recent developments in this field, and in this Lecture I shall confine myself mainly to the bonding of hydrogen to the transition metal and the properties of hydrogen as an anionic ligand in its most stable complexes.

The formation of metal-metal bonds has not yet been studied systematically, but the bonds are surprisingly long, e.g., $Mn-Mn = 2.93 \text{ Å}^1$ All transition-metal complexes containing these bonds as an essential link in the structure also contain carbon monoxide as one of the ligands or as the sole ligand.

Hydrido-,²⁻⁵ alkyl, and aryl complexes⁵⁻⁷ have been studied much more extensively and useful correlations are appearing. The most stable of these complexes have the general formulæ $[MR_xX_yL_z]_n$, where R is hydrogen or an alkyl or an aryl radical, X is an anionic ligand, usually halide or cyanide ions, L is an uncharged ligand, and n is usually 1. Many of these new compounds and certainly all of the most stable of them are diamagnetic. The ligands L which give the best stabilisation are those which cause electron-pairing in the complex molecule, *i.e.*, those of high ligand-field strength, such as the cyclopentadienyl anion, carbon monoxide, nitric oxide, tertiary phosphines, and less so, tertiary arsines. The metal atom in these complexes usually has the effective atomic number of the next inert gas, or, more rarely, has only a few electrons less than the next inert gas. The non-bonding *d*-orbitals are thus occupied by at least one electron each, except in the organotitanium compounds simple [TiMe₄], $[TiCl_3R]$, and $[TiCl_2R_2]$. These are of the same type

as those obtained from the corresponding non-transition metals, such as germanium and tin, but they are very much less stable. As would be expected, the formulæ of the more stable alkyl and aryl complexes of the transition metals are closely similar to those of the stable hydrido-complexes; a selection of the more stable hydrido-complexes is given in Table 1.

Since I have already discussed the organocomplexes of the transition metals in considerable detail and these discussions have been published,⁶ I shall concentrate my attention largely on hydridocomplexes. The history and chemistry of the two series of complexes are very similar.^{2,6}. Fig. 1, similar to that in a review by Wiberg,⁸ shows that the transition elements provided the main gap in our knowledge of the hydrides of the elements in 1952. No molecular hydrides were known, apart from the very unstable carbonyl hydrides of which only two, cobalt and iron carbonyl hydrides, CoH(CO)₄ and $FeH_2(CO)_4$, had been extensively studied. These are very unstable volatile substances, decomposing even at -20° and behaving as weak acids in water.

The present phase of the chemistry of the hydridocomplexes of transition metals started in 1955 with the discovery of hydridobiscyclopentadienylrhenium, $ReH(C_5H_5)_2$. This was discovered by accident during the attempted preparation of biscyclopentadienylrhenium and, in contrast to the carbonyl hydrides, it is basic with a strength about equal to that of ammonia. This was followed by the discovery of the relatively stable cyclopentadienylcarbonyl hydrides, e.g., [CrH(C₅H₅)(CO)₃], which are weakly acidic and much more stable than the carbonyl hydrides themselves. The above hydrides are sensitive to air.

Carbonyl	$[MH(CO)_5] M = Mn, Re$
Cyclopentadienyl	$[TaH_3(C_5H_5)_2], [WH_2(C_5H_5)_2], [ReH(C_5H_5)_2]$
Carbonyl cyclopentadienyl	$[MH(C_5H_5)(CO)_3] M = Cr, Mo, W.$
Tertiary phosphine and arsine*	$[MH_xCl_{2-x}(R_2PCH_2CH_2PR_2)_2] x \le 2, M = Fe, Ru, Os$
	$[RhHCl_2(AsPh_2Me)_3]^{\dagger}$
	$[IrH_x Cl_{3-x}(PR_3)_3] x \leq 3$
	$[PtHCl(PR_3)_2]$
Tertiary phosphine- and arsine-carbonyl*	$[MHCl(CO)(PR_3)_3] M = Ru, Os$

TABLE 1. Some stable and well-defined hydrido-complexes.^{2,5}

* Examples similar to those given but containing tertiary arsines are known.

† A phosphine analogue is not yet known.

¹ See Corcy and Dahl, J. Amer. Chem. Soc., 1961, 83, 2203, and references therein, for examples. ² Chatt and Shaw, Proceedings of the XVIIth International Congress of Pure and Applied Chemistry, 1959, Butterworths Scientific Publ., London, 1961, p. 147. ³ Green, Angew. Chem., 1960, 72, 719. ⁴ Wilkinson, "Advances in the Chemistry of the Co-ordination Compounds," ed. S. Kirschner, Macmillan Co., New York, 1961, p. 50.

⁵ Sharp, Ann. Reports, 1960, 57, 150, 152.

⁶ Chatt, Record of Chemical Progress, 1960, 21, 147; "Chimica Inorganica," Accad. Naz. Lincei, 1961, p. 121. ⁷ Coates and Glocklin, "Organometallic Chemistry," Amer. Chem. Soc. Monograph No. 147, ed. Zeiss, Reinhold Publ. Corp., New York, 1960, p. 426.

⁸ Wiberg, Angew. Chem., 1953, 65, 16.



FIG. 1. Elements which were known in 1962 to form simple hydrides.

1957 saw the discovery of transition-metal hydrides stabilised by tertiary phosphines, *e.g.*, *trans*-[PtHCl(PEt₃)₂], and to a smaller extent by tertiary arsines. Many of these are sufficiently stable to air and moisture to allow a more complete study of the nature of the metal-hydrogen bond, and of the properties of the hydride ion when co-ordinated to the metal. These hydrides are neutral in their reaction.

Finally in 1960 an even more stable type of hydrido-complex was discovered. It is stabilised by tertiary phosphines or arsines, and carbon monoxide. Its members are neutral in reaction, resembling the phosphine- and arsine-stabilised hydrides rather than the carbonyl hydrides. All isolated so far are stable to air and moisture.

In addition to the above well-defined substances a number of less well-defined transition-metal hydrides have been detected by means of their nuclear magnetic spectra in the solutions where they had been produced, either by reduction or protonation of other complexes.^{4,5}

For the purpose of this Lecture we shall consider mainly the stable hydrido-complexes containing tertiary phosphines. Since 1957 some fifteen notes have appeared describing new compounds of this type, but hardly any detail has yet been published and scarcely anything at all about the properties of the hydrogen in these compounds. I propose therefore to concentrate almost entirely on the hydrogen and its bonding; but, first, a word or two should be said about the preparations. The hydrides are generally obtained by reduction of the corresponding halogeno-complexes, *e.g.*, [PtCl₂(PEt₃)₂], and, depending on the ease of reduction and sensitivity of the hydrido-complex to moisture, various reducing agents and solvent media have been used. These range from the strictly anhydrous lithium aluminium hydride in tetrahydrofuran, through alcoholic potassium hydroxide and alcoholic hypophosphorous acid, to aqueous hydrazine. Even hydrogen has been used.

Hydrogen as a Ligand in Transition-metal Complexes.—Many of the hydrido-complexes stabilised by tertiary phosphines have sufficient stability and resistance to oxidation to allow a study of their physical properties. The following discussion is based entirely on data collected for such complexes, where the hydrogen takes the place of an anionic ligand; and the conclusions may not apply to complexes where the hydrogen appears to be protonic, *e.g.*, the carbonyl hydrides.

Hydrogen as an Anionic Ligand.—The evidence that the hydrogen takes the place of an anionic ligand is as follows. In the platinum complex, trans-[PtHBr(PEt₃)₂], the planar arrangement of the three heavy ligand atoms around the platinum has been shown by X-rays, and, although there is some slight distortion from a square arrangement, it seems reasonable to suppose that the hydrogen atom completes the square co-ordination as shown in Fig. 2. It is to be noted that the platinum-bromine distance



FIG. 2. Structure of trans-[PtBrH(PEt)₂].

is slightly longer than the sum of the covalent radii (2.43 Å) which can be correlated with the high reactivity of the bromine ligand in this complex.

Further evidence is provided by the fact that all the hydrido-complexes stabilised by tertiary phosphines can be accounted for on the assumption that the hydrogen is anionic and that the metals have normal valencies, co-ordination numbers, and configurations. In particular, in the iridium series where a number of isomers are known, they can all be accounted for, and their properties such as dipole moments and nuclear magnetic resonance spectra interpreted, by assuming that they are normal octahedral complexes of tervalent iridium as shown in Fig. 3.⁹ [FeHCl{ $C_2H_4(PEt_2)_2$], but generally they range from 20 to 30 p.p.m. The large shift ensures that the resonance of the hydridic proton is well removed from that due to the organic part of the molecule, as shown in the spectrum of *trans*-[PtHCl(PEt_3)_2] in benzene (Fig. 4). This also shows the splitting of the hydrogen resonance into a triplet by the two equivalent phosphorus nuclei (spin = $\frac{1}{2}$) and further large splitting by platinum-195, first observed by Dr. N. Sheppard. The coupling constant J_{Pt-H} of 1276 c./sec. is also very large.⁹ The splitting of the proton resonance by the phosphorus atoms together with the dipole moments are invaluable in deciding the configurations of the complexes.

The Infrared Spectrum.-This usually shows a



FIG. 3. Some hydride complexes of iridium and their dipole moments. ($P = PEt_2Ph$).



FIG. 4. The proton magnetic resonance spectrum of trans-[PtHCl(PEt)₂].

Nuclear Magnetic Resonance Spectrum.—The hydridic hydrogen in transition-metal hydridocomplexes always shows a very large chemical shift, and in the phosphine-stabilised hydrides we have some of the largest proton shifts ever observed. The shifts range from $\sigma = 13.1$ p.p.m. relative to water in [PtH(CN)(PEt_3)_2] to $\sigma = 39.1$ in

strong sharp band due to the metal-hydrogen stretching vibration. The position of this band varies widely and the range observed to the present is from 1726 cm.^{-1} in *trans*-[FeH₂{ $o-C_6H_4(PEt_2)_2$ }]¹⁰ to 2242 cm.^{-1} in *trans*-[PtH(NO₃)(PEt₃)₂]. The absorption due to the bending mode of vibration is sometimes observed around the 800 cm.⁻¹ region. Fig. 5

⁹ Chatt and Shaw, unpublished work.

¹⁰ Chatt, Hart, and Rosevear, J., 1961, 5504.



FIG. 5. Infrared spectrum of (a) trans-[PtHCl(PEt₃)₂] and (b) trans-[PtDCl(PEt₃)₂], in Nujol.

(Reproduced by permission of the International Union of Pure and Applied Chemistry and Butterworths Scientific Publications Ltd., from Chatt and Shaw, Proceedings of the XVIIth International Congress of Pure and Applied Chemistry, 1959, Butterworths Scientific Publications Ltd., London, 1961, p. 147.)

shows typical spectra of a hydride and the corresponding deuteride.²

Electric-charge Distribution.—Although the hydrogen takes the place of an anionic ligand in the complex, and its nuclear magnetic resonance spectrum shows a large positive chemical shift, it appears to carry a slight positive charge relative to the rest of the molecule. The direction of the dipole is evident from the moments of the isomers in Fig. 6,⁹ where



FIG. 6. Apparent polarity of the hydrogen.

the positively charged phosphorus and arsenic atoms in *trans*-position to hydrogen in an otherwise symmetrical molecule produces a relatively small dipole moment, in contrast to that of the corresponding chloro-complex.

Complexes with the hydrogen atom in *trans*position to a chlorine atom in otherwise symmetrical complexes have moments of 4—5 D (Table 2). We

¹¹ Chatt and Hayter, J., 1961, 2605, 5507.

TABLE 2.

Dipole moments (D) of some hydrido-complexes.^{9,11} trans-[PtHCl(PEt₃)₂] $4\cdot 2$

trans-[PtHCl(PPh ₃) ₂]	4.4
trans-[FeHCl(Et ₂ PCH ₂ CH ₂ PEt ₂) ₂]	4.25
trans-[RuHCl(Et ₂ PCH ₂ CH ₂ PEt ₂) ₂]	4∙9
trans-[OsHCl(Et ₂ PCH ₂ CH ₂ PEt ₂) ₂]	4∙6

have found that we can make a reasonable prediction of the moment of phosphine-chloro-complexes of the platinum metals in their normal-valent states by assuming the phosphorus-metal bond moment to be about 6 D, and the metal-chlorine bond moment to be about 2 D. On this basis it appears that the metalhydrogen bond has a dipole moment of the order of 2-3 D with the hydrogen positive. However, we can expect a considerable distortion of the bond angles in hydrogen complexes because of the very small size of the hydrogen atom and, since the phosphorusmetal bonds have high moments, a slight distortion might produce an appreciable moment in the molecule. Thus a distortion such as shown in Fig. 2 where the positively charged phosphorus atoms have moved towards the hydrogen atom would introduce a resultant moment of just under 1 D, making it appear that the hydrogen were positively charged. Even allowing for this effect, the metal-hydrogen bond moment appears to be of the order of 1-2 D with the hydrogen positive, and this cannot be correlated with the anionic character of the hydride. The only

logical conclusion is, therefore, that the *trans*-halogen has become more negative under the influence of the hydride ligand. This can be correlated with the long Pt-Br bond observed in *trans*-[PtHBr(PEt₃)₂] (Fig. 2) and the apparently greater ionic character of the *trans*-halogen as shown in displacement reactions (see "*trans*-effect of hydrogen" below).

It is also evident that the hydrogen does not carry an unduly high negative charge. Thus the large positive chemical shifts cannot be due to exceptional electron screening of the proton.

Ligand-field Strength.-The hydrogen ion in transition-metal complexes has a very large ligandfield strength and the hydrogen complexes are much paler than the corresponding dichloro-complexes. It has been difficult to get quantitative data on the ligand-field strength of the hydride ligand because its strength is so high that bands due to the $d \rightarrow d$ transitions are shifted into the ultraviolet region and hidden by strong charge-transfer bands. Nevertheless, a lower limit can be set. Thus in trans- $[\operatorname{RuCl}_2(\operatorname{Me}_2\operatorname{P}\cdot\operatorname{CH}_2\cdot\operatorname{CH}_2\cdot\operatorname{PMe}_2)_2]$ the lowest $d \to d$ transition occurs at 411 m μ (24,300 cm.⁻¹). In trans- $[\operatorname{RuHCl}(\operatorname{Me}_2\operatorname{P}\cdot\operatorname{CH}_2\cdot\operatorname{CH}_2\cdot\operatorname{PMe}_2)_2]$ the $d \to d$ transition is shifted into the charge-transfer region and certainly does not occur below 364 m μ (27,500 cm.⁻¹). Thus the shift is at least 29,000 cm.⁻¹. This is rather greater than the shift produced by a methyl group in the corresponding methyl complex, and perhaps similar to that of cyanide ion which is the common anionic ligand of greatest ligand-field strength. It is evident that hydrogen ion is to be classed with methyl and cyanide ion in the spectrochemical series.12

us a measure of the magnitude of this effect.¹³ Pyridine and the platinum complexes undergo the following equilibrium reaction:

trans-[PtXCl(PEt₃)₂] + py \Rightarrow [PtXpy(PEt₃)₂]⁺ Cl⁻

The rate law for its attainment can be expressed by the equation:

$$k_{\rm obs} = k_1 + k_2[\rm py]$$

where k_{obs} is a pseudo-first-order rate constant, k_1 is a first-order rate constant for solvent-controlled reaction, and k_2 is a second-order rate constant for reaction with pyridine. For the hydride, trans- $[PtXCl(PEt_3)_2]$ (X = H), $k_1 = 1.1$ and $k_2 = 2.25$ imes 10² at 0°, and for the corresponding chloride (X = Cl), $k_1 = 6 \times 10^{-5}$ and $k_2 = 2.4 \times 10^{-2}$ at 25°. It is evident that the rate is increased some million times by the presence of the hydrogen atom in place of chlorine. This great lability is correlated with the rather long platinum-bromine bond found in the corresponding bromide *trans*-[PtHBr(PEt₂)₂] (Fig. 2) and the enhanced polarity of the metal-halogen bond, indicating that the presence of the hydrogen has increased the ionic character of the metalhalogen bond.

Sensitivity of Hydrogen to its Environment in the Complex.—The hydrogen atom is very sensitive to its environment in the complex. As we have seen the hydrogen atom in the platinum complex has a very high *trans*-effect and labilises the anionic ligand in *trans*-position to itself. Conversely, the anionic ligand has an influence on the hydrogen atom and this is seen in the infrared spectra of the series of compounds recorded in Table $3.^2$ Here the anionic

TABLE 3. Influence of trans-ligands (X) on the hydrogen atom as shown by v_{M-H} (cm,⁻¹) in hexane

trans-	NO ₂	Cl	Br	I	NO ₂	SCN	CN
[PtHX(PEt ₃) ₂]	2242	2183	2178	2156	215Õ	2112	2041
$[PtHX(AsEt_3)_2]$		2174	2167	2139		2108	
[FeHX(diphos) ₂]		1849*		1872*			
$[RuHX(diphos)_2]$		1938	1945	1948		1919	1803
[OsHX(diphos),]		2039		2051		2009	

diphos = $Et_2P \cdot CH_2 \cdot CH_2 \cdot PEt_2$. * Nujol mull.

trans-Effect of Hydrogen.—The hydrogen atom in the tertiary phosphine complexes has a very high *trans*-effect and greatly labilises the ligand in *trans*position to itself. This is very obvious in both the platinum and the ruthenium series of complexes where hydrogen and chlorine atoms occur in mutually *trans*-positions and the chloride ion is very rapidly replaced in metathetical reactions by other anionic ligands. One series of quantitative experiments gives

ligands have been placed in order of their *trans*-effects. It will be seen that the hydrogen stretching frequency, as noted in the infrared spectrum, decreases with increasing *trans*-effect. Since the platinum atom is so heavy this decrease must represent a true weakening of the platinum-hydrogen bond under the influence of the anionic ligands as one passes along the *trans*-effect series from NO_3^- to CN^- . Moreover, the hydrogen atom is not always

¹² Chatt and Hayter, J., 1961, 772.

¹³ Basolo, Chatt, Gray, Pearson, and Shaw, J., 1961, 2207.

affected in the same way by its co-ligands in transposition. Thus in the iron, ruthenium, and osmium series of complexes shown in Table 3 it will be noted that the trans-halogens produce a smaller effect on the vibration frequency of the hydrogen, and that it is in the opposite direction to that observed in the platinum series.¹⁰ The fact that the halogens produce a different effect on the trans-hydrogen atom according to whether they occur in the platinum- or iron-Group complexes suggests that there are at least two mechanisms for the transmission of this effect. Their relative importance must be different in the two series of complexes, and it is suggested that the more readily polarisable d⁸-platinum ion, by virtue of $p_z d_c$ -hybridisation, transmits a stronger mesomeric effect than the d^6 -ruthenium ion. Thus, in the platinum complexes, the iodine atom exerts its greater lowering of v_{Pt-H} by virtue of its ability to withdraw electrons mesomerically into its d-orbitals more strongly than chlorine can. In the ruthenium complexes, where mesomeric withdrawal is not so easy, the effect of the halogens is largely inductive and the more electronegative chloride ion exerts the greater electron-withdrawing effect in the o-bond. Further evidence is needed on this point, and it will be interesting, when a trans-effect series has been established for the octahedral d⁶-complexes of the iron(II)-Group of metals to see whether the halogens in that series will be in the reverse order to that found in trans-effect series for platinum(II).

Sensitivity of the Hydrogen to Solvent Effects.— The stretching frequency of the metal-hydrogen bond is sensitive not only to the other ligands in the molecule, but also to the solvent in which the spectra are measured. Fig. 7 illustrates this, using a series of compounds where hydrogen is found in *trans*position to chlorine, phosphorus, or arsenic.¹⁴ The infrared spectrum was examined in a number of solvents and the stretching frequency found to be lowest in hexane and highest in chloroform. However, the

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shift in frequency in passing from one solvent to the other is not the same in every compound. In compounds having the hydrogen in trans-positions to a phosphorus or arsenic atom only a very small shift $(\Delta \nu)$ occurs. On the other hand when the hydrogen atom is in trans-position to a chlorine the shift is large. In the third compound where both types of hydrogen atom occur both types of shifts are observed. It seems likely that the shift is mainly caused by solvation of the anionic chloride ligand by the more polar solvents and especially chloroform. This would assist the accommodation of negative charge by the chloride ligand and so increase the ionic character of the Pt-Cl bonds, i.e., there would be electron drift towards the chlorine. Thus the chlorine would behave more like a nitrate group and, as shown in Table 3, v_{Pt-H} would move to a higher frequency. Such solvation of the organic phosphine or arsine ligands is unlikely to occur because of the bulky organic groups, but if it did occur it would help the positively charged ligand atoms to accommodate more positive charge, *i.e.*, release electrons to the metal atom and so lower the v_{Pt-H} .

We see that in some ways the binding of the hydrogen atom is very sensitive to its co-ligands. Perhaps the acidity of the hydrogen atom in the purely carbonyl hydrides, *e.g.*, $[CoH(CO)_4]$, is a special example of this. The hydrogen atom attached to the metal is in an environment of delocalised π -bonds along the M=C=O groups. These might provide an ideal system whereby the proton could migrate along the π -bonds from the metal atom *via* the carbon and oxygen atoms, so escaping into a suitably receptive solvent.

The reactions of the hydrido-complexes have not been studied very extensively as yet, and most reported reactions are somewhat trivial, *e.g.*, reaction with halogen to form hydrogen halide. Perhaps the most interesting is the reversible reaction with ethylene at $45^{\circ}/40$ atm. (reversed by pyrolysis) where



* $P = PEt_2Ph. \dagger P - P = Me_2P \cdot CH_2 \cdot CH_2 \cdot PMe_2.$

FIG. 7. Influence of solvent on v_{M-H} (M = Pt,Ir,Ru). $\Delta v = v_{M-H}$ in chloroform $-v_{M-H}$ in hexane.

¹⁴ Adams, Proc. Chem. Soc., 1961, 431.

it seems likely that the β -hydrogen atom of the ethyl group becomes the hydride ligand and vice versa.⁹

 $\textit{trans-[PtHCl(PEt_3)_2]} + C_2H_4 \rightleftharpoons \textit{trans-[PtClEt(PEt_3)_2]}$

The Stability of the Hydrido-complexes. The stabilities of analogous hydrido-complexes in any group of transition elements generally rise in passing from the lighter to the heavier element. Carbonyl hydrides appear to be the only exceptions. Thus manganese carbonyl hydride, $[MnH(CO)_5]$, is known to be more stable that its rhenium analogue, $[ReH(CO)_5]$, and, whereas the very unstable iron and cobalt carbonyl hydrides have been extensively studied, their analogues containing the heavier metals are scarcely known.

The thermal stabilities of the hydrido-complexes stabilised by tertiary phosphines certainly rises on ascending the group, and the similar increase in M-H stretching frequency would indicate also increasing M-H bond strength. Thus, in the nickel group we have a series of compounds [MHCl(PR₃)₂], the platinum compound (R = Et) is sufficiently stable to be distilled under a high vacuum (at 130°/0.01 mm.) and $v_{Pt-H} = 2183$ cm.⁻¹. The corresponding palladium compound can be isolated as a solid, but is contaminated with decomposition products, and it is rapidly destroyed on recrystallisation. Moreover, $\nu_{Pd-H} = 2053 \text{ cm.}^{-1}$. The nickel compound (R = Prⁿ) has never been isolated, but it has been detected by its nuclear magnetic resonance spectrum in the solution which results when the nickel dichloro-complex is reduced with lithium borohydride. In the iron group similar series of stabilities and metal-hydrogen stretching frequencies are observed, as shown in Table 4, except that the very stable ruthenium and osmium compounds are about equally stable.

TABLE 4. v_{M-H} and Decomposition points of some iron Group hydrido-complexes,

[MHCl(Et₂P·CH₂·CH₂·PEt₂)₂].^{2,13}

M ν (cm, ⁻¹)	Decomp. pt.	M.p.
Fe 1849 (n)	155°	155°
Ru 1938 (h)	310	175
Os 2039 (h)	315	171

n = Nujol mull; h = hexane.

This increase in stability of the transition-metal hydrido-complexes in passing from the light to the heavy elements is in sharp contrast to the behaviour of the covalent hydrides of the non-transition metals, for example in the series methane, silane, germane, stannane, and plumbane. The hydrogen in the hydrido-complexes is certainly covalently bound because the complexes show none of the high sensitivity to water associated with the ionic metal hydrides, such as those of sodium and calcium. The

¹⁶ Chatt and Shaw, J., 1961, 285, and references therein.
¹⁶ Wilkinson, Proc. Chem. Soc., 1961, 72.

increase in stability of the hydrido-complexes as one ascends a Group of transition metals in the Periodic Table is paralleled exactly by an increase in stability of the corresponding organo-derivatives on ascending the Group, again in contrast to the behaviour of covalent organic derivatives of other elements of the Periodic Table.

These facts suggest that the stability of the hydrido-complexes and of the corresponding organocomplexes is mainly due to the total ligand-field stabilisation energy of the ligands in the complex, so preventing dissociation to produce the reactive entities H⁻ or R⁻ which would be immediately destroyed by air or moisture. The chance of homolytic dissociation would also be reduced by the large splitting in the *d*-energy levels, which would hinder the thermal promotion of electrons from the bonding orbitals of the metal-hydrogen or metal-carbon bond into the antibonding orbitals or, on the basis of ligand-field theory, into the high-energy d-orbitals of the metal ion. Thus, the crucial factor in the stabilisation of the hydrido- and organo-complexes is probably the energy separation between the occupied non-bonding d-orbital energy levels and the vacant anti-bonding levels.¹⁵ This energy separation must be greater than some crucial value before stability is achieved and with the lighter elements only ligands of high ligand-field strength will cause stability. On the other hand, in the heavier transition metals where the energy separations are in any case considerably greater, ligands of only moderately ligand-field strength may be sufficient to stabilise the hydrido-complexes. In agreement with this, Wilkinson has recently found a somewhat unstable complex [RhHClen₂]Cl containing only chlorine and an aliphatic amine.16

A further consequence of the above hypothesis is the expectation that hydrido- and related organocomplexes with ligands in orthogonal relationship will be more stable than those with tetrahedral or other non-orthogonal configurations. This appears to be so; all of the very stable hydrido- and organocomplexes have octahedral configurations or, in the case of platinum, square-planar. Amongst the alkyl and aryl complexes, where the variety of organic groups allows a more systematic study there is no doubt about the preferences for the orthogonal arrangement. Thus the organo-complexes, e.g., $[M(C_6Cl_5)_2(PEt_2Ph)_2]$ (M = Fe or Co) derived tetrahedral halogeno-complexes from the [MCl₂(PEt₂Ph)₂] have trans-planar configurations.

The ligand-field stabilisation energy appears to be the most important factor in the stabilisation of hydrido- and related organo-complexes, and the

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hydrogen and organo-ligands themselves also contribute to this by virtue of their high ligand-field strengths. Thus there is a tightening of the whole complex when the halogen is replaced by hydrogen or carbon. This is strikingly demonstrated in the organo-complexes of iron and cobalt mentioned above. These are completely free from any smell of the phosphine, although the corresponding crystalline halogeno-complexes dissociate sufficiently to provide a continual odour of the phosphine, and indeed the iron complex dissociates completely in hydroxylic solvents.

Thus not only does the presence of the phosphorus or similar ligand atom stabilise the M-C and M-Hbonds, but the presence of the carbon and hydrogen ligands stabilises the M-P bonds, all of which emphasises the importance of a high total ligandfield stabilisation energy in hydrido- and organocomplexes.

This has been only a very incomplete story. Hardly anything is known of the reactions of the hydridocomplexes or the behaviour of the hydrogen in transition-metal complexes. Many compounds have been prepared but there has been little study of their properties. The same applies to the organo-complexes and even less is known of complexes containing metal-metal bonds. In fact, the chemistry of transition metals in compounds containing ligands of high ligand-field strength is only just beginning. The subject is full of problems, such as how does the hydrogen atom labilise so strongly the group in *trans*position to itself? to what does it owe its very high ligand-field strength? what exactly causes the very high chemical shifts in the proton magnetic resonance spectrum? All these need answers and I am sure that when we have found them our knowledge of valency theory and the action of hydrogen and hydrocarbons on metal catalysts will be enormously enhanced.

In conclusion, I thank all my collaborators, particularly Dr. B. L. Shaw and Dr. R. G. Hayter whose contributions from my laboratory were almost entirely in the field of hydrido- and organo-complexes.

To keep the number of references to a minimum only relevant original papers published during 1961 are given. References to earlier work are available in the reviews (refs. 2–8).

COMMUNICATIONS

Tricarbonyl-π-pyrrolylmanganese

By K. K. JOSHI and P. L. PAUSON

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VERY few π -complexes of transition metals with heterocycles have been described.¹ We now report the preparation of the first pyrrole complex of this type, tricarbonyl- π -pyrrolylmanganese.

This complex was prepared by heating decacarbonyldimanganese (1.60 g.) with pyrrole (6.0 ml.) in light petroleum or ethylene glycol diethyl ether (25 ml.) at 130° for 6 hours. Separation and purification were effected by chromatography on alumina. The complex sublimes at 0.2 mm. at room temperature as bright orange crystals (0.6 g.), m.p. 40.5°— 41.0° [Found: C, 41.0; H, 1.8; N, 6.7; O, 23.8%; *M* (cryoscopic in benzene), 213. C₇H₄MnNO₃ requires C, 41.0; H, 2.0; N, 6.8; O, 23.4%; *M*, 205].

The nuclear magnetic resonance spectrum (in CCl₄) shows singlet peaks at 3.9 and 4.8 τ corresponding to the protons α and β to the nitrogen atom.

The ultraviolet and infrared spectra are both remarkably similar to those of tricarbonylcyclopentadienylmanganese and thus strongly support an analogous structure, $(\pi$ -C₄H₄N)Mn(CO)₃ for the pyrrolyl complex. The infrared spectrum even includes peaks at 1109 and 1006 cm.⁻¹ corresponding to the "9 and 10 μ bands" which were hitherto regarded as characteristic of an unsubstituted cyclopentadienyl ring.² The compound is at most weakly basic and forms neither a methiodide nor a complex with aluminium chloride under mild conditions. Preliminary experiments (with W. H. Stubbs) indicate that not only substituted pyrroles, but also pyrazoles and triazoles, form related complexes with various transition metals.

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¹ Zeiss, "Organometallic Chemistry," Reinhold, New York, 1960; Wilkinson and Cotton, in "Progress in Inorganic Chemistry," Vol. I, ed. Cotton, Interscience Publ. Inc., New York, 1959.

² Rosenblum and Woodward, J. Amer. Chem. Soc., 1958, 80, 5443.

The Structure of Xylindein

By G. M. BLACKBURN, A. H. NEILSON, and Lord TODD

(UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE)

XYLINDEIN, the green pigment of *Chlorociboria* aeruginosa (formerly described as Peziza aeruginosa or Chlorosplenium aeruginosum) was first isolated from wood infected with the fungus¹ but is more conveniently obtained from C. aeruginosa cultures grown on a cellulose base in aqueous malt extract. Xylindein was investigated by Kögl and his co-workers who assigned² to it a formula $C_{34}H_{26}O_{11}$ but were unable to determine its structure although they established³ the existence in the molecule of two lactone groupings and an extended quinone system.

We have evidence that the pigment as obtained by simple extraction either of cultures or of the infected wood is not as a rule homogeneous, the major component, for which we retain the name xylindein, being accompanied by smaller amounts of closely related substances whose presence may account for some of the difficulties experienced by earlier workers. The molecular weight of xylindein obtained by extracting the culture mycelium with phenol was found by mass spectrometry to be 568-570 (quinone-quinol) and this, together with the analytical values for xylindein derivatives, accords best with a formula C₃₂H₂₀O₁₀. As a result of our investigations we now propose structure (I) for xylindein.



Xylindein shows infrared bands at 1720 and 1625 cm.⁻¹ which we assign, respectively, to the two identical $\alpha\beta$ -unsaturated δ -lactone groupings and a hydrogen-bonded extended quinone system. It contains two hydroxyl groups [diacetate, dimethyl ether

(II)] which appear to be situated *peri* to the quinone carbonyl group (boroacetate reaction and infrared absorption). The light-absorption curve of xylindeol dimethyl ether, the product of reduction of the ether (II) with lithium aluminium hydride, has maxima at 563, 522, and 490 m μ . The close similarity in form between this spectrum and that of *peri*-xanthenoxanthene-4,10-quinone⁴ (λ_{max} . 522, 484, and 451 m μ) strongly supports the view that the central chromophore of xylindein is that of 3,9-dihydroxy-perixanthenoxanthene-4.10-quinone. Moreover, zincdust distillation of tetra-O-acetyldihydro-xylindein yields a yellow, crystalline product shown by highresolution mass spectrometry⁵ to be either 1,7-di-npentyl-peri-xanthenoxanthene (III) or the 5,11isomer; of these, only the former is compatible with the chemical behaviour of xylindein. Further support is found in a comparison of the light absorption of the zinc dust distillation product (λ_{max} . 444, 416, 391, and 368 m μ) with that of *peri*-xanthenoxanthene $(\lambda_{\text{max}}, 439.5, 412, 389, \text{ and } 368 \text{ m}\mu).$

Kögl considered that xylindein contained two enolic lactone groupings, but the dominant mass peak at 568 in the mass spectrum of xylindein and the absence of ketonic infrared absorption in chromatographically pure xylindeic acid dimethyl ester indicate that they are saturated. Chromic acid oxidation of xylindein gives 1.3-1.5 mol. of volatile acid containing n-butyric acid as major component with only minor amounts of propionic and acetic acid. Clearly the n-butyric acid must originate in that part of the xylindein molecule which yields the n-pentyl group in the degradation product (III), and its production thus indicates that in xylindein there are two 3,4-dihydro-3-n-propylisocoumarin systems. The absence of infrared absorption corresponding to a phenol acetate grouping in the acetate of dihydro-3,4,9,10-tetra-O-methylxylindeol (ν_{max} . 1732 cm.⁻¹) shows that the lactone systems cannot be of the dihydrocoumarin type and the change in the 340 m μ region of the absorption spectra of xylindein derivatives on reduction of the lactone groupings is evidence for the attachment of the carbonyl groups in them to the chromophore. We regard the lactones, therefore, as being of the dihydroisocoumarin type and formulate xylindein as (I).

² Kögl and von Tacuffenbach, *Annalen*, 1925, 445, 170. ³ Kögl and Erxleben, *Annalen*, 1930, 484, 65.

- ⁴ Pummerer, Rieche, von Krudener, Pfeiffer, Prell, Tuchmann, and Wilsing, Annalen, 1933, 503, 40.
- ⁵ Benyon, Proc. Xth Colloquium Spectroscopium Internationale, Maryland, 1962.

¹ Döbereiner, Schweiggers Journal, 1813, 9, 160; Rommeir, Compt. rend., 1868, 60, 108; Liebermann, Ber., 1874, 7, 1102.

The structure can be built up from two acetatederived naphthalene units and a successful model coupling of units of this type will be reported later.

We are indebted to Dr. J. H. Beynon for the mass-

spectrometric data on (I) and (III) and to Dr. R. I. Reed for preliminary mass-spectrometric examination of (III).

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The Free-radical Reactions of Co-ordination Compounds: Pentane-2,4-dione Chelates By ROY J. GRITTER and EDWIN L. PATMORE

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Some ionic substitutions of pentane-2,4-dione chelates have been reported;¹ we now relate some results on the free-radical reactions of the organic portions of these compounds, involving hydrogenatom abstraction; both the ease of carbon-hydrogen bond breaking and the structure of the intermediate radicals have been determined.

When t-butyl peroxide is heated in a substrate, the t-butoxy-radicals obtained either abstract a hydrogen atom to form t-butyl alcohol or decompose to acetone and a methyl radical. Thus the alcohol : acetone ratio indicates the strength of the carbon-hydrogen bond being broken.²

Such measurements on a number of pentane-2,4dione chelates and other compounds in bromobenzene (see Table) show the great effect of the structure of the chelates and the properties of the metal. The rate ratios from the substituted toluenes were used to determine the Hammett³ ρ value for the reaction (-0.77). The Hammett³ m- σ values for the chelate rings were calculated from this ρ value, and these are also listed in the Table.

Correlation of the rates with such properties of the metals as electronegativity, ionisation potential, ionic radius, and ligand-field effect shows that the rates increase with the increasing energy of the metaloxygen bond. The increase of rate with increasing number of *d*-electrons of the metal ion suggests that the back-donation of electrons from the metal to the organic ligand is very important in determining the relative reactivities. This is true because the more reactive the chelate the greater the electron density at the site of the radical reaction.⁴

The studies on the site of attack with a t-butoxyradical have shown that a hydrogen atom is abstracted from the 1-position of the chelate (from a methyl group). It had been previously found that a hydrogen atom is abstracted from the 3-position of unco-ordinated pentane-2,4-dione under the same conditions.⁵ Thus, co-ordination changes the site of radical attack. The intermediate chelate radical has been found to add to other intact chelate molecules

Reactivities	and	Hammett	σ	values	of	chelates	and
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	Rate	<i>m</i> -σ
Compound	ratios*	values [†]
Pentane-2,4-dione	5.00	
$Na(C_5H_7O_2)$	0.515	+0.681
$Mg(C_5H_7O_2)_2$	8·85	-0.528
$Cr(C_5H_7O_2)_3$	5.70	-0.023
$Co(C_5H_7O_2)_3$	27.9	- 0 ·947
$Mn(C_5H_7O_2)_3$	11.6	-0.455
$Fe(C_5H_7O_2)_3$	6.54	-0.130
$Al(C_5H_7O_2)_3$	5.62	-0.043
$Cu(C_5H_7O_2)_2$	21.0	-1.02
$Be(C_5H_7O_2)_2$	31.8	-1.25
$Ni(C_5H_7O_2)_2$	9.14	- 0 ·548
$Co(C_5H_7O_2)_2$	4.59	-0·157
$Zn(C_5H_7O_2)_2$	2.76	+0.125
$Mn(C_5H_7O_2)_2$	19.7	-0.981
$Cu(C_5H_6O_2-3-Me)_2$	77.7	
$Cu(C_3H_6ClO_2)_2$	45.1	
$Cr(C_3H_3O_2)_3$	10.1	
Toluene	1.55	
<i>m</i> -Xylene	1.73	0.000
p-Bromotoluene	1.01	
p-Tolunitrile	0.207	

* Calc. from the ratios of t-butyl alcohol : acetone obtained.

† Corr. for the no. of chelate rings.

‡ Min. values because of poor solubility in bromohenzene.

in the 3-position; therefore, the product obtained after hydrolysis of the reaction mixture is the 1,3'dimer; 3-acetyloctane-2,5,7-trione. It was determined that the best method of hydrolysis was by using an ion-exchange resin. The authentic dimer was prepared by the reaction of 1-bromopentane-2,4dione and the sodium salt of pentane-2,4-dione. It was also synthesised from the 1,3-dipotassio-derivative of pentane-2,4-dione and 3-chloropentane-2,4dione.6

We thank the National Science Foundation for financial assistance. (Received, August 20th, 1962.)

¹ For a review see Collman and Kittleman, Inorg. Chem., 1962, 1, 499.
² Williams, Oberright, and Brooks, J. Amer. Chem. Soc., 1956, 78, 1190.
³ Jaffe, Chem. Rev., 1953, 53, 191.
⁴ Russell, J. Org. Chem., 1958, 23, 1407.
⁵ Gritter, Ph.D. Dissertation, University of Chicago, 1955.
⁶ Hours and Harris L. Anger Chem. 2052, 200 (200).

⁶ Hauser and Harris, J. Amer. Chem. Soc., 1958, 80, 6360.

Cascarillin

By J. S. BIRTWISTLE, D. E. CASE, P. C. DUTTA, T. G. HALSALL, G. MATHEWS, H. D. SABEL, and V. THALLER

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THE bitter principle cascarillin^{1,2} from cascarilla bark (*Croton eleuteria*) was formulated in 1896 as $C_{16}H_{24}O_5$ by Naylor and Littlefield.² It has now been found to be a diterpene monoacetate, $C_{22}H_{32}O_7$, which is in agreement with the original analysis.²

Spectroscopic evidence, including nuclear magnetic resonance and mass spectral data obtained by Mr. J. H. Beynon and Mr. A. E. Williams (Imperial Chemical Industries Limited, Dyestuffs Division), and degradative experiments indicate³ that cascarillin is a β -monosubstituted furan and that the oxygen atoms are accounted for by the furan ring, one axial acetoxy-group, two secondary hydroxyl groups (one of which is attached equatorially to a six-membered ring and the other to the carbon atom next to the furan ring), one tertiary hydroxyl group, and a tertiary aldehyde group which forms a hemiacetal link with the furfuryl hydroxyl group. The nuclear magnetic resonance spectra indicate that there is a CH₂ group next to the CH·OH group attached to the furan ring. They also indicate that three methyl groups are present, two tertiary and one secondary. The high-resolution infrared spectrum of cascarillin diacetate showed the absence of a gem-dimethyl group. The τ value (8.60) of the hydrogen atoms of one of the tertiary methyl groups suggests that it is attached to carbon carrying oxygen.

The acetate group of cascarillin is very easily hydrolysed (7% sodium carbonate solution in 1:1 aqueous methanol at 20° overnight). The resulting deacetyl compound, $C_{20}H_{30}O_6$, $[\alpha]_D - 19^\circ$, when treated with acid very readily loses one mole of water to give a stable acetal, $C_{20}H_{28}O_5$, m.p. 160.5—162°, $[\alpha]_{\rm D} - 11^{\circ}$. This on oxidation gives a monoketone, m.p. 159.5—161°, $[\alpha]_{\rm D} + 23^{\circ}$ (O.R.D. curve: amplitude + 64°), which still has the tertiary hydroxyl group. Reduction of cascarillin with lithium aluminium hydride gives a pentaol which is not oxidised by sodium periodate. Treatment of cascarillin with ethanolic hydrogen chloride leads to a monoethyl acetal, C₂₄H₃₆O₇, m.p. 173·5-176°, $[\alpha]_{\rm p} - 13^{\circ}$, which on hydrolysis with base followed by oxidation with chromic oxide-pyridine gives a diketone, $C_{22}H_{30}O_6$, m.p. 185–188°, $[\alpha]_p + 33°$ (in dimethylformamide). Its ultraviolet spectrum shows that it is not an enolisable α - or β -diketone. Other evidence indicates that the acetoxy- and the furfuryl hydroxy-group are both attached to carbon atoms γ disposed to the aldehyde group. These results imply the partial structure (I). Dehydrogenation of the acetal with 30% palladium/charcoal gave a small amount of a neutral fraction which was purified by preparative gas-chromatography. Its ultraviolet spectrum indicated that it was a mixture of diand tri-alkylnaphthalenes.



The results are further consistent with cascarillin belonging to the group of diterpenes of which clerodin⁴ (II) is an example. In view also of the likely biogenesis of cascarillin a possible structure for it is (III) (or its mirror image), the acetal then being (IV) and the diketone (V). An iodoacetate of the acetal has been prepared and may well be a suitable compound for crystallographic examination. Two less likely structures for cascarillin are: (*a*) (III) with the 6-hydroxyl group moved to C-7; and (*b*) (III) with the acetoxy-group moved to C-7 and the 6-hydroxyl group to C-1.

The authors thank Dr. L. M. Jackman for valuable assistance in the determination and interpretation of some of the nuclear magnetic resonance spectra, and Mr. J. H. Beynon and Mr. A. E. Williams for the mass spectrum.

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¹ Garcias-Salat, "Unica quaestiuncula in qua examinatur pulvis de quarango vulgo cascarilla in curatione tertianae," Valentiae, 1692; Duval, J. Pharm., 1845. 8, 91; Gerhardt, "Traité de Chimie organique," 1862, Vol. IV, p. 279; Mylius and Mylius, Ber., 1873, 6, 1051.

- ² Naylor and Littlefield, Pharm. J., 1896, 57, 95.
- ³ Cf. J. S. Birtwistle, D.Phil. Thesis, Oxford, 1962.
- ⁴ Barton, Cheung, Cross, Jackman, and Martin-Smith, J., 1961, 5061.

Solvolysis of the Toluene-p-sulphonate of 3α -Hydroxymethyl-A-norcholest-5-ene

By G. H. WHITHAM

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the toluene - p - sulphonate (I; R WHEN _ p-CH₃·C₆H₄·SO₂) of 3α -hydroxymethyl-A-norcholest-5-ene¹ is heated with buffered aqueous acetone, the alcoholic product consists of 3β ,5-cyclo- 5β cholestan-6-ol (II; 89%), m.p. 98–100.5°, $[\alpha]_{p}$ + 23°, together with the unrearranged alcohol (I; R =H; 11%). The structure of the alcohol (II) follows from (i) reconversion into the alcohol (I; R = H) on treatment with aqueous mineral acid, and (ii) oxidation to the corresponding ketone, m.p. 109-110°, $[\alpha]_{\rm p}$ + 80°, $\nu_{\rm max}$ 1710 cm.⁻¹ (in carbon disulphide).

There is, therefore, no detectable conversion into the cholesteryl system, and this presumably reflects the relatively high energy of the boat conformation of the cholesteryl cation (III). A possible representation of the intermediate cation involved in the solvo-

¹ Dauben and Ross, J. Amer. Chem. Soc., 1959, 81, 6521.

lysis reaction is (IV). The 6β -orientation of the hydroxyl group in the alcohol (II) is assigned on the basis that attack of water should involve maximum overlap with the vacant orbital on C-6.



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A Convenient New Synthesis of the Hydrocarbon Reported to be Octaphenylcubane

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A HIGH-MELTING dimer of tetraphenylcyclobutadiene has recently been characterised as octaphenylcubane.¹ We now report a new and convenient synthesis of this novel compound.

Triphenylphosphine (2 mols.) in benzene was slowly added to tetraphenylcyclobutadienepalladium chloride² (1 mol.) in boiling benzene. The tetraphenylcyclobutadiene-palladium chloride(I) dissolved rapidly, the solution assuming a dark greenish-brown colour which after a few minutes faded to yellow-orange with deposition of crystals. The mixture was refluxed for 6 hr., cooled, and filtered. The crystals were boiled with chloroform and collected, affording colourless octaphenylcubane (II) ($\sim 70\%$).¹ Further purification was by crystallisation from diphenyl ether followed by vacuum-sublimation (Found: C, 94.2; H, 5.7. C₅₆H₄₀ requires C, 94.4; H, 5.7%). The identity of the material was established by comparison of its infrared spectrum with that of an authentic sample¹ and by its m.p. and mixed m.p. 426-428°.

The chloroform solution, on cooling, deposited bistriphenylphosphinepalladium chloride (III) in 80% yield (Found: C, 61.6; H, 4.3; Pd, 15.4. Calcd. for C₃₆H₃₀Cl₂P₂Pd: C, 61.6; H, 4.3; Pd., 15.2%), m.p. and mixed m.p. 297-298°.

Trimethyl phosphite may be used, instead of triphenylphosphine, to convert compound (I) into (II). Since compound (I) may be readily obtained from diphenylacetylene this represents a convenient route to octaphenylcubane.

Reactions carried out in the presence of oxygen yielded no octaphenylcubane, but instead afforded the chloride (III) (85%) and tetraphenylfuran (12%), the latter being an expected oxidation product of tetraphenylcyclobutadiene.³ At room temperature, even in the absence of oxygen, yields of the cubane dropped to near 10%. Under these conditions, as in reactions carried out under nitrogen at reflux temperatures, addition of the phosphine or phosphite was followed by the appearance of a green colour. In the cold the green colour persisted for a considerable time, and the electron-spin resonance of the solution showed the presence of a free-radical species, probably associated with transient formation of tetraphenylcyclobutadiene by displacement from compound (I) by the phosphorus ligands.

We thank Dr. H. H. Freedman for a sample of octaphenylcubane, Dr. E. Stone for recording the electron spin resonance spectrum, and the National Science Foundation for support.

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- [†] Present address: Department of Chemistry, Queen Mary College, London, E.1, England.
 ¹ Freedman and Petersen, J. Amer. Chem. Soc., 1962, 84, 2837.
 ² Blomquist and Maitlis, J. Amer. Chem Soc., 1962, 84, 2329.

- ³ Freedman, J. Amer. Chem. Soc., 1961, 83, 2195.

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A New Criterion for the Absolute Configuration of Dihedral Metal Complexes

By R. E. BALLARD, A. J. MCCAFFERY, and S. F. MASON (CHEMISTRY DEPARTMENT, THE UNIVERSITY OF EXETER)

HITHERTO, the absolute configuration of dihedral transition-metal complexes have been related by solubility methods,1,2 which agree in their assignments,3 but they are at variance with methods based upon the optical rotatory properties of the complexes.³ However, the solubility methods cannot link the chiralities of the cationic, neutral, and anionic complexes, whereas an optical method may afford such a connection. The suggested optical methods have been based upon the sign of the rotation given by the complexes at the sodium D-line,⁴ or, more significantly, upon the sign of the long-wavelength Cotton effect, measured by the circular dichroism or the anomalous rotatory dispersion.³ The spinallowed transition of lowest energy in an octahedral complex breaks down, in a dihedral d^3 or d^6 complex, into A_2 and E components, which necessarily have rotatory powers of opposite signs,⁵ and the long-wavelength Cotton effect is determined by the component transition having the lower energy.

The crystal spectra, measured with planepolarised light, give the A_2 transition the lower energy in the oxalate,⁶ and the acetylacetonate⁷ complexes of chromium(III) and the acetylacetonate⁷ complex of cobalt(III), but in the corresponding ethylenediamine complexes the splittings⁸ are small and ambiguous. The X-ray diffraction study⁹ of the 2[d-Coen₃Cl₃], NaCl, 6H₂O crystal gives the absolute configuration (I) to the d-Corn₃³⁺ ion, and shows



that the C_3 axes of the complex ions are parallel to the optic axis of the uniaxial crystal. The circular dichroism of this crystal has now been measured with the circularly polarised light directed along the optic

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 ⁸ Yamada and Tsuchida, Bull. Chem. Soc. Japan, 1960, 33, 98.
 ⁹ Nukura Shira Saita and Vanana Bull. Chem. Soc. Japan, 1067, 20, 168

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- ¹⁰ Mathieu, J. Chim. phys., 1936, 33, 78.
- ¹¹ Unpublished measurements by the authors.
- ¹² McCaffery and Mason, Trans. Faraday Soc., in the press.



The circular dichroism, the electronic absorption spectrum - - - - - of the d-Coen₃³⁺ ion in solution, and the circular dichroism------ of the 2[d-Coen₃Cl₃],NaCl,6H₂O crystal with radiation propagated along the optic axis.

axis so that the radiation field can give rise only to transitions of E symmetry. The results (Figure) establish that the E transition has a positive rotational strength and, by comparison with the solution circular dichroism, that it has the lower energy in the d-Coen₃³⁺ ion.

It is suggested that dihedral d^3 and d^6 complexes have the same absolute configuration as the d-Coen₃³⁺ ion (I) if the spin-allowed transition of lowest energy has an E component with a positive rotatory power. This criterion is in accord with the solubility assignments of chirality to dihedral complexes. The E component of the long-wavelength circular dichroism absorption given by a dihedral complex in solution^{10,11} can be identified¹² not only from the energy-splitting, but also from the polarisation ratio of the A_2 and the E transitions observed⁶⁻⁸ in the spectra of the crystal. The identifications show

¹ Werner, Ber., 1912, 45, 1229.

that the complexes of chromium(III) and cobalt(III) with the absolute configuration (I) are the ethylenediamine complexes with the less-soluble chloro-(+)tartrate, the oxalate complexes with the less soluble (-)-strychnine salt, and the more stable of the neutral enantiomeric complexes formed with (+)hydroxymethylenecamphor, a β -dicarbonyl ligand. By using the solubility relations^{1,2} the assignment of chirality (I) can be extended to the corresponding

ethylenediamine and oxalate complexes of rhodium-(III) and iridium(III).

The authors are indebted to the Royal Society, Imperial Chemical Industries Limited, and Messrs. Albright and Wilson Ltd., for the components used in the construction of the circular dichroism spectrophotometer.

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The Absolute Configuration of Prostaglandin F₂₋₁

By SIXTEN ABRAHAMSSON, SUNE BERGSTRÖM, and BENGT SAMUELSSON (CRYSTALLOGRAPHY GROUP, INSTITUTE OF MEDICAL BIOCHEMISTRY, UNIVERSITY OF GÖTEBORG AND INSTITUTE OF CHEMISTRY, KAROLINSKA INSTITUTET, STOCKHOLM, SWEDEN)

A MATERIAL stimulating smooth muscle and depressing blood pressure was discovered in human semen by Goldblatt¹ and by von Euler² who also found a similar activity in sheep sperm and named the factor "prostaglandin."

In 1960 Bergström and Sjövall³ isolated two active crystalline compounds, PGE_1 ($C_{20}H_{34}O_5$) and PGF_1 $(C_{20}H_{36}O_5)$, from sheep prostate glands. The molecular weight was determined by mass spectrometry. X-Ray methods³ indicated a molecular weight of $353 \pm 5.$

Reduction of the first compound (PGE_1) with borohydride yielded the second (PGF₁), together with an isomer (PGF₂).⁴ The structure of compound PGE₁ was recently shown⁵ to be (I) and consequently the two PGF compounds are the isomeric alcohols formed by reduction of the carbonyl group.

$$HO_{2}C \cdot [CH_{2}]_{4} \cdot CH - CH \cdot CH \stackrel{i}{=} CH \cdot CH(OH) \cdot [CH_{2}]_{4} \cdot CH_{3}$$

A three-dimensional single crystal analysis of the tri-p-bromobenzoate of the methyl ester⁶ of compound PGF₂ has now independently confirmed this molecular structure and, in addition, given the stereochemistry of the molecule (Figure). This derivative is orthorhombic $(P2_12_12_1)$ with a = 26.14, b =33.93, and c = 4.76 Å. The parameters of the mole-

- Bergström, Krabisch, Samuelsson, and Sjövall, Acta Chem. Scand., 1962, 16, 969. 4
- Bergström, Ryhage, Samuelsson, and Sjövall, Acta Chem. Scand., 1962, 16, 501.
- Abrahamsson, Acta Cryst., in the press.
- Bergström, Ryhage, Samuelsson, and Sjövall, Acta Chem. Scand., 1962, 16, in the press.
- ⁸ Baker and Meister, J. Amer. Chem. Soc., 1951, 73, 1336.



Scale drawing of the tri-p-bromobenzoate of the methyl ester of compound PGF₂, in the correct absolute configuration; deduced from the electron density map.

cule, which shows large anisotropic vibrations, have been refined by least-squares treatment to R =10.9% for the 1776 observed independent reflexions.

Ozonolysis of the three compounds yielded7 2-hydroxyheptanoic acid, $[\alpha]_{D}^{23} + 9.0^{\circ}$ in aqueous sodium hydroxide. According to Baker and Meister,⁸ the acid has then the (R)-configuration. The absolute configuration of the three molecules is thereby known and is given for the PGF₂ derivative in the Figure.

(Received, July 24th, 1962.)

¹ Goldblatt, Chem. and Ind., 1933, 52, 1056.

Von Euler, Arch. Exp. Path. Pharmakol., 1934, 175, 78; J. Physiol., 1935, 84, 21P. Bergström and Sjövall, Acta Chem. Scand., 1960, 14, 1993, 1701. 2

The Structure of Hydridobromocarbonyltris(triphenylphosphine)osmium(II)

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SPECTRAL and chemical studies have supplied substantial evidence for a direct linkage between the central atom and hydrogen in transition-metal hydrido-complexes, but have fallen short of establishing the stereochemical role of this bond. Only one X-ray crystal structure of a complex hydride, $[PtHBr(Et_3P)_2]$,¹ has been determined: Owston et al.² report that the molecule has a trans squareplanar configuration with hydrogen apparently occupying a normal co-ordinated position. Although hydrogen is not detected by X-rays, the study shows that this method provides an insight into the character of the metal-hydrogen bond.

We have examined the stereochemistry of another hydride, OsHBr(CO)(PPh₃)₃.³ The hydride and carbonyl ligands in this compound originate from the solvent used in the synthesis,3 and their presence was not recognised when the complex was first reported {as [OsBr(PPh₃)₃]}.⁴ The present results strongly suggest an octahedral co-ordination for the osmium atom (see Figure), supporting the revised formulation, and thereby contributing to the new chemistry of metal hydride and carbonyl formation by reaction with alcohols.⁵

Results.— $[OsHBr(CO)(PPh_3)_3], M = 1086$, orthorhombic, a = 19.5, b = 18.7, c = 25.6 Å, $D_{m} = 1.52$, Z = 8, $D_c = 1.55$. Space group *Pbca* (No. 61).⁶ 326 h0l and 275 0kl reflections were measured photographically, $Cu-K_{\alpha}$ radiation being used. The osmium positions were located from Patterson projections; electron-density projections, it being assumed that phase domination was by osmium, showed maxima attributable to bromine and three phosphorus. Because of the large number of carbon atoms, no further attempt was made for a complete structural analysis. R was 0.29 and 0.32 for the hol and 0kl zones, respectively.

The essential features of the structure are shown in the Figure. The phosphorus atoms lie at the corners of a triangle with osmium approximately on one of the edges. In the [100] projection no definite maximum of electron density is found corresponding to the fourth corner of the quadrangle. In [010] a rather diffuse maximum is evident in the octahedral position trans to bromine, attributable to overlapping of two carbonyl groups belonging to different molecules.



Molecular configuration of [OsHBr(CO)(PPh₃)₃] (bond lengths in Å).

The bond trans to the assumed position of hydrogen, Os-P₃, is longer than expected from the sum of covalent radii; the Os-P1 and Os-P2 bonds are shorter than expected, and they are bent toward Os-H. These observations show an analogy with the structure of [PtHBr(Et₃P)₂] (quoted above).²

The X-ray evidence for the structure (Figure) is compatible with the magnetic properties of $[OsHBr(CO)(PPh_3)_3]$ (diamagnetic, 76-400°K) and its isostructural analogues $[MHX(CO)L_3]$ (M = Os, Ru; X = Cl, Br; L = PPh₃, AsPh₃).^{3,7} These data agree with the formulation of the compounds as octahedral M(II) complexes of spin-paired d_{e}^{6} configuration, and, together with isotopic and infrared spectral evidence,3 eliminate a square-pyramidal structure of an Os(I) species (i.e., without hydrogen) that might have appeared possible solely on the basis of X-ray data. (Received, August 20th, 1962.)

Vaska and DiLuzio, J. Amer. Chem. Soc., 1961, 83, 1262.

- ⁵ (a) Chat and Shaw, *Chem. and Ind.*, 1960, 931; (b) Vaska, *ibid.*, 1961, 1402, and refs. quoted ⁶ These were determined initially by Dr. S. S. Pollack, ref. 4.

⁷ Unpublished results.

¹ Chatt, Duncanson, and Shaw, Proc. Chem. Soc., 1957, 343.

² Owston, Partridge, and Rowe, Acta Cryst., 1960, 13, 246. 3

⁴ Vaska, Z. Naturforsch., 1960. 15b, 56.

Synthesis of Benzocyclobutene from Cyclo-octane Derivatives

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THE previously-described base-catalysed aromatisation¹ of diacetylenes prompted an extension of the process with tetrabromo-derivatives as precursors. In one example the readily-available cis, cis-cycloocta-1,5-diene was converted in 83% yield into homogeneous 1,2,5,6-tetrabromocyclo-octane (m.p. 147-148°) by treatment with pyridinium bromide perbromide. Heating with excess of potassium t-butoxide in 2,2'-dimethoxydiethyl ether at 120° produced a mixture of hydrocarbons which, by gasliquid chromatography in conjunction with chemical methods, was shown to consist of benzocyclobutene (\sim 30%), an unidentified isomeric non-benzenoid hydrocarbon (\sim 50%), styrene (\sim 10%), and traces of cyclo-octatetraene and another unidentified hydrocarbon. Preparative isolation of benzocyclobutene indicated an overall yield of 20% from the diene. Its ultraviolet, infrared, nuclear magnetic

resonance, and mass spectra were identical with those of an authentic sample of benzocyclobutene derived from benzenoid precursors.²

The isolation of a trace of cyclo-octatetraene from the reaction suggested the possibility of this hydrocarbon's functioning as an intermediate in the process. Indeed, base-catalysed rearrangement of cyclooctatetraene itself by this method gave a similar mixture of benzocyclobutene ($\sim 44\%$), the first of the above unidentified hydrocarbons ($\sim 40\%$), styrene ($\sim 13\%$), and a trace of unchanged cyclooctatetraene.

We are now engaged in studying the mechanism of these transformations. We thank the Institute of Petroleum Hydrocarbon Chemistry Panel for a grant.

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¹ Eglinton, Raphael, and Willis, Proc. Chem. Soc., 1960, 247.

² We thank Prof. L. Horner of the University of Mainz for a generous sample of benzocyclobutene.

The Synthesis of Cyclobutenes by Photoisomerisation* By K. J. CROWLEY

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ALTHOUGH the photoisomerisation of myrcene (I) follows a foreseeable course to some extent,¹ the main product (54%) is the unexpected cyclobutene (II). The latter showed no ultraviolet maximum (ϵ_{191} 16,000 in C₈H₁₈) and had infrared absorptions indicative of trisubstituted double bonds. It took up two equivalents of hydrogen (Pt-AcOH) with the disappearance of these absorptions and the appearance of the isopropyl doublet (1385 and 1368 cm.⁻¹). The photoproduct was reconverted into myrcene by heat (3 min. at 215° gave 95% conversion), and, on ozonolysis, yielded γ -ketopimelic acid (infrared spectrum and mixed m.p.).

On irradiation of isoprene as a 1% solution in hexane until the ultraviolet absorption of the diene had disappeared, 1-methylcyclobutene (b.p., $n_{\rm D}$, infrared spectrum²) was obtained in 36% yield after distillation. 2,3-Dimethylbutadiene gave the corresponding dimethylcyclobutene in 70% yield when irradiated as a 1% solution in ether. The product

 $^{(\}epsilon_{191} 8100 \text{ in } C_8H_{18}; \nu_{max.} 1689 \text{ cm.}^{-1})$ absorbed one equivalent of hydrogen to give a saturated derivative $(\epsilon_{191} 50 \text{ in } C_8H_{18})$, was oxidised by permanganate to hexane-2,5-dione, and yielded the parent diene when heated for 10 min. at 210°.



Similarly, the photoproduct (IV) of bi(cyclohex-1enyl) (III) showed λ_{max} . 204 m μ (ϵ 10,400 in C₉H₁₈) and ν_{max} . 1703 cm.⁻¹, required one equivalent of hydrogen to give the saturated derivative, and was isomerised to the diene (III) when heated for 2.5 hr. at 280°.

^{*} Presented at the Second Internat. Symposium on the Chemistry of Natural Products, Prague, August 27th— September 2nd, 1962. ¹ Crowley, Proc. Chem. Soc., 1962, 245.

² Cleveland, Murray, and Gallaway, J. Chem. Phys., 1947, 15, 742.

The formation of cyclobutene rings fused in a variety of polycyclic systems on irradiation of conjugatedly unsaturated six-, seven-, and eightmembered rings has recently been reported.³ The present work, in conjunction with these results, suggests that cyclobutene formation on irradiation of conjugated dienes is a general reaction, provided that steric factors permit, and that competing reactions do not excessively interfere.

In this work the irradiations were carried out at room temperature, with a 450-w Hanovia mercuryarc lamp in a water-cooled "Vycor" glass internal probe. Under these conditions approximately 5, 15,

and 40 hours' irradiation were required to produce one gram of products (II) and (IV) and 1-methylcyclobutene, respectively, but irradiation times should be considerably reduced by the use of a quartz probe, coupled, if necessary, with a suitable light-filter. This reaction, which, at least in simple cases, gives unusually clean products, offers an attractive approach to the synthesis of simple cyclobutene compounds from readily available starting materials. It should, in some instances, afford the most direct route to the corresponding cyclobutanes.

(Received, August 21st, 1962.)

³ de Mayo and Reid, Quart. Rev., 1961, 15, 393; Schuller, Moore, Hawkins, and Lawrence, J. Org. Chem., 1962, 27, 1178; Chapman, Pasto, Borden, and Griswold, J. Amer. Chem. Soc., 1962, 84, 1220; Dauben and Cargill, J. Org. Chem., 1962, 27, 1910; Chappell and Clark, Chem. and Ind., 1962, 1198.

The Stereochemistry of α -Santonin By J. D. M. ASHER and G. A. SIM (CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW, W.2)

WE recently reported¹ that bromodihydroisophoto- α -santonic lactone acetate has the stereochemistry defined in (I) with the configuration of the 13-methyl group opposite to that generally $accepted^2$ for α -santonin (II; R = H). Synthetic studies by Barton and his collaborators3 indicated that inversion of



configuration at position 11 does not occur in the conversion of santonin into bromodihydroisophotosantonic lactone acetate and the revised stereochemistry shown in (II; R = H) was therefore attributed to α -santonin. At about the same time Nakazaki and Arakawa⁴ provided further support for the revised configuration at position 11 by the degradation of α -santonin to (+)-benzoylalanine.

We have now obtained incontrovertible proof of the revised configuration: X-ray analysis of 2-bromo- α -santonin defines its constitution and relative stereochemistry to be as in (II; R = Br), and

- ² See Cocker and McMurry, *Tetrahedron*, 1960, **8**, 181. ³ Barton, Miki, Pinhey, and Wells, *Proc. Chem. Soc.*, 1962, 112.
- ⁴ Nakazaki and Arakawa, Proc. Chem. Soc., 1962, 151.

 α -santonin must therefore have the stereochemistry shown in (II; R = H), the absolute configuration shown being firmly established chemically.²

Crystals of 2-bromo- α -santonin are orthorhombic, with space group $P2_12_12_1$, and four molecules of $C_{15}H_{17}BrO_3$ in the unit cell of dimensions a = 7.34, b = 23.34, c = 8.28 Å. From equi-inclination Weissenberg photographs 1300 independent structure amplitudes were evaluated. The crystal, and hence molecular, structure was determined by threedimensional Patterson and Fourier methods. Subsequent refinement of the atomic positions by the method of least squares has reduced the value of Rto 17%.

For the calculations on the Glasgow University DEUCE computer programmes devised by Dr. J. S. Rollett⁵ and Dr. J. G. Sime⁶ were employed. We are grateful to Professor D. H. R. Barton, F.R.S., for supplies of 2-bromo- α -santonin, to Professor J. Monteath Robertson, F.R.S., for his encouragement, and to Mr. A. C. Macdonald for assistance in the early stages of the analysis. One of us (J.D.M.A.) is indebted to the Department of Scientific and Industrial Research for financial support.

(Received, August 3rd, 1962.)

¹ Asher and Sim, Proc. Chem. Soc., 1962, 111.

⁵ Rollett in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 87.

⁶ Sime, ref. 5, p. 301.

Infrared and Nuclear Magnetic Resonance Studies of α-Amino-polycarboxylic Acids in Aqueous Solution

By D. CHAPMAN, D. R. LLOYD, and R. H. PRINCE (UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE)

THE infrared spectra^{1a} of salts of iminodiacetic and nitrilotriacetic acid are in good agreement with measurements that we have made. We have, however, obtained the infrared spectrum of the latter acid itself in D_2O solution and shown that the acid is present in a zwitterion form (bands at 1730 and 1635 cm.⁻¹) in contrast to its existence in the crystal as a "normal" carboxylic acid (single band at 1736 cm.⁻¹). The acid hydrochloride in D_2O also has a single band at 1732 cm.⁻¹. We find that methyliminodiacetic acid and ethylenediaminetetra-acetic acid also undergo this change from a normal to a zwitterion form when dissolved in water. Apparently the hydrogen-bonded systems available in the crystal are energetically favourable for the existence of the normal type of acid structure.

Disodium hydrogen nitrilotriacetate shows only one infrared band, at 1625 cm.⁻¹, among the carboxylate (asymmetric stretching) frequencies when one proton is added to the molecule. This is a shift of some 37 cm.⁻¹ from the band position for the trisodium salt containing the anion (I).

(I)
$$N(CH_2 \cdot CO_2)_3$$
 $RN^+(CH_2 \cdot CO_2)_3$ (II)

Apparently the single proton is attached to the nitrogen atom as in (II; R = H), and the frequency shift arises from an inductive effect.¹ Similar shifts occur with methyliminodiacetic (42 cm.⁻¹) and ethylenediaminetetra-acetic acid (43 cm.⁻¹ for the disodium salt). With dimethylglycine and glycine they are 47 and 33 cm.⁻¹, respectively.

Whilst inductive effects may operate in all these cases, direct interaction of the CO_2^- group with the NH⁺ group may be more important for the following reasons:

(a) A greater inductive effect might be expected for the betaine system Me^{.+}N \leftarrow than for the system H⁺N \leftarrow ; consequently the CO₂⁻ (as) frequency difference between ions (I) and (II; R = Me) should be greater than that between (I) and (II; R = H). The converse is observed: the betaine shows a frequency shift 10 cm.⁻¹ less than that of the monoprotonated anion. The chemical shift, τ , of the CH₂ protons suggests, however, that there is a larger inductive effect operating in the betaine since we observe a larger difference in τ between (I) and (II; R = Me) than between (I) and (II; R = H). (b) A purely inductive effect should affect each of the two C–O bonds of the CO_2^- group equally, the (sym) and (as) frequencies of the carboxylate group moving in the same sense,^{1b} but in all the examples cited the (as) carboxylate frequency increases whereas the associated (sym) frequency decreases. This would be expected if the NH⁺ group has an unsymmetrical influence on the carboxylate group. If the monoprotonated anion of nitrilotriacetic acid has the structure (III) such an effect is to be expected.

(c) An electrostatic (or hydrogen-bonded) model (III) is a compact sterically permissible structure, the proton lying in a cage of CO_2^- groups. This may be compared with the situation of the proton in di-



methylglycine, methyliminodiacetic acid, and trimethylamine conjugate acid in which the proton is exposed to solvent. The rates of proton exchange in the systems $Me_n(^+NH\cdot CH_2\cdot CO_2^-)_{3-n}/OH^-$ where n= 3, 2, and 1 are very similar, but for n = 0 the rate decreases² by a factor of 10². This is consistent with proton transfer from a structure such as (III).

Changes in the nuclear magnetic resonance chemical shifts, $\Delta \tau$, of the CH₂ and the CH₃ protons (if any) adjacent to the nitrogen atom and carboxylate groups when protonation occurs give additional information on structural changes during stepwise protonation. With ethylenediaminetetra-acetic acid the values for the "outer" CH2 groups are large for the first two proton additions and much smaller for each of the next four. This is consistent with attachment of the first two protons to nitrogen, giving a double zwitterion, and substantiates ionisation schemes based on pK data.³ This large change in proton chemical shift of the CH₂ adjacent to nitrogen on proton addition, and a small shift of these protons on protonation of the carboxylate groups, are observed with a number of α -amino-polycarboxylic acids and related compounds.

(Received, August 1st, 1962.)

² Eigen and Kruse, unpublished work.

¹ Nakamoto, Morimoto, and Martell, J. Amer. Chem. Soc., (a) 1962, 84, 2081; (b) 1961, 83, 4528.

⁸ Schwarzenbach and Ackermann, Helv. Chim. Acta, 1947, 30, 1798; Olsen and Margerum, J. Amer. Chem. Soc., 1960, 82, 5602; cf. "Stability Constants," Chem. Soc. Special Publ., No. 6, Part I, pp. 47, 49.

An Improved Platinum Catalyst for Hydrogenation of an Olefin

By R. W. BOTT, C. EABORN, E. R. A. PEELING, and DENNIS E. WEBSTER

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BROWN and BROWN recently described the preparation of a "highly active" platinum catalyst for olefin hydrogenation;¹ it was made from hexachloroplatinic acid and sodium borohydride in ethanol in the presence of hydrochloric acid, and was about 1.6times as active as commercial Adams catalyst (PtO₂) in hydrogenation of oct-1-ene under their conditions. We find that reduction of hexachloroplatinic acid with a silicon hydride gives a catalyst many times more active than either Adams catalyst or Brown and Brown's catalyst.

Thus, hexachloroplatinic acid (0.01 mmole) in 95% aqueous ethanol (1 ml.) was added to a solution of tribenzylsilane (0.1 mmole) in 95% aqueous ethanol (20 ml.) at 70°, contained in a 250-ml. flask. The mixture, which became brown, was allowed to cool for 10 min. and the flask was placed in a thermostat-bath at 30°. Some minutes later a solution of oct-1-ene (40 mmole) in 95% aqueous ethanol (29 ml.) was added, the system was thrice flushed with hydrogen, and the flask was connected to a hydrogen reservoir (kept at atmospheric pressure) and shaken at 300 cycles/min. The expected quantity of hydrogen was absorbed, at 78 ml./min. (corrected to s.t.p.), which is 1.5 times as fast as in Brown and Brown's experiment with 20 times as much hexachloroplatinic acid. With Adams catalyst (0.09 mmole) containing 9 times as much platinum, in

presence of a little hydrochloric acid (0.1 mmole), hydrogen was absorbed at 67 ml./min. [Silicon hydrides have a promoting effect on Adams catalyst, and the rate was 117 ml./min. when tribenzylsilane (1 mmole) was present.]

We have also used trichloro-, triethyl-, tributyl-, triphenyl-silane. They reduce hexachloroplatinic acid with differing ease (reaction is fast with the three triorganosilanes at room temperature, while boiling is required with trichlorosilane), but the formed catalysts have much the same activity as that from tribenzylsilane.

The catalyst from a silicon hydride and hexachloroplatinic acid is several times *less* active than Adams catalyst in hydrogenation of benzene, and the presence of a silicon hydride markedly retards the hydrogenation of benzene over Adams catalyst.

These results have immediate practical value, but also interesting theoretical implications, and the investigation continues.

We thank Dr. D. L. Bailey, of the Silicones Division, Union Carbide Corporation, for valuable discussions which led to this investigation, and D.S.I.R. for a maintenance grant to one of us (D.E.W.).

(Received, August 9th, 1962.)

¹ Brown and Brown, J. Amer. Chem. Soc., 1962, 84, 1494.

A Stereospecific Epimerisation of Cyclitols

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It was found that cyclitols, or cyclitol acetates, are epimerised on being refluxed in 95% acetic acid containing 1.5% sulphuric acid. The reaction is reversible, and in most of our cases equilibrium was established. The reaction is stereospecific: epimerisation occurs only on those carbon atoms whose hydroxyl group is flanked by a *cis*-hydroxyl group on one side and by a *trans*-hydroxyl group on the other. Thus, epi-inositol (I) is converted into alloinositol (II) which in turn is changed into neoinositol (III); the proportion of these isomers in equilibrium, as determined by gas-liquid chromatography,¹ was 17:23:60.

¹ Angyal and Krzeminski, J., 1962, 3251.

Similarly, myo-, (\pm) -, and muco-inositol are interconvertible, but scylloinositol (in which all the hydroxyl groups are *trans* to each other) and cisinositol (all-*cis*) are not changed. The reaction was



also applied to several cyclohexane-pentols and -tetrols, and the position of the equilibria was determined, although in these cases the stereospecific epimerisation was accompanied by some slower. random epimerisation.

The stereospecificity of the reaction is explained by assuming that it occurs by a nucleophilic attack of a neighbouring acetate group on a carbon atom which is attached to a cyclic acetoxonium ion:



The reaction appears to be related to two other recently described processes: to the epimerisation of acetylated 6-deoxy-6-iodo-aldehydo-sugars in the

² Micheel and Böhm, Tetrahedron Letters, 1962, 107.

³ Hedgley and Fletcher, J. Amer. Chem. Soc., 1962, in the press. (We thank Dr. H. G. Fletcher, Jr., for allowing us to study the manuscript of this paper before publication.)

kcal./mole.

⁴ Cf. Angyal and McHugh, Chem. and Ind., 1956, 1147.

The Catalytic Action of Anionic Catalysts

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WE have shown¹ that steric hindrance prevents addition of a butyl anion to tetraphenylethylene and 1,1,3,3-tetraphenylbut-1-ene. An electron can be added to these olefins, however, either by use of sodium metal or of sodium naphthalene in tetrahydrofuran.² This electron transfer occurs immediately the sodium naphthalene and olefin solutions

are mixed. If the sodium naphthalene and 1,1,3,3tetraphenylbut-1-ene solutions are mixed at -70° , the green colour of the sodium naphthalene remains; when the solution warms, the green colour is slowly replaced by the red of the olefin anion.

presence of zinc chloride and acetic anhydride² (in

which stereospecificity was not observed, since the compounds were acyclic), and to the reaction of

inositol acetates with liquid hydrogen fluoride³

which gave the same products as our reaction but

For the six cases in which we established equilibrium, it was possible to calculate the differences in the free-energy content of the isomers in agreement with the experimental data, mostly within 0.1 kcal./mole, by the assumption that the interaction energies between non-bonded groups are additive, and by using the following values for the interaction energies:⁴ $(O_1:O_2)$ 0.5, $(O_a:H_a)$ 0.4, $(O_a:O_a)$ 2.1

(Received, August 17th, 1962.)

did not proceed to equilibrium.

We have now studied the electron transfer to these two olefins from a variety of sodium hydrocarbons

Electron	Aromatic	Concentrations (mole $1.^{-1}$)		Rate of electron transfer to	
affinity (ev)	hydrocarbon ArH	10 ³ [Na+ HAr-]	10 ³ [Olefin]	Tetraphenyl- butene	Tetraphenyl- ethylene
2.59	Naphthalene	0.380	1.07	Rapid	-
		0.282	0.742		Rapid
2.63	Phenanthrene	34.3	42.7	Rapid	
		16.5	16-9	-	Rapid
2.76	Chrysene	0.414	5.62	Slow	-
	•	2.38	9.35		Rapid
2.78	Picene	1.52	8.23	Slow	-
		1.74	2.06		Rapid
2.96	Pyrene	0.755	9.05	No transfer	-
	·	0.878	6.49		No transfer
3.04	1,2-Benzanthracene	1.37	2.72		No transfer
3.11	Anthracene	2.15	7.70	No transfer	
		2.85	3.87		No transfer
3.32	Perylene	2.88	7.60	No transfer	
	•	3.27	4.55		No transfer

¹ Evans and George, J., 1961, 4753. ² Evans, Evans, Owen, Tabner, and Bennett, Proc. Chem. Soc., 1962, 226.

³ Matsen, J. Chem. Phys., 1956, 24, 602.

in tetrahydrofuran, and our results at room temperature are given in the Table, together with the electron affinities calculated for the hydrocarbons. It is seen that as the electron affinity increases there is a change from rapid electron transfer to absence of electron transfer.

For 1,1,3,3-tetraphenylbut-1-ene, electron transfers from sodium chrysene and sodium picene are slow enough to be measured spectroscopically; for chrysene the transfer reaction is first order in sodium chrysene and in olefin. The velocity constant at 30° is 4.4×10^{-1} moles⁻¹ min.⁻¹ l., and its activation energy is 14 kcal. mole⁻¹. Electron transfer from sodium picene is much slower; for sodium chryseen and sodium picene to tetraphenylethylene it is much faster than to 1,1,3,3-tetraphenylbut-1-ene.

We thank D.S.I.R. for a Research Studentship (to J.C.E.) and the University of Wales for a University Studentship (to B.J.T.).

(Received, July 30th, 1962.)

Absorption Spectrum of the Tropyl (Cycloheptatrienyl) Radical By B. A. THRUSH and J. J. ZWOLENIK

(DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF CAMBRIDGE)

THE properties of cyclic polyenes are of particular interest since they lend themselves readily to theoretical treatment. Application of simple molecular orbital theory to π -electron systems, notably by Hückel,¹ predicted the relatively high stability of the cyclopentadienyl anion and of the tropylium cation. The free radicals cyclopentadienyl and tropyl are not expected to be unusually stable, but should be detectable by flash photolysis. The absorption spectrum attributed² to the cyclopentadienyl radical agrees well with theoretical predictions.³ The spectrum of the tropyl radical is of particular interest since this species is predicted to have an ionisation potential as low as 6.41 ev;⁴ a mass-spectrometric value of 6.6 ± 0.1 ev has been reported⁵ for these radicals produced by the pyrolysis of bitropyl.

We have observed a transient absorption spectrum attributed to the tropyl radical in the flash photolysis of bitropyl (biscycloheptatrien-7-yl) and of ditropyl sulphide (bis-cycloheptatrien-7-yl sulphide) using ca. 0.1 mm. Hg of vapour in a great excess of nitrogen. This spectrum consists of three members of a Rydberg series ν (cm.⁻¹) = 50,325 - R/(n + 0.043)², converging to an ionisation threshold of 6.23_7 ev.

Appearance	$\nu_{\rm obs.}$	$\nu_{\rm calc.}$	Diff.
of band	(cm1)	(cm1)	(cm1)
Diffuse	38,450	38,474	-24
Narrow	43,654	43,612	+42
Narrow	45,991	46,010	-19
	Appearance of band Diffuse Narrow Narrow	Appearance $\nu_{obs.}$ of band(cm. ⁻¹)Diffuse38,450Narrow43,654Narrow45,991	Appearance $\nu_{obs.}$ $\nu_{calc.}$ of band(cm. ⁻¹)(cm. ⁻¹)Diffuse38,45038,474Narrow43,65443,612Narrow45,99146,010

The low ionisation potential and the absence of strong vibrational structure show that the electron

- 4 Streitwieser, J. Amer. Chem. Soc., 1960, 82, 4123.
- ⁶ Harrison, Honnen, Dauben, and Lossing, J. Amer. Chem. Soc., 1960, 82, 5593.
 ⁶ Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, 1961, p. 188. ⁷ Meyerson and Rylander, J. Chem. Phys., 1957, 27, 901.
- ⁸ Meyerson, Rylander, Eliel, and McCollum, J. Amer. Chem. Soc., 1959, 81, 2606.

excited is antibonding, and that the ion and the radical formed have similar configurations. This evidence, and the production of the same transient spectrum in the photolysis of two parent molecules concerned, leave little doubt that this spectrum is due to the tropyl radical, since the difference between the spectroscopic and the mass-spectrometric ionisation potential is of the magnitude and sign frequently encountered with aromatic species.⁶ This is thought to be the first observation of a molecular Rydberg series outside the vacuum ultraviolet.

Combining Lossing's value⁵ for $\Delta H_{\rm f}$ (cyclo-C₇H₇.) = 65 kcal./mole with our value for the ionisation potential of the tropyl radical gives $\Delta H_{\rm f}$ (cyclo- $C_7H_7^+$ = 209 kcal./mole. This is significantly below the best value⁵ of $\Delta H_f(C_6H_5 \cdot CH_2^+) = 222$ kcal./mole and shows that the formation of the symmetrical $C_7H_7^+$ ions observed in the mass spectra of toluene derivatives7 is favoured energetically. It also supports evidence that this rearrangement is not confined to species with an excess of energy, in that the symmetrical ion is formed from benzyl halides at the ionisation threshold.8

The authors thank Professor Hyp J. Dauben, Jr., of the University of Washington for generously supplying the specimens of bitropyl and ditropyl sulphide. J.J.Z. thanks the National Science Foundation for a Postdoctoral Fellowship.

(Received, August 2nd, 1962.)

¹ Hückel, Z. Phys., 1931, 70, 204. ² Thrush, Nature, 1956, 178, 155.

³ Longuet-Higgins and McEwen, J. Chem. Phys., 1957, 26, 719.

Conversion of Alkoxyphosphazenes into 1,3,5-Triazines

By B. W. FITZSIMMONS, C. HEWLETT, and R. A. SHAW

(DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE, MALET STREET, LONDON, W.C.1)

As part of an investigation of alkoxyphosphazenes,^{1,2} reactions with a number of reactive halogen compounds have been studied. Hexaethoxycyclotriphosphazatriene (I) when heated with benzoyl chloride for 1 hr. at 130-140° gives ethyl chloride, ethyl metaphosphate³ (identified by infrared spectroscopy), and 2,4,6-triphenyl-1,3,5-triazine (II) (identified by analysis, infrared spectrum, and mixed m.p.). Octaethoxy-



cyclotetraphosphazatetraene, $N_4P_4(OEt)_8$ undergoes this transformation during 5 hr. at 140-160°, giving the same products. This conversion can be understood

- Fitzsimmons and Shaw, Chem. and Ind., 1961, 109.
 Fitzsimmons and Shaw, Proc. Chem. Soc., 1961, 258.
 Cramer and Hettler, Chem. Ber., 1958, 91, 1181.
- ⁴ Smolin and Rappoport, "s-Triazines and Derivatives," Interscience Publishers Inc., New York, 1959, p. 178.

On the Origin of Methylenedioxy-groups in Nature

By D. H. R. BARTON, G. W. KIRBY, and J. B. TAYLOR

(IMPERIAL COLLEGE, LONDON, S.W.7)

DURING recent studies^{1,2} on the biosynthesis of Amaryllidaceae alkaloids we examined the incorporation of the phenol (I) into the alkaloids of the King Alfred daffodil. Unlike norbelladine and its N-methyl and ON-dimethyl derivatives, the phenol (I), labelled in the carbon chain with carbon-14 as indicated, was not incorporated significantly into galanthamine or galanthine. However, efficient incorporation (highest value, 1.0% into haemanthamine (II) was observed. It being accepted^{2,3} that the phenol (I) is not extensively degraded in the plant before transformation into haemanthamine, the methylenedioxy-group of the latter must be formed either by demethylation followed by reaction with a suitable formaldehyde equivalent, or by oxidative cyclisation of methoxyl to methylenedioxy. Since demethylation before alkaloid formation does not occur² with galanthamine we were led to favour the latter possibility.

The following critical experiments proved this hypothesis for haemanthamine.

¹ Barton, Kirby, Taylor, and Thomas, Proc. Chem. Soc., 1961, 254.

- ² Barton, Kirby, Taylor, and Thomas, Proc. Chem. Soc., 1962, 179.
- Wildman, Fales, Highet, Breuer, and Battersby, Proc. Chem. Soc., 1962, 180.

⁴ Sribney and Kirkwood, Nature, 1953, 171, 931; we thank Dr. Kirkwood cordially for sending us details of his hydrolysis procedure.

on the basis of an attack of the nitrogen atom on the carbonyl group:



It may be that reaction then proceeds by formation of ethyl metaphosphate with concomitant splitting out of benzonitrile, which is known to trimerise in the presence of benzoyl chloride to the triazine (II).⁴

Receipt of financial assistance from the U.S. Department of Agriculture is gratefully acknowledged.

The phenol (I) was labelled in both the carbon

chain (81%) and in the methoxyl group (19%). The

(I)

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(Received, September 4th, 1962.)

(II)

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biogenetically derived haemanthamine had 20% of

its activity in the methylenedioxy-group, the

methylene carbon being isolated as formaldehyde after hydrolysis with 20% sulphuric acid.⁴ In another

experiment, haemanthamine, derived from the doub-

ly labelled precursor (I) containing 4.6% of the

activity in the methoxyl group, was degraded to the amino-acid (III).⁵ Cleavage with lead tetra-acetate then gave inactive carbon dioxide, formaldehyde (94% of total activity), and *N*-methyl-6-phenyl-piperonylamine⁶ (4.3% of total activity). Hydrolysis of the haemanthamine liberated 4.7% of its activity as formaldehyde.

be derived biogenetically from *o*-methoxyphenols was first mentioned by Sribney and Kirkwood,⁴ who found that methionine, but not formate, was a precursor for the methylenedioxy-group of protopine.* We are not aware, however, of any definite evidence on this question apart from that reported in the present communication.

The hypothesis that methylenedioxy-groups could

(Received, August 22nd, 1962.)

* At the Meeting of the Chemical Society in Sheffield, 1962, Professors A. J. Birch and A. R. Battersby stated that they had also independently conceived that methylenedioxy-groups could be biosynthesised in this way. ⁵ Fales and Wildman, J. Amer. Chem. Soc., 1960, 82, 197; Battersby, Fales, and Wildman, J. Amer. Chem. Soc.,

1961, 83, 4098. ⁶ Warren and Wright, J., 1958, 4696.

NEWS AND ANNOUNCEMENTS

Editorial Office: Change of Address.—The Editorial Office of the Chemical Society has moved to 20—21 Cornwall Terrace, Regent's Park, London, N.W.1. The telephone number remains the same, WELbeck 1707.

Liaison Officer.—Mr. D. W. Wilson has agreed to serve as a Chemical Society Liaison Officer at Sir John Cass Technical College in place of Dr. A. J. Lindsey who has resigned.

Local Representative for Melbourne.—The resignation of Dr. J. F. Duncan, who has been appointed to the Chair of Inorganic and Theoretical Chemistry at Victoria University, New Zealand, has been accepted, and the Council has appointed Professor R. L. Martin as Local Representative for Melbourne.

Election of New Fellows.—66 Candidates, whose names were published in *Proceedings* for August, have been elected to the Fellowship.

Death of Honorary Fellow.—We regret to announce the death (28.8.62) of *Dr. E. W. R. Steacie*, President of the National Research Council of Canada, who was elected an Honorary Fellow of the Society in 1958.

Deaths.—We regret to announce the deaths of the following Fellows: *The Rev. Canon F. G. Belton* (29.4.62) of Birmingham; *Dr. C. M. French* (6.8.62), Lecturer in Chemistry at Queen Mary College, London; and *Dr. H. McCombie* (31.5.62), Reader, Emeritus, in Chemistry, University of Cambridge.

Royal Society Delegation to Peking.—*Mr. H. M. Powell* and *Dr. H. W. Thompson* were members of a Royal Society Delegation visiting Peking recently on the invitation of the President of the Academia Sinica in exchange for a similar visit of Chinese Academicians to the Royal Society last year.

Ethel Behrens Fund.—This is a new fund, the purpose of which is to provide grants towards the travelling expenses, including maintenance, of Fellows of the Society studying at a University or Technical College in the British Isles for the first University degree, or other equivalent qualification, to enable them to attend the Anniversary Meetings of the Society and any Scientific Symposia or Discussions in conjunction therewith. The first awards are to be made in connection with the Anniversary Meetings to be held in Cardiff in March, 1963.

Forms of application, together with regulations governing the award of travel grants, may be obtained from the General Secretary and must be returned by February 15th, 1963.

Research Fund.—The Research Fund of the Chemical Society provides grants for the assistance of research in all branches of Chemistry. Applications for grants will be considered in December, 1962, and should be submitted on the appropriate form not later than November 15th, 1962. The total amount available for distribution is approximately £1,000, and applications from Fellows will receive prior consideration.

Forms of application, together with the regulations governing the award of grants, may be obtained from the General Secretary.

The Harrison Memorial Prize.—The Selection Committee, consisting of the Presidents of The Chemical Society, The Royal Institute of Chemistry, The Society of Chemical Industry, and The Pharmaceutical Society, will, in 1963, consider making an award of the Harrison Memorial Prize.

The Prize, which consists of a bronze plaque and a monetary payment of 100 guineas, will be awarded to the chemist of either sex who, being a natural-born British subject and not at the time over thirty years of age, shall, in the opinion of the Selection Committee, during the five years ending December 1st, 1962, have conducted the most meritorious and promising original investigations in Chemistry and published the results of those investigations in a scientific periodical or periodicals.

Applications, five copies of which must be sub-

PROCEEDINGS

mitted, should include the full names of the applicant; age (birth certificate to be enclosed); any other qualifications and experience; titles, and reprints if available, of published papers (with co-authors' names); where research was carried out; testimonials and references, and any other relevant particulars.

The Selection Committee is prepared to consider applications, nominations, or information as to candidates who have not attained the age of thirty years at December 1st, 1962, and are otherwise eligible for the Prize.

Any such communications must be received by the President of the Chemical Society, Burlington House, London, W.1, not later than December 31st, 1962.

The Corday-Morgan Medal and Prize.—This Award, consisting of a Silver Medal and a monetary Prize, is made annually to the Chemist of either sex and of British Nationality who, in the judgement of the Council of the Chemical Society, has published during the year in question the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years. Copies of the rules governing the Award may be obtained from the General Secretary. Applications or recommendations in respect of the Award for the year 1961 must be received not later than December 31st, 1962, and applications for the Award for 1962 are due before the end of 1963.

The Perkin Centenary Trust.—The Trust was established to commemorate the centenary of the discovery, by William Henry Perkin in 1856, of Mauveine, the first important synthetic dye. Its purpose is to promote technical education in all aspects of the manufacture and the application of colouring matters.

The Trustees invite applications for the following awards for the Academic Year 1963—64 to be submitted on forms available from the Secretary.

The Perkin Centenary Fellowship.—This award is offered normally for one or two years but is renewable exceptionally for a third year, for the purpose of higher study of any subject approved by the Trustees. Candidates will be required to show either that they have had experience in an industrial firm or other institution concerned in the manufacture or the application of colouring matters, or that their intended field of study has a direct bearing on these subjects. The maximum value of the Fellowship is £750 per annum with an additional grant of up to £100 per annum towards certain designated expenses. In each case the stipend will be determined by the Trustees in relation to the age and experience of the candidate and to other circumstances. It may be tenable, from October, 1963, at any university, technical college, or other institution approved by the Trustees. Applications must be received not later than May 1st, 1963.

The Perkin Centenary Scholarship.---Two such awards are offered, each for one or two years, renewable at the discretion of the Trustees for one further year, to enable candidates employed in an industrial firm or other institution concerned with the manufacture or the application of colouring matters to receive an education at a university or technical college. Each award will have a value of £350 per annum. This may be increased, at the discretion of the Trustees, to £400 per annum if the candidate appointed is required to live away from his normal place of residence. There is no means test and a successful candidate is not debarred from receiving the whole or a part of his normal salary from his employers during his tenure of the Scholarship. Applications must be received not later than May 1st, 1963.

Perkin Travel Grants.—A number of these grants are offered to teachers at universities, technical colleges or other institutions in order to provide an opportunity for them to widen their experience. Full details and forms of application, which are returnable not later than December 1st, 1962, are available from the Secretary.

Enquiries relating to these awards should be addressed to: The Secretary, The Perkin Centenary Trust, c/o The Chemical Society, Burlington House, London, W.1.

Symposia, etc.—An International Symposium on Boron-nitrogen Chemistry will be held on April 23rd—24th, 1963, at Duke University, Durham, North Carolina, sponsored by the U.S. Army Research Office (Durham). Participation is by invitation only and further information can be obtained from Dr. Kurt Niedenzu, U.S. Army Research Office (Durham), Box CM, Duke Station, Durham, North Carolina.

An International Symposium on Macromolecular Chemistry, sponsored by I.U.P.A.C., will be held in Paris from July 1st—5th, 1963. Further enquiries should be addressed to the Organising Committee of the Symposium, 11, Rue Pierre-Curie, Paris 5^e, France.

A Symposium on Thermodynamics and Thermochemistry, sponsored jointly by the I.U.P.A.C. commission on the Thermodynamics and Thermochemistry and by the Swedish Chemical Association, will be held in Lund, Sweden, on July 18th–23rd, 1963. Further enquiries should be addressed to Dr. S. Sunner, Thermochemical Laboratory, The University, Lund, Sweden.

Personal.—Dr. W. Blakey has been appointed Chairman of British Industrial Plastics Ltd.

Mr. K. W. DeWitt has been appointed Chief Chemist of the Halifax Toffee and Chocolate Laboratories of John Mackintosh and Sons Limited.

Dr. G. F. Kirby, formerly of Bechtel International

Corporation, has joined the Board of Industrial and Engineering Consultants Limited.

Dr. R. V. Parish has taken a post as Senior Research Associate with Professor N. N. Greenwood at King's College, Newcastle upon Tyne. Dr. G. P. Pearson has been appointed Lecturer at Bradford Institute of Technology.

Dr. D. S. P. Roebuck has been appointed to the position of Senior Scientist of Monsanto Chemicals Ltd.

FORTHCOMING SCIENTIFIC MEETINGS

London

Thursday, November 15th, 1962, at 6 p.m.

Tilden Lecture, "Nuclear Magnetic Resonance Spectroscopy," by Dr. R. E. Richards, M.A., F.R.S. To be given in the Anatomy Lecture Theatre, King's College, Strand, W.C.2.

(British Railways are offering concessionary fares for this meeting and a travel voucher will be sent by the General Secretary on receipt of a stamped and addressed envelope.)

Aberdeen

Friday, November 23rd, 1962, at 8 p.m.

Lecture, "The Prospects for Leaf Protein as a Food in Various Parts of the World," by N. W. Pirie, F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Medical Physics Lecture Theatre, Marischal College.

Aberystwyth

(Joint Meetings with the University College of Wales Chemical Society, to be held in the Edward Davies Chemical Laboratory.)

Tuesday, November 6th, 1962, at 5 p.m.

Lecture, "Mechanisms of Inorganic Redox Reactions," by Professor F. S. Dainton, Sc.D., F.R.S. Thursday, November 22nd, at 5 p.m.

Lecture, "Directive Effects in Addition Reactions," by Professor H. B. Henbest, D.Sc., F.R.I.C.

Thursday, December 6th, at 5 p.m.

Lecture, "Champagne," by Professor F. Mackenzie, M.A., D. ès l.

Belfast

Thursday, December 6th, 1962, at 7.45 p.m.

Lecture, "Catalytic Superactivity of Metal Wires," by Dr. A. J. B. Robertson, M.A. 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.

Birmingham

Friday, November 9th, 1962, at 4.30 p.m.

Lecture, "The Simplest Charge, Atom, and Molecule," by Professor F. S. Dainton, Sc.D., F.R.S, Joint Meeting with the University Chemical Society. to be held in the Chemistry Department, The University.

Bristol

(Joint Meetings with the Society of Chemical Industry and the Royal Institute of Chemistry, to be held in the Department of Chemistry, The University, unless otherwise stated.)

Thursday, November 1st, 1962, at 6.30 p.m.

Pedler Lecture, "Amino-acid Sequences in Certain Enzymes," by Dr. F. Sanger, F.R.S.

Thursday, November 15th, at 5.15 p.m.

Lecture, "Some Problems in the Chemistry of Cellwall Materials," by Professor E. L. Hirst, C.B.E., D.Sc., F.R.S.

Thursday, November 15th, at 6.30 p.m.

Social Evening (Films and Talk), to be held at Cheltenham.

Thursday, November 22nd, at 6.30 p.m.

Ladies' Night: "Perfumes," arranged by Dr. R. Favre of Proprietry Perfumes Ltd. To be held at the College of Science and Technology, Ashley Down.

Thursday, December 6th, at 6.30 p.m.

Lecture, "Modern Methods of Aluminium Production," by A. R. Carr, B.Sc., A.R.I.C., and Dr. C. E. Ransley, F.I.M. Joint Meeting with the Royal Institute of Chemistry and the Chemical Engineering Group of the Society of Chemical Industry.

Cambridge

(Joint Meetings with the University Chemical Society, to be held in the University Chemical Laboratory, Lensfield Road.)

Friday, November 2nd, 1962, at 8.30 p.m.

Lecture, "Oxidative Cyclisation," by Professor G. W. Kenner, Ph.D., Sc.D.

Friday, November 16th, at 8.30 p.m.

Lecture, "Euclid and the Chemist," by Dr. A. F. Wells, M.A.

Cardiff

Monday, November 19th, 1962, at 5 p.m.

Lecture, "Non-stoicheiometric Compounds," by Dr. J. S. Anderson, F.R.S., to be given in the Department of Chemistry, University College, Cathays Park.

Dublin

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Wednesday, November 28th, 1962, at 5.30 p.m. Lecture, "The Periodate Oxidation of Disaccharides," by Dr. J. M. Clancy, to be given in the Department of Chemistry, Trinity College.

Durham

(Joint Meetings with the Durham Colleges Chemical Society, to be held in the Science Laboratories, The University.)

Monday, November 12th, 1962, at 5 p.m.

Lecture, "The Benzidine Rearrangement," by Sir Christopher Ingold, D.Sc., F.R.S.

Monday, November 26th, at 5 p.m.

Lecture, "The Electronic Structure of Molecules," by Dr. J. W. Linnett, M.A., F.R.S.

Monday, December 3rd, at 5 p.m.

Lecture, "Unusual Co-ordination Numbers of the Transition Metals," by Professor R. S. Nyholm, D.Sc., F.R.S.

Edinburgh

Tuesday, November 20th, 1962, at 4.30 p.m.

Lecture, "Some Theoretical and Practical Aspects of Conducting Flames," by Dr. T. M. Sugden, M.A. Joint Meeting with the University Chemical Society, to be held in the Department of Chemistry, The University.

Thursday, November 22nd, at 7.30 p.m.

Lecture, "Some Chemotherapeutic Topics," by Dr. F. L. Rose, O.B.E., F.R.I.C., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Heriot-Watt College.

Thursday, December 6th, at 7.30 p.m.

Lecture, "Solid-state Polymerisation," by Professor C. H. Bamford, M.A., Sc.D., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Heriot-Watt College.

Exeter

(Meetings will be held in the Washington Singer Laboratories, Prince of Wales Road.)

Friday, November 16th, 1962, at 5.15 p.m.

Lecture, "The Recombination of Atoms—The Simplest Chemical Reaction," by Professor G. Porter, Ph.D., F.R.S. Joint Meeting with the Exeter University Chemical Society.

Friday, November 30th, at 5.15 p.m.

Lecture, "Oxidative Cyclisation," by Professor G. W. Kenner, Ph.D., Sc.D.

Friday, December 7th, at 5.15 p.m.

Lecture, "The Benzidine Rearrangement," by Sir Christopher Ingold, D.Sc., F.R.S.

Glasgow

Thursday, November 15th, 1962, at 4 p.m. Lecture, "Spectroscopic Aspects of Optical Rotatory Power," by Dr. S. F. Mason, M.A. Joint Meeting with the Alchemists' Club, to be held in the Chemistry Department, The University.

Hull

Thursday, November 8th, 1962, at 5 p.m.

Pedler Lecture, "Amino-acid Sequences in Certain Enzymes," by Dr. F. Sanger, F.R.S. To be given in the Physics Lecture Theatre, The University.

Tuesday, November 20th, at 5 p.m.

Lecture, "Electrochemical Methods of Studying Reactions," by Professor W. F. K. Wynne-Jones, D.Sc. Joint Meeting with University Students Chemical Society, to be held in the Organic Lecture Theatre, The University.

Keele

Thursday, December 6th, 1962, at 8.15 p.m.

Lecture, "Some Aspects of Di- and Tri-terpene Synthesis," by Dr. J. A. Barltrop, M.A. Joint Meeting with the Royal Institute of Chemistry, to be held in the Department of Chemistry, The University.

Leicester

Thursday, November 1st, 1962, at 4.30 p.m.

Lecture, "The Electronic Structure of Molecules," by Dr. J. W. Linnett, M.A., F.R.S. Joint Meeting with the University Chemical Society, to be held in the Department of Chemistry, The University.

Wednesday, November 14th, at 3.30 p.m.

Lecture, "Nuclear Magnetic Resonance in Organic Chemistry," by Dr. R. A. Y. Jones, M.A., M.S. Joint Meeting with the Colleges of Art and Technology Chemical Society, to be held in the Colleges of Art and Technology.

Monday, December 3rd, at 4.30 p.m.

Lecture, "Aromatic Fluorine Compounds," by Professor M. Stacey, D.Sc., F.R.S. Joint Meeting with the University Chemical Society, to be held at the Department of Chemistry, The University.

Liverpool

Thursday, November 29th, 1962, at 5 p.m.

Lecture, "Organic Reactions in Strong Alkalis," by Professor B. C. L. Weedon, D.Sc., F.R.I.C. Joint Meeting with the University Chemical Society, to be held in the Donnan Laboratories, The Chemistry Department, The University.

Manchester

Thursday, November 1st, 1962, at 6.30 p.m.

Lecture, "Some New Horizons in Reaction Kinetics," by Professor F. S. Dainton, Sc.D., F.R.S. To be given at the Manchester College of Science and Technology. Thursday, November 29th, at 5 p.m.

Lecture, "New Thoughts on Old Dyes," by Dr. E. N. Abrahart. Joint Meeting with Students Union Chemical Society of the Royal College of Advanced Technology, to be held at the Royal College of Advanced Technology, Salford.

Tuesday, December 4th, at 4 p.m.

Lecture, "The Chemistry of Bacterial Walls and Membranes," by Professor J. Baddiley, D.Sc., F.R.S. Joint Meeting with the University Chemical Society to be held in the Large Chemistry Theatre, The University.

Nottingham

(Joint Meetings with the University Chemical Society, to be held in the Chemistry Department, The University.)

Tuesday, November 13th, 1962, at 5 p.m.

Lecture, "Cationic Polymerisation," by Professor D. C. Pepper, M.A., Ph.D.

Tuesday, November 20th, at 5 p.m.

Lecture, "The Study of Molecular Structure by Infrared Spectroscopy," by Dr. N. Sheppard, M.A.

Tuesday, November 27th, at 5 p.m.

Lecture by Dame Kathleen Lonsdale, D.Sc., F.R.S.

Oxford

Monday, November 19th, 1962, at 8.30 p.m. Lecture, "The Nature of the Intermediates formed by Hydrocarbons in Catalytic Reactions on Metals," by Professor C. Kemball, M.A., Ph.D., F.R.I.C. Joint Meeting with the Alembic Club, to be held in the Inorganic Chemistry Laboratory.

Reading

Tuesday, November 27th, 1962, at 5.45 p.m.

Lecture, "Application of Nuclear Magnetic Resonance to Organic Chemistry," by Dr. A. R. Katritzky, M.A. Joint Meeting with the Royal Institute of Chemistry to be held in the Main Chemistry Lecture Theatre, The University.

St. Andrews and Dundee

(Meetings will be held in the Chemistry Department, Queen's College, Dundee.)

Tuesday, November 13th, 1962, at 5 p.m.

Lecture, "Electron-spin Resonance Studies of Simple Inorganic Oxy-radicals," by Professor M. C. R. Symons, D.Sc., F.R.I.C.

Tuesday, December 4th, at 5 p.m.

Lecture, "A few Chemical Problems Connected with Cancer Chemotherapy," by Professor F. Bergel, D.Sc., F.R.S.

Sheffield

(Joint Meetings with the Royal Institute of Chemistry and the University Chemical Society, to be held in the Department of Chemistry, The University.)

Thursday, November 22nd, 1962, at 4.30 p.m.

Lecture, "The Electrochemistry of Flames," by Dr. T. M. Sugden, M.A.

Thursday, November 29th, at 4.30 p.m.

Lecture, "Enol Elimination Reactions," by Dr. J. Harley-Mason, M.A., F.R.I.C.

Southampton

Friday, November 16th, 1962, at 5 p.m.

Lecture, "Biosynthetic Pathways in Amaryllidaceae," by Professor A. R. Battersby, Ph.D. To be given in the Chemistry Department, The University.

Friday, November 23rd, at 5 p.m.

Lecture, "Aliphatic Electrophilic Substitution," by Sir Christopher Ingold, D.Sc., F.R.S. Joint Meeting with the Royal Institute of Chemistry, to be held in the Chemistry Department, The University.

Wednesday, December 5th, at 7 p.m.

Lecture, "Platinum Group Metals," by E. C. Davies. To be given at the College of Technology, Portsmouth.

Friday, December 7th, at 5 p.m.

Lecture, "The Reactivity of Solids," by Dr. F. S. Stone. Joint Meeting with the Royal Institute of Chemistry, to be held in the Chemistry Department, The University.

Swansea

Monday, November 19th, 1962, at 4.30 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 Student Chemical Society, to be held in the Chemistry Lecture Theatre, University College.

Tees-side

(Joint Meetings with the Royal Institute of Chemistry, the Society of Chemical Industry, and the Society for Analytical Chemists.)

Wednesday, November 7th, 1962, at 7.30 p.m.

Annual Dinner Dance, to be held at the Billingham Arms, Billingham.

Monday, November 12th, at 8 p.m.

Lecture, "Solvent Extraction of Inorganic Compounds; Some Recent Developments," by Professor H. M. N. H. Irving, M.A., D.Sc., F.R.I.C. To be given at the Constantine Technical College, Middlesbrough.

Wednesday, December 5th, at 8 p.m.

Lecture, "Organometallic Co-ordination Complexes of Some Group II and III Elements," by Professor G. E. Coates, M.A., D.Sc. To be given at the William Newton School, Norton.

APPLICATIONS FOR FELLOWSHIP

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

Achmad, Siamsul Arifin, B.Sc. 127 Links Avenue, Concord, New South Wales, Australia.

- Allum, Keith George, B.Sc. "Park Gate," London Road, Bagshot, Surrey.
- Arendt, John Harry, B.Sc. 93 Brim Hill, London, N.2.
- Atkinson, Ivor Benjamin. 32 Mount Road, Chessington, Surrey.

Bahl, Om. P., Ph.D. Veterans Administration Hospital,

- 54th St. and 48th Ave., Minneapolis 17, Minn., U.S.A. Berry, George Kenneth, B.Sc. 13 Sherington Road, Charlton, S.E.7
- Bezzi, Silvio, Dr. Via Sografi 15, Padova, Italy.
- Billing, David Edward. 138 Albert Road, Wellingborough, Northants.
- Blundell, Thomas Leon. 13 Adur Avenue, Shoreham-by-Sea, Sussex.
- Boswell, Colin Ralph, B.Sc. 2 Lochiel Flats, Old Karori Road, Wellington, W.3, New Zealand.
- Castro, Albert J., A.M., Ph.D. Department of Chemistry, San Jose State College, San Jose 14, Calif., U.S.A.
- Cereghetti, Marco, Dr.sc. Department of Chemistry, Stanford University, Stanford, Calif., U.S.A
- Cuthrell, Robert Eugene, B.A., B.S. 3112 Walling Drive, Austin 5, Texas, Ŭ.S.Á.
- Davis, Michael I., Ph.D. Department of Chemistry, University of Texas, Austin 12, Texas, U.S.A.
- Deshprabhu, Prabhakak K., B.Sc. 29 Corringham Road, N.W.11.
- Dessau, Ralph M., A.M. Box 756, Havemeyer Hall, Columbia University, New York 27, N.Y., U.S.A.
- DeWitt, Walter Groesbeck, B.S. 450 Noyes Laboratory, University of Illinois, Urbana, Ill., U.S.A.
- Driver, William John Bernard, 8 Bramshill Mansions, Dartmouth Park Hill, N.W.5.
- Dyson, Walter Raymond, B.Sc. 100 Teignmouth Road, Willesden Green, N.W.2.
- Edwards, Anthony Gilbert, B.Sc., M.A. 217A Eisenhower Street, Princeton, New Jersey, U.S.A.
- Fields, Ellis Kirby, Ph.D. 63 Princes Park Avenue, N.W.11.
- Foxman, Bruce Mayer. P.O. Box 122, I.S.U. Station, Ames, Iowa, U.S.A.
- Gandini, Alessandro. Department of Chemistry, University of Keele, Keele, Staffs.
- Gier, Thurman E., Ph.D. Central Research Department, E.I. du Pont de Nemours & Co., Wilmington 98, Delaware, U.S.A.
- Goldsmith, John Anthony, B.Sc. Research Department, Parke-Davis & Co., Ltd., Staines Road, Hounslow, Middlesex.

- Gopalarao, Mallavarapu, M.Sc. Department of Chemistry, Andhra University, Waltair, India.
- Gordon, Arnold Jacob, B.Sc. Department of Chemistry, New York University, University Heights, Bronx 53, N.Y., U.S.A. ray, Terence Joseph William. 18 Albion Road,
- Gray, Kettering, Northants.
- Haysom, John Trevor, B.Sc. St. Stephen's College, Delhi-6, India.
- Joshi, Balawant Shankar, Ph.D. Ciba Pharmaceutical Company, 556 Morris Avenue, Summit, New Jersey, U.S.Ä.
- Kepert, David Leslie, M.Sc. Chemistry Department, University College, Gower Street, W.C.1
- Leeming, Michael Raymond Graves, B.Sc. Department of Organic Chemistry, The Robert Robinson Labs., The University of Liverpool, Liverpool 7.
- Lewis, Phillip, B.Sc. 113 Otley Drive, Barkingside, Ilford, Essex.
- Melrose, Barbara Margaret, B.Sc. 98 Randolph Drive, Clarkston, Glasgow.
- lousseron, Magdeleine, Dr.sc. Ecole Nationale Superieure de Chimie, 8 Rue Ecole Normale, Mont-Mousseron, pellier (Herault), France.
- Nazeeri, Makeen Ahsan, M.Sc. Chemistry Department,
- Oregon State University, Corvallis, Oregon, U.S.A. Nunn, Dennis Michael, B.Sc., F.R.I.C. 31 Saltburn Place, Toller Lane, Bradford 9, Yorks.
- Patel, Kantilal Shanabhai, M.Sc. 103 Castle Road, N.W.1
- Paudler, William W., Ph.D. College of Arts and Science, Department of Chemistry, Ohio University, Athens, Ohio, U.S.A.
- Peterson, Peter John, M.Sc. Department of Botany, University College, Gower Street, W.C.1.
- Rosenberg, Richard Martin, Ph.D. Central Research Department, E.I. du Pont de Nemours & Co., Wilmington 98, Delaware, U.S.A.
- Searle, Terence, Ph.D. Messrs. T. Wall & Sons (Meat & Handy Foods) Ltd., Atlas Road, Willesden, N.W.10.
- Smith, Patrick Edmund, B.Sc. 59 London Road, Gravesend, Kent.
- Tutt, Kenneth James, B.Sc. 20 Wordsworth Road, Salisbury, Wilts.
- Walden, Terence Anthony. 422 Kingston Road, S.W.20. White, Danny V., B.A. 132 South—3rd West, Logan, Utah, U.S.A.
- Wright, Alan Carl, B.S. Department of Chemistry, University of Florida, Gainesville, Florida, U.S.A.
- Woodcock, David John, B.Sc. 13 East Parade, Heworth, York.

OBITUARY NOTICE

ERIC ARTHUR HOUGHTON ROBERTS 1910-1962

ERIC ARTHUR HOUGHTON ROBERTS was born at Broadstairs on March 23rd, 1910 and died in London on March 13th, 1962. He was educated at Chatham House School, Ramsgate, gaining an open scholarship to Brasenose, Oxford, in 1928. He gained First Class Honours in chemistry in 1932 and with a Hulme Travelling Scholarship worked in Munich under Professor Wieland.

Returning to Oxford, he gained his D.Phil. with Professor Peters in the Biochemical Laboratory, and then for a year worked on lysozyme under Professor Florey in the Department of Pathology. From that time onwards until his death he was Biochemist to the Indian Tea Association, first at Tocklai in Assam, and later in London.

Roberts will always be remembered for his contribution to the chemistry of tea fermentation. The door was opened to the essential chemistry of the tannins of tea by A. E. Bradfield, his predecessor in the London laboratory of the Association. The tannins were known to be a complex mixture of catechins and related substances, and it was the painstaking work carried out in Bradfield's laboratory in separating and characterising the individual constituents, eventually with the aid of paper chromatography, that put into Roberts' hands the means of following the changes taking place in them during the manufacturing process.

Except for a break during the war with the Indian Ordnance Service, Roberts served for fourteen years as biochemist. He was thus intimately familiar with the operations of tea manufacture, with the vagaries of the raw material, and with the tie-up between quality of green leaf and quality of made tea. His work during this time was concerned with the fermentation process: the enzymes, their action, and the significance of variation in processing conditions on the properties of the manufactured tea. His researches were published, the later ones with D. J. Wood, in a series of papers in the Biochemical Journal. He and Wood made the notable discovery of the resolution of optical isomers when chromatographed on paper with aqueous solvents (Biochem. J., 1953, 53, 332).

His use of paper chromatography in the elucidation of a complex natural system is indeed a model of the disciplined use of a new technique in chemical research. It may seem commonplace now, but the impetus given to the chemists' acceptance of this method by Roberts' success in employing it, backed at all times by rigorous chemical verification, cannot be overstressed. In this way he discovered theogallin, an ester of gallic acid with quinic acid, identified theanine, was a co-discoverer of p-coumarylquinic acid, and gained a considerable measure of insight into the structures of the theaflavins and thearubigins (his own terminology), the complex coloured products of the oxidative fermentation of tea. At rockbottom he had at all times the relationship of what he was finding out about the chemistry of tea and the changes brought about during its manufacture to the qualities which brought enjoyment and appreciation to the palate of the consumer and the expert taster. His last papers—in process of publication in the Journal of the Science of Food and Agriculture under the heading of the Chemical Basis of Quality in Tea -were designed to bring all the threads of his work together, almost as if he were aware that the consummation were imminent. An excellent summary of

his work may be found in a chapter by him in the recently published "Chemistry of Flavonoid Compounds," edited by T. A. Geissman.

Although through-and-through a chemist, Roberts found the biological implications of his work immensely attractive. He delighted in contemplating the way in which his exploration of the chemistry of the different forms of Camellia sinensis L. was helping to illuminate their botanical origin and affinities, his contributions finding a place in discussions of the taxonomy of the species (E. A. H. Roberts, W. Wight, and D. J. Wood, New Phytologist, 1958, 57, 233). He was an enthusiastic founder-member of the Plant Phenolics group, in which his dual interest found a natural outlet, and at the time of his death had almost completed his term of office as Chairman of the group. He had the satisfaction not only of seeing the growth in membership of the group under his chairmanship, but also of learning of the founding of similar groups in North America and Japan. signalling the success which had attended his own considerable contribution to the activities of the British group during the first four years of its existence.

Roberts is in many ways to be envied. He found his métier and was given the opportunity to exploit it. He seized the opportunity and was handsomely rewarded with the products of his enthusiasm and devotion. To the writer it was a perpetual pleasure to look in at his laboratory in the London dockland, occupying a penthouse at the top of Butler's Wharf, and reached by a dark and devious route through warehouses stacked with tea-chests. There was a suggestion of the glamorous, the macabre, and the gently comic in the setting, the last place one would expect to find a laboratory. It was a source of wonder to his friends how he succeeded in producing so much with so little assistant labour at his disposal, until one realised the amount of personal effort he was prepared to devote to the work. He provided an objectlesson in how to set up a small research unit, the lesson consisting of course in getting just the right man to run it that Roberts self-evidently was.

He himself was always genial, always imperturbable (if a man so bursting with enthusiasm and so ready for lively discussion can properly be so described). It is impossible to imagine that he could ever have made an enemy. We who are left working in similar fields of research, and with similar aspirations for the future development of phytochemistry, have lost not only a colleague but also, we feel, a potential leader. We can only be grateful for the splendid contribution he had already made to the fulfilment of our plans, and sorrowful that he had not the opportunity given him to carry them still further

ADDITIONS TO THE LIBRARY

Historical studies in the language of chemistry. M. P. Crosland. Pp. 406. Heinemann. London. 1962. (Presented by the publisher.)

International tables for X-ray crystallography. Vol. 3. Pp. 362. Kynoch Press. Birmingham. 1962.

Calculations in advanced physical chemistry. P. J. F. Griffiths and J. D. R. Thomas. Pp. 215. Edward Arnold. London. 1962. (Presented by the publisher.)

London. 1962. (Presented by the publisher.) Unified organic chemistry. C. A. MacKenzie. Pp. 586. Harper & Bros. New York. 1962. (Presented by the publisher.)

The pyrimidines. D. J. Brown. (Chemistry of heterocyclic compounds. Edited by A. Weissberger. Vol. 16). Pp. 774. Interscience Publishers Inc. New York. 1962.

Contribution à la synthèse et à l'étude physicochimique de quelques cyano-2 propène-2-oates d'éthyle et de leurs dérivés. R. Carrie. Bulletin de la Société Scientifique de Bretagne. 1962. Vol. 37 (special issue). Pp. 135. Centre National de la Recherche Scientifique. Rennes. 1962. (Presented by the publisher.)

Treatise on analytical chemistry. Edited by I. M. Kolthoff, P. J. Elving, and E. B. Sandell. Part 2. Vol.2. Pp. 471. Vol. 9. Pp. 490. Interscience Publishers Inc. New York. 1962

Practical clinical biochemistry. H. Varley. 3rd edn. Pp. 689. Heinemann. London. 1962.

The chemistry and chemotherapy of tuberculosis. E. R. Long. 3rd edn. Pp. 450. Bailliere, Tindall and Cox. London. 1958.

Gesammelte Abhandlungen zur Kenntuis der Kohle. Edited by F. Fischer. 6 vols. Verlag-Gebruder Borntraeger. Berlin. 1917–23. (Presented by Dr. Lessing.) Materials of construction for chemical plant. Edited by I. L. Hepner. Pp. 197. L. Hill. London. 1962. (Presented by the publisher.)

Advances in polarography: proceedings of the second International Congress held at Cambridge, 1959. Edited by I. S. Longmuir. 3 Vols. Pp. 1204. Pergamon Press. Oxford. 1960.

Chemie und Biochemie der Solanum-Alkaloide: Vortrage und Diskussionsbeitrage des Internationalen Symposiums der Deutschen Akadmie der Landwirtschaftswissenschaften zu Berlin, Berlin, 1959. (Tagungsberichte nr. 27). Pp. 336. Deutsche Akad. der Landwirtschaftswissenschaften. Berlin. 1961. (Presented by Dr. F. Callow).

The molecular basis of neoplasis; collection of papers presented at the Fifteenth Annual Symposium on Fundamental Cancer Research, 1961, at the University of Texas M.D. Anderson Hospital and Tumor Institute. Pp. 614. University of Texas Press. Houston, Texas. 1962. (Presented by the publisher.)

Polymerisation and polycondensation processes: papers based on the symposium presented by the Division of Industrial and Engineering Chemistry at the 140th Meeting of the American Chemical Society, Chicago, 1961. (Advances in Chemistry Series, No. 34). Pp. 260. A.C.S. Washington. 1962.

NEW JOURNALS

Chemical Processing (Chicago), from 1962, 25. Fortschritte der Arzneimittelforschung, from 1959, 1. Bulletin of the Royal Society International Scientific Information Services, from 1962, 1.

CHRISTMAS COMPETITION

THE following little poem is probably quite well known:

The Fisherman's Prayer

God grant me strength to catch a fish So large that even I When telling of it afterwards May never need to lie.

A prize (book token for two guineas) is offered for a quatrain giving a Chemist's Prayer. The verse may be in any metre and may concern any aspect of a chemist's work.

Entries must reach the Editor (The Chemical Society, 20—21 Cornwall Terrace, Regent's Park, London, N.W.1) not later than December 31st, 1962, and may be accompanied by a pseudonym for publication. It is hoped to issue a report in the January 1963 issue of *Proceedings*.

The Editor's decision will be final.