NOTES.

911. *Some Halogenocarbonylmanganese Complexes.*

By A. G. OSBORNE and M. H. B. STIDDARD.

ABEL and WILKINSON [1] and Hieber and Schropp [2] have examined the reactions of halogenocarbonylmanganese compounds with various ligands to produce compounds of the type $Mn(CO)_3L_2X$ ($X =$ halogen; $L = C_5H_5N$, Ph_3P, Ph_3As, etc.). However, except for 2,2′-bipyridyl and 1,10-phenanthroline, bidentate ligands were not examined. As part of a general study we have extended this series by examining the reactions of the ligands *o*-phenylenebisdimethylarsine (diars), 1,2-bisdiphenylphosphinoethane (diphos), and 1,2-bisphenylthioethane (disulph). These three react readily with the carbonyl halides at >120° under nitrogen to produce the compounds $Mn(CO)_3$(ligand)I and

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[1] Abel and Wilkinson, *J.*, 1959, 1501.
[2] Hieber and Schropp, *Z. Naturforsch.*, 1959, **14**b, **460**.

$Mn(CO)_3(ligand)Br$. Reactions with the carbonyl chloride appear more complex and will be reported later. We report these compounds, in particular, in order to draw attention to the fact that sulphur-containing bidentate ligands seem to have properties comparable to those of their extensively studied phosphorus and arsenic analogues. Cotton and Zingales[3] have reported products from hexacarbonylmolybdenum containing monodentate sulphur ligands. Independently of us, Mannerskantz and Wilkinson[4] have also been examining sulphur polydentate ligands; their work is now reported elsewhere.[5]

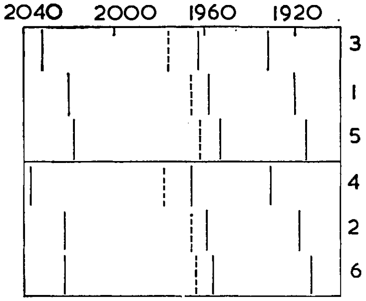
TABLE 1.

Halogenocarbonylmanganese complexes.

No.	Compound	Colour	M. p.	Conductances in $PhNO_2$ Λ_M (Ω^{-1} cm.^{2})	Conductances in $PhNO_2$ Concn. (10^{-3}M)	C–O stretching frequencies (cm.$^{-1}$) in $CHCl_3$	Mol. wt. Found	Mol. wt. Calc.
1	$Mn(CO)_3(diphos)I$	Orange	179°	0·045	2·10	2020, 1958, 1920	700 ‡	664
2	$Mn(CO)_3(diphos)Br$	Light orange	182—183	0·029	2·44	2022, 1959, 1918	580 ‡	617
3	$Mn(CO)_3(disulph)I$	Yellow	170—171 †	0·46	0·92	2032, 1963, 1932	490 ‡	512
4	$Mn(CO)_3(disulph)Br$	Yellow	165 †	0·24	1·75	2037, 1966, 1931	450 ‡	465
5	$Mn(CO)_3(diars)I$ *	Orange	183—184	0·97	0·87	2018, 1953, 1915	520 **	552
6	$Mn(CO)_3(diars)Br$	Light orange	185	1·58	1·37	2022, 1956, 1913	504 **	505

All compounds are diamagnetic in the solid state at 20°. All C–O frequencies are strong.

* Nyholm and Ramana Rao (*Proc. Chem. Soc.*, 1959, **130**) obtained this compound by halogen oxidation of $Mn(CO)_3(diars)$. † With decomposition. ‡ Cryoscopically in benzene. ** Ebullioscopically in chloroform.



C–O Stretching frequencies (cm.$^{-1}$). Numbers refer to Table 1. Broken lines represent averages.

The properties of the complexes $Mn(CO)_3(ligand)X$ are shown in Table 1. Clearly they are monomeric, octahedral, non-electrolytes containing manganese(I) (d_ϵ^6) though the values of Λ_M vary by an unexpectedly large factor (it is difficult to know whether this variation is significant, except that presumably solvolysis is increasingly evident in the order phosphorus $<$ sulphur $<$ arsenic complexes). Any discussion of the infrared data must be rather speculative. Cotton and Zingales,[3] studying the infrared spectra of the compounds $Mo(CO)_3L_3$ ($L =$ sulphur ligand), suggested that sulphur has a π-bonding capacity similar to, or slightly less than, that of phosphorus. The Figure shows the phosphorus, arsenic, and sulphur compounds to have similar spectra. As mentioned in the preceding paper, Orgel suggests that similar carbonyl compounds are best compared by considering the average values of the C–O stretching modes. It is clear from the Figure that these average values are very similar, indicating that the ligands have similar π-bonding

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[3] Cotton and Zingales, *Inorg. Chem.*, 1962, **1**, 145.
[4] Wilkinson, personal communication.
[5] Mannerskantz and Wilkinson, *J.*, 1962, 4454.

properties. Further, this comparison could indicate that sulphur acts as a somewhat better π-acceptor than phosphorus in these compounds. Such an interpretation must not be taken as final, however, since (*a*) it is not easy to assess how significant are these differences of a few wave numbers and (*b*) the polarity of the metal–halogen bonds may not be constant in this series. Finally it should be emphasised that this suggestion is not necessarily at variance with that of Cotton and Zingales since there is no reason why relative π-character of metal–ligand bonds should not vary with the charge on the metal atom.

Experimental.—Interaction of the ligands with manganese carbonyl halides. The carbonyl halide (*ca.* 0·2 g.) was heated with an excess of the ligand (*ca.* 1·5 equiv.) under nitrogen at the temperatures indicated in Table 2 until carbon monoxide evolution had ceased (*ca.* 30 min.). After cooling, the product was dissolved in chloroform (15 ml.). The solution was filtered and, after addition of light petroleum (10 ml.), the *compound* crystallised overnight. It was washed with light petroleum (5 ml.) and dried *in vacuo*. In some cases, a recrystallisation from methanol was necessary to obtain the pure product, as shown in Table 2.

TABLE 2.

Preparation and analysis of complexes.

			Found (%)				Required (%)			
Compound	Reaction temp.	Yield (%)	C	H	P/S	Hal	C	H	P/S	Hal
$Mn(CO)_3(diphos)I$	150°	58 *	52·7	4·2	9·2	19·4	52·5	3·7	9·3	19·1
$Mn(CO)_3(diphos)Br$	150	50 *	56·5	4·2	9·6	12·7	56·4	3·9	10·0	12·9
$Mn(CO)_3(disulph)I$	120	61	39·9	2·7	12·7	24·5	39·9	2·7	12·5	24·8
$Mn(CO)_3(disulph)Br$	120	60	43·8	2·9	13·7	17·8	43·9	3·0	13·8	17·2
$Mn(CO)_3(diars)I$	120	69	28·6	2·8	—	22·6	28·3	2·9	—	23·0
$Mn(CO)_3(diars)Br$	120	58 *	31·0	3·2	—	15·9	30·9	3·2	—	15·9

* Recrystallised from methanol.

Preparation of the ligands. The diarsine was prepared by Chatt and Mann's method,[6] the diphosphine as described by Chatt and Hart,[7] and the disulphide as described by Brooks *et al.*[8]

We thank the Ethyl Corporation for the gift of carbonylmangenese, Dr. G. W. Gray for the infrared spectra, and D.S.I.R. for a maintenance grant (to A. G. O.).

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, HULL.

[*Received, June 5th,* 1962.]

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[6] Chatt and Mann, *J.*, 1939, 610.
[7] Chatt and Hart, *J.*, 1960, 1378.
[8] Brooks, Cranham, Cummings, Greenwood, Jackson, and Stevenson, *J. Sci. Food Agric.*, 1957, **8**, 31.

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912. *The Reduction of* S-*Alkenyl* NN-*Dimethyl-dithiocarbamates and -thiocarbamates and Tetramethylthiourea with Lithium Aluminium Hydride.*

By A. A. WATSON.

LITHIUM ALUMINIUM HYDRIDE reduces *S*-alkenyl *NN*-dimethyldithiocarbamates quantitatively to alkenethiol, hydrogen sulphide, and trimethylamine: the reaction steps, each involving H^-, are:

$$RS{\cdot}CS{\cdot}NMe_2 \longrightarrow RS^- + HCS{\cdot}NMe_2 \longrightarrow {}^-S{\cdot}CH_2{\cdot}NMe_2 \longrightarrow CH_3{\cdot}NMe_2 + S^{2-},$$

where $R = Me_2C{:}CH{\cdot}CHMe$ or $MeCH_2{\cdot}CH{:}CMeCH_2$. The first stage is analogous to reduction of an ester[1] or thiolester,[2] and subsequent stages are formally similar to reduction of *N*-formylamines to methylamines.[3]

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[1] Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197.
[2] Bobbio, *J. Org. Chem.*, 1961, **26**, 3023.
[3] Bory and Mentzer, *Bull. Soc. chim. France*, 1953, 814.

S-1,3-Dimethylbut-2-enyl is reduced more slowly than *S*-2-methylpent-2-enyl dimethyldithiocarbamate, which is consistent with the greater stability of the leaving 2-methylpent-2-enethiolate ion, although steric hindrance to the approach of the ion AlH_4^- by the 3-methyl substituent may be a retarding factor.

Comparable reduction of *S*-2-methylpent-2-enyl dimethylthiocarbamate gave 2-methylpent-2-ene-1-thiol, a negligible amount of hydrogen sulphide, trimethylamine, and (presumably) water, indicating that the reaction followed a similar course to that of the dithiocarbamate.

Neither dimethylamine nor methanethiol, which would result from carbon–nitrogen bond cleavage, was detected in these reductions. Fission of the carbon–nitrogen bond in t-amides, to form dialkylamine and the alcohol or aldehyde, though not an easy process, sometimes occurs.[4] This stability of the carbamates is ascribed to strong resonance contributions of the form $^-O{\cdot}C(SR){:}NMe_2^+$ and $^-S{\cdot}C(SR){:}NMe_2^+$.

These quantitative reductions provide a useful route to pure disubstituted methylamines from secondary amines by the formation of a dithiocarbamate from amine, carbon disulphide, and alkyl halide followed by reduction.

Tetramethylthiourea, on reduction for 2 hours, yielded dimethylamine and 0·73 mol. of hydrogen sulphide. Although these products are consistent with carbon–nitrogen bond cleavage the amine probably results from hydrolysis of tetramethylmethylenediamine[5] which is first formed (with hydrogen sulphide).

Experimental.—S-2-*Methylpent*-2-*enyl dimethyldithiocarbamate*, prepared by reaction of sodium dimethyldithiocarbamate with 1-chloro-2-methylpent-2-ene,[6] had b. p. 100°/0·001 mm., n_D^{20} 1·5770 (Found: C, 53·15; H, 8·4; N, 6·8; S, 31·6. $C_9H_{17}NS_2$ requires C, 53·15; H, 8·45; N, 6·9; S, 31·5%). *S*-1,3-Dimethylbut-2-enyl dimethyldithiocarbamate, m. p. 56—57°, was prepared according to Saville's method.[7] S-2-*Methylpent*-2-*enyl dimethylthiocarbamate*, formed in 40% yield by Tilles's procedure,[8] had b. p. 79°/0·005 mm., n_D^{20} 1·5110 (Found: C, 57·7; H, 9·15; N, 7·1; S, 17·05. $C_9H_{17}NOS$ requires C, 57·7; H, 9·15; N, 7·5; S, 17·1%). Other materials were purified commercial samples.

General procedure. The technique was similar to that described for the semimicro-scale reduction of dialk(en)yl sulphides by lithium aluminium hydride.[9] The sample (100—200 mg.) was weighed into a suspension of lithium aluminium hydride (200 mg.) in tetrahydrofuran (10 ml.), contained in a three-necked flask fitted with a nitrogen inlet, a 10-ml. dropping funnel, and a reflux condenser (packed with glass helices) attached to a tube dipping into 0·1N-sulphuric acid (30 ml.) and chloroform (20 ml.). The reactants were heated at 75° for the specified times, then cooled in ice, and the excess of reagent was destroyed by water (10 ml.). The amine was removed by passing nitrogen through the reaction mixture at 75° for 90 min. and was estimated by titration, with alkali (Methyl Red), of the sulphuric acid–chloroform mixture. After the reaction mixture had again been cooled in ice, the metal salts were hydrolysed with 20 ml. of pyridine–sulphuric acid solution (sulphuric acid 20 ml., water 230 ml., and pyridine 250 ml.). Nitrogen was passed through the hydrolysed mixture at 80° for 60 min., the displaced hydrogen sulphide passed into buffered cadmium acetate solution, and the precipitated cadmium sulphide estimated iodometrically.[10] In reductions where thiol was liberated, the reflux condenser was washed with tetrahydrofuran (3 ml.) and replaced by a distillation unit having a still-head 10 cm. long. The thiol was rapidly co-distilled with the tetrahydrofuran–pyridine–water azeotrope into 0·4N-silver nitrate (10 ml.) and pyridine (10 ml.). After dilution of the silver nitrate mixture with water (100 ml.) the thiol was estimated by

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[4] Nystrom and Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738; Weygand and Tietjen, *Chem. Ber.*, 1951, **84**, 625; Micović and Mihailović, *J. Org. Chem.*, 1953, **18**, 1190; Brown and Tsukamoto, *J. Amer. Chem. Soc.*, 1961, **83**, 4549.

[5] Isham, U.S.P. 2,657,239/1953.

[6] Evans, Higgins, Saville, and Watson, *J.*, 1962, in the press.

[7] Saville, *Proc. Chem. Soc.*, 1961, 214.

[8] Tilles, *J. Amer. Chem. Soc.*, 1959, **81**, 714.

[9] Porter, Saville, and Watson, *J.*, 1962, in the press.

[10] B.S. 903: 1950, Section 3.5 (London: British Standards Institution).

Saville's method.[11] Amine was not trapped or estimated where reliable estimates of hydrogen sulphide were required, in which case the acidification and removal of hydrogen sulphide was performed directly after decomposition of the excess of reagent.

The results are tabulated.

Products of reduction by lithium aluminium hydride.

Reactant	Time (min.)	Thiol (%)	H_2S (%)	NMe_3 (%)
S-2-Methylpent-2-enyl dimethyldithiocarbamate	5	47·4	40·6	Present
	60	101·9	97·0	Present
	60	102·9	88·7 *	94·4
S-1,3-Dimethylbut-2-enyl dimethyldithiocarbamate	60	100·0	92·2	Present
	120	100·7	96·1	Present
S-2-Methylpent-2-enyl dimethylthiocarbamate	60	102·3	1·9	Present
	60	97·2	$<1·0$	93·6
Tetramethylthiourea	120	—	73·2	$NHMe_2$ only

* Some lost on removal of the amine.

Identification of products. Thiols were regenerated from the filtered, water-washed, silver mercaptides by use of a sulphuric acid–thiourea reagent.[9] Gas–liquid chromatography of the thiols was carried out at 65° with 20% dinonyl phthalate on acid-washed Celite, and the thiols identified by comparison of their R_{x9} values [12] with those of samples prepared otherwise.[6,13] *S*-1,3-Dimethylbut-2-enyl dimethyldithiocarbamate yielded only 4-methylpent-3-ene-2-thiol; *S*-2-methylpent-2-enyl dimethyl-thio- and dithio-carbamate yielded *cis*- + *trans*-2-methylpent-2-ene-1-thiol containing *ca.* 3% of 2-methylpent-1-ene-3-thiol. The impurity probably originated from *S*-1-ethyl-2-methylallyl *NN*-dimethylthio and -dithiocarbamate in the starting compounds, their presence being expected as 3-chloro-2-methylpent-1-ene is a likely contaminant of the chloro-olefin from which the compounds were made.

Trimethylamine was liberated by boiling the neutralised amine sulphate solution with alkali and characterised as picrate, m. p. and mixed m. p. 224·5—226°. The presence or absence of dimethylamine was established by passing the liberated amine into a chloroform solution of carbon disulphide, which was then shaken with ammoniacal copper sulphate which gave the brown colour of copper dimethyldithiocarbamate if dimethylamine was present.

THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION,
48—56 TEWIN ROAD, WELWYN GARDEN CITY, HERTS.
[*Received, May* 30*th*, 1962.]

[11] Saville, *Analyst*, 1961, **86**, 29.

[12] Smith, *Chem. and Ind.*, 1960, 1024; Evans and Smith, *J. Chromatog.*, 1961, **6**, 293.

[13] Saville, *J.*, 1962, in the press.

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913. *The Structure of the Self-condensation Products of Glutaconic Esters.*

By JOHN HARLEY-MASON and JOHN C. W. TIMS.

IN 1903, Blaise[1] treated diethyl glutaconate with ethanolic sodium ethoxide, and formulated his product as glutaconoyl glutaconate. von Pechmann, Bauer, and Obermiller[2] carried out a similar condensation, but used an ethereal suspension of sodium ethoxide. They concluded that their product was probably an ethyl dihydro-2,4-diethoxycarbonyl-5-hydroxyphenylacetate, but the position of the double bonds and the relative positions of the ethoxycarbonyl groups were not unambiguously determined. Later workers[3] proved that the two preparations gave the same substance, but suggested that the ethoxycarbonyl groups were in the 2,6-positions.

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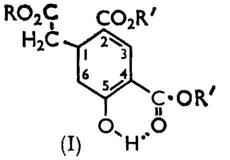
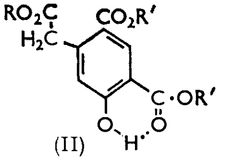
[1] Blaise, *Bull. Soc. chim. France*, 1903, **29**, 1028.

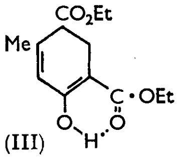
[2] von Pechmann, Bauer, and Obermiller, *Ber.*, 1904, **37**, 2113.

[3] Curtis and Kenner, *J.*, 1914, **105**, 282.

Our experiments were conducted on the methyl and the ethyl triesters (I). The triethyl ester was prepared [3] by using one mole of condensing agent per mole of glutaconic ester. We have conclusively shown that the triethyl ester is ethyl 1,6-dihydro-2,4-diethoxycarbonyl-5-hydroxyphenylacetate, on the basis of the following evidence:


(I)


(II)


(III)

(*a*) Infrared spectra of the triesters were consistent with structure (I). The triethyl ester showed broad absorption around 3000 cm.$^{-1}$ in its infrared spectrum, obtained in carbon tetrachloride solution. This indicates a chelated hydroxyl group. Moreover, no keto-group could be deduced from infrared or nuclear magnetic resonance spectroscopy. In the latter case, a 5-keto-group should lead to splitting of the 3-ethylenic proton absorption, owing to the associated change in conjugation.

(*b*) The ultraviolet spectra of the triesters were different from that of compound (III), previously isolated both by Knoevenagel and Klages and by Rabe.[4] This is consistent with the branched type of conjugation in (I), as compared with the linear type of conjugation in (III).

(*c*) The nuclear magnetic resonance spectrum of the triethyl ester showed a singlet at chemical shift τ —2·85, due to a chelated hydroxyl-proton. The spectra of both triesters showed the same asymmetric quartet centred at τ 7·43, which we attribute to the grouping, $-CH_2{\cdot}CH{\cdot}CH_2-$, and a sharp singlet at τ 2·53 (triethyl ester) or 2·60 (trimethyl ester). This singlet is due to the one 3-ethylenic proton; its low τ value is noteworthy and results from the combined effect of two *cis*-carbonyl groups,[5] adjacent on either side of the ethylenic proton.

(*d*) The aromatised product, (II; R = H, R′ = Me) obtained by bromine oxidation [2,3] of the dimethyl ester (I; R = H, R′ = Me), in chloroform solution, showed two sharp singlets at τ 3·07 and 1·60 in its nuclear magnetic resonance spectrum. The lower value of τ 1·60 is again due to the 3-proton which has a *cis*-carbonyl group adjacent on either side. This result is consistent with a benzene ring that has only two protons, placed *para* with respect to one another. Hence the two conjugated ester groups R′ are in positions 2 and 4.

We have also confirmed that selective hydrolysis of the trimethyl ester (I; R = R′ = Me), with cold aqueous-methanolic sodium hydroxide,[2] or the use of an excess (2·3 mol.) of sodium methoxide with dimethyl glutaconate, yields the diester (I; R = H, R′ = Me). This acid diester is easier to isolate than the triester, which is best obtained pure by methylation of the diester. The following additional evidence confirms the structure of the dimethyl ester: (i) The infrared spectrum of the diester showed no saturated ester carbonyl absorption but showed broad absorption at 3000 cm.$^{-1}$ and a peak at 3020 cm.$^{-1}$, characteristic of a chelated hydroxyl and a carboxylic group. (ii) Attempted decarboxylation of the diester, by heating it with a mixture of glass and copper powder, caused the elimination of acetic acid and aromatisation, to give dimethyl 4-hydroxyisophthalate in low yield.

Experimental.—Nuclear magnetic resonance spectra were obtained at 40 Mc./sec. by using a Varian Associates V.4300B spectrometer and 12″ electromagnet with flux stabilisation and sample spinning. Positions of reference are quoted on the τ scale [τ ($SiMe_4$) = 10·00] and

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[4] Rabe, *Annalen*, 1908, **360**, 289; Knoevenagel and Klages, *ibid.*, 1894, **281**, 96.

[5] Jackman and Wiley, *J.*, 1960, 2886.

have been measured against tetramethylsilane as an internal reference, with side-bands generated by a Muirhead-Wigan D.695A decade oscillator. Infrared spectra were recorded on a Perkin-Elmer model 21 instrument, with a sodium chloride prism, for Nujol or hexachlorobutadiene mulls, unless otherwise stated. Ultraviolet spectra were measured for 95% ethanol solutions with a Cary model 14 recording spectrophotometer.

Ethyl 1,6-*dihydro*-2,4-*diethoxycarbonyl*-5-*hydroxyphenylacetate* (I; R = R′ = Et). The triethyl ester, prepared in poor yield by Curtis and Kenner's method,[3] had m. p. 79—79·3° (lit., 82° [2] and 78·5° [3]) (Found: C, 58·3; H, 6·65. Calc. for $C_{16}H_{22}O_7$: C, 58·6; H, 6·75%), $\nu_{max.}$ (in CCl_4) 3000 (broad; chelated OH), 1737 (saturated ester), 1705 (conjugated ester), 1654 (chelated ester), 1637, 1578 (C=C–C=C) cm.$^{-1}$, $\lambda_{max.}$ 262 mμ (ε 13,400), and 318 mμ (ε 7450), $\lambda_{min.}$ 224 mμ (ε 2180) and 287 mμ (ε 5300). Compound (III) had $\lambda_{max.}$ 233 mμ (ε 7680) and 297 mμ (ε 493), $\lambda_{min.}$ 292 mμ (ε 491). The nuclear magnetic resonance spectrum of ester (I; R = R′ = Et) was recorded in (*a*) chloroform, showing peaks at τ 8·69 (three overlapping triplets due to $\cdot CH_3$ of ethoxyl groups), τ 7·43 (quartet) ($-CH_2\cdot CH\cdot CH_2-$), τ 5·73 (three overlapping quartets, due to CH_2 of ethoxyl groups), and τ 2·53 (C=CH), and (*b*) carbon tetrachloride, which, in addition, showed τ −2·85 (chelated OH).

1,6-*Dihydro*-5-*hydroxy*-2,4-*dimethoxycarbonylphenylacetic acid* (I; R = H, R′ = Me). To a solution of sodium (7·5 g., 2·3 mol.) in dry methanol (80 ml.) dimethyl glutaconate, prepared by Kohler and Reid's method [6] (21·9 g., 1 mol.), was added dropwise at 0—5°, causing an immediate orange colour. Next day, excess of ether was added and after 24 hr. the solid product was filtered off and the ethereal solution was extracted twice with water and once with dilute sodium hydroxide solution. The solid was dissolved in the combined aqueous extracts, which were then acidified with dilute hydrochloric acid. The precipitated *diester* (13·8 g., 70%) was collected and recrystallised from aqueous methanol. A sublimed sample had m. p. 146·5—147·5° (Found: C, 53·35; H, 5·4. $C_{12}H_{14}O_7$ requires C, 53·3; H, 5·2%), $\nu_{max.}$ 3020, 2970, 2680 (broad), 1700, 1656, 1634, 1570, and 756 cm.$^{-1}$, $\lambda_{max.}$ 262 mμ (ε 13,900) and 319 mμ (ε 7310), $\lambda_{min.}$ 225 mμ (ε 1710) and 287 mμ (ε 4420).

Methyl 1,6-*dihydro*-5-*hydroxy*-2,4-*dimethoxycarbonylphenylacetate*. This *triester* was prepared from the diester by treatment with methanolic hydrogen chloride and purified by sublimation as prisms m. p. 85—85·5° (Found: C, 55·3; H, 5·9. $C_{13}H_{16}O_7$ requires C, 54·95; H, 5·5%), $\nu_{max.}$ 1722, 1703, 1647, 1634, 1573, and 761 cm.$^{-1}$, $\lambda_{max.}$ 262 mμ (ε 12,600) and 319 mμ (ε 6850), $\lambda_{min.}$ 224 mμ (ε 1730) and 286 mμ (ε 5050).

5-*Hydroxy*-2,4-*dimethoxycarbonylphenylacetic acid* (II; R = H, R′ = Me). The aromatised *diester* was prepared by the method that von Pechmann *et al.* used for the triethyl ester. It crystallised from aqueous methanol and it sublimed, giving needles, m. p. 173—174° (Found: C, 52·1; H, 4·7. $C_{12}H_{12}O_7,0·5H_2O$ requires C, 52·0; H, 4·7%), $\nu_{max.}$ 3240—2640 (broad) (acidic and chelated OH), 1719 (ester C=O), 1707 (acidic C=O), 1682 (chelated C=O), 1645, 1620, and 1573 (Ar) cm.$^{-1}$, $\lambda_{max.}$ 225 mμ (ε 42,200) and 306 mμ (ε 3185), $\lambda_{infl.}$ 244—251 mμ (ε 12,170), and $\lambda_{min.}$ 278 mμ (ε 975).

Dimethyl 4-*hydroxyisophthalate*. The dimethyl ester (I; R = H, R′ = Me) (200 mg.) was heated with glass powder and copper powder to 230° ± 10° for 30 min. After cooling, the melt was sublimed at 50—85°/0·1 mm., giving oily rosettes (average yield, 10 mg., 7%). Further sublimations yielded the isophthalate as rosettes, m. p. 95—96° (lit.,[7] 94—96°) (Found: C, 57·3; H, 4·85. Calc. for $C_{10}H_{10}O_5$: C, 57·15; H, 4·75%), $\nu_{max.}$ 3200 (chelated OH), 1729 (ester C=O), 1687 (chelated ester), 1616, 1589 and 1496 (Ar) cm.$^{-1}$. Its ultraviolet spectrum agreed with that reported.[8]

One of us (J. C. W. T.) acknowledges a maintenance grant from the Department of Scientific and Industrial Research.

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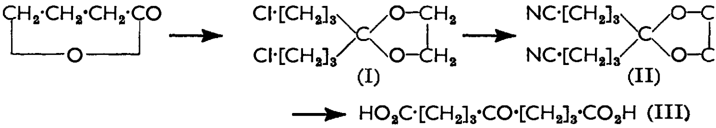
[6] Kohler and Reid, *J. Amer. Chem. Soc.*, 1925, **47**, 2803.
[7] Freeman, *J. Amer. Chem. Soc.*, 1952, **74**, 6257.
[8] Hunt, Jones, and Lindsey, *J.*, 1956, 3099.

914. *The Preparation of δ-Oxoazelaic Acid.*

By David Hartley.

δ-Oxoazelaic acid (III) has been prepared in low yields from disodioacetonedicarboxylic ester and β-iodopropionic acid,[1,2] and by intermolecular Claisen condensation of glutaric esters,[3] as well as by the general diketen synthesis of symmetrical oxo-dicarboxylic acids,[4] a method which is the least efficient in this case.[5]

The need for experimental quantities of δ-oxoazelaic acid prompted development of a simple synthesis from butyrolactone; this was converted into 1,7-dichloroheptan-4-one,[6] and thence into the ethylene ketal (I), to reduce the anionoid reactivity at positions 3 and 5. The dichloro-ketal with sodium cyanide in dimethyl sulphoxide[7] gave the crystalline dinitrile (II), which was hydrolysed by 40% aqueous potassium hydroxide in satisfactory yield to the acid (III). The overall process was improved when the dinitrile was subjected to a preliminary oxidation with hydrogen peroxide to convert the cyano- into amide groups. The acid is obtained reasonably pure in an overall yield from butyrolactone consistently greater than 55%.



While this work was in progress two further preparations of δ-oxoazelaic acid were reported, one starting from cyclohexane-1,3-dione (38% yield)[8] and the other from glutaric acid (no yield given).[9] A four-stage synthesis of diethyl δ-oxoazelate from ethyl 2-oxocyclopentanecarboxylate with an overall yield of 18% has also been described.[10]

Experimental.—*2,2-Di-(3-chloropropyl)-1,3-dioxolan* (I). Freshly prepared 1,7-dichloroheptan-4-one[6] (120 g.), benzene (400 ml.), ethylene glycol (60 g.), and toluene *p*-sulphonic acid (0·2 g.) were heated under reflux in a Dean and Stark apparatus. When no more water distilled, the cooled solution was washed with water, saturated sodium hydrogen carbonate solution, and water, dried (Na_2SO_4), filtered, and evaporated. Distillation gave *2,2-di-(3-chloropropyl)-1,3-dioxolan* (131 g., 93%), b. p. 98—104°/0·4 mm. (Found: C, 47·5; H, 7·1. $C_9H_{16}Cl_2O_2$ requires C, 47·6; H, 7·05%).

2,2-Di-(3-cyanopropyl)-1,3-dioxolan (II). Dimethyl sulphoxide (310 ml.), dried over calcium hydride, was added to sodium cyanide (73 g.), pre-dried overnight at 100°/16 mm., and the slurry heated to 90° with stirring. The heat was removed and 2,2-di-(3-chloropropyl)-1,3-dioxolan (116 g.) added dropwise. After an induction period, the temperature rose suddenly to 160°, at which it was maintained during the rest of the addition (10 min.). Stirring was continued for a further $\frac{1}{2}$ hr. and the cooled mixture poured into chloroform (300 ml.). The precipitated salt was dissolved in water and the organic layer separated. The aqueous layer was extracted with chloroform (2 × 100 ml.) and the combined extracts were washed with saturated brine, dried ($MgSO_4$), and evaporated. Distillation of the residue from a Hickman flask gave *2,2-di-(3-cyanopropyl)-1,3-dioxolan* (102 g., 96%), m. p. 40—42°. A sample redistilled for analysis had b. p. 151—152°/0·2 mm., m. p. 42—42·5° (Found: C, 63·55; H, 7·85. $C_{11}H_{16}N_2O_2$ requires C, 63·4; H, 7·7%).

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[1] von Pechmann and Sidgwick, *Ber.*, 1904, **37**, 3817.
[2] Goode and Leonard, *J. Amer. Chem. Soc.*, 1950, **72**, 5404.
[3] Sórm, *Coll. Czech. Chem. Comm.*, 1947, **12**, 150.
[4] Sauer, *J. Amer. Chem. Soc.*, 1947, **69**, 2444.
[5] Blomquist, Dinguid, Johnson, Shillington, and Spencer, *J. Amer. Chem. Soc.*, 1952, **74**, 4203.
[6] Curtis, Crocket, Hart, and Sandri, *Org. Synth.*, 1958, **38**, 19.
[7] Arnold and Smiley, *J. Org. Chem.*, 1960, **25**, 257.
[8] Stetter, *Chem. Ber.*, 1958, **91**, 2543.
[9] Gilbey, *J. Org. Chem.*, 1961, **26**, 2982.
[10] Huisgen and Pawellak, *Annalen*, 1961, **641**, 71.

δ-Oxoazelaic acid. Hydrogen peroxide (13 ml.; 100-vol.) was added to a stirred suspension of the dinitrile (II) (30·2 g.) in 30% potassium hydroxide solution (200 ml.), and a stream of nitrogen bubbled through the mixture. After 1 hour's heating at 40° the mixture was refluxed until the exit gases were free from ammonia (~3 hr.). The hot solution was poured into 40% phosphoric acid (200 ml.) and set aside for 2 hr. Continuous ether-extraction of this solution and crystallisation of the product from ether gave δ-oxoazelaic acid (23 g., 85%), m. p. 109—111° (lit.,[5] m. p. 109—109·6°) (Found: C, 53·6; H, 7·15%; equivl, 102. Calc. for $C_9H_{14}O_5$: C, 53·5; H, 7·0%; equiv., 101).

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915. *Dichlorobisdialkylnitrosaminepalladium Complexes.*

By R. D. Brown and G. E. Coates.

A yellow crystalline complex, *trans*-$(Et_2N_2O)_2PdCl_2$, is precipitated when diethylnitrosamine is added to an aqueous solution of sodium tetrachloropalladate(II). Similar complexes have been prepared from dimethyl- and di-n-butyl-nitrosamine. The methyl complex is moderately soluble in cold water, and practically insoluble in non-polar solvents, but the butyl complex is insoluble in water and readily soluble in most organic solvents. Resonance between the forms $R_2N{-}N{=}O$ and $R_2N^+{=}N{-}O^-$ is likely to make the oxygen atom a stronger donor than either nitrogen atom. The infrared spectra of the palladium complexes all contain a very strong band close to 1490 cm.$^{-1}$, which is the frequency of the asymmetric N–N–O vibration in gaseous monomeric dialkylnitrosamines.[1] We conclude that, in the palladium complexes, co-ordination is from the oxygen atoms, since co-ordination from the tertiary nitrogen would result in an increased N–O bond order and the complexes contained no strong band in the 1550—1600 cm.$^{-1}$ region. The spectra of the complexes, $(R_2N_2O)_2PdCl_2$, contained weak bands at 447 ($R = Me$), 498 ($R = Et$), and 459 cm.$^{-1}$ ($R = Bu^n$) in the region where metal–oxygen (or nitrogen) stretching bands would be expected.[2] The spectra are less complex above 20 μ, and the main feature is a very strong band at 362 ($R =$ Me or Et) and 351 cm.$^{-1}$ ($R = Bu^n$). A single strong band in the 350—360 cm.$^{-1}$ region is characteristic of *trans*-dichloropalladium(II) complexes;[3] *cis*-dichloro-complexes have two bands in the range 270—335 cm.$^{-1}$.

Dialkylnitrosamines do not displace diethyl sulphide from its palladium chloride complex. The nitrosamines are not strong ligands when bonded to palladium since they are themselves displaced by a variety of other ligands. For example, addition of pyridine to a cold methanolic solution of $(Et_2N_2O)_2PdCl_2$ causes immediate precipitation of *trans*-py_2PdCl_2 (identified by comparison of infrared spectrum in the 5—40 μ region with an authentic specimen).

Experimental.—Infrared spectra were recorded with a Grubb–Parsons GS2A prism-grating spectrometer (wavelength below 23 μ) and a Grubb–Parsons DB3/DM2 200-line per cm. grating instrument (wavelengths between 22 and 50 μ). Spectra at shorter wavelengths were taken on specimens pressed in alkali halide discs, but at longer wavelengths Nujol mulls mounted between

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[1] Haszeldine and Mattinson, *J.*, 1955, 4172; Tarte, *J. Chem. Phys.*, 1955, **23**, 979.

[2] Cotton, "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960, Chapter 5.

[3] Coates and Parkin, unpublished work.

cæsium iodide discs were used, the mulls being separated from the cæsium iodide by Polythene films to prevent halogen exchange.

trans-*Dichlorobisdimethylnitrosaminepalladium*(II). This *complex* was prepared from the nitrosamine (2 mol.) and a concentrated aqueous solution of sodium tetrachloropalladate(II), and recrystallized from water as brown prisms, m. p. 168° (decomp.) (Found: C, 14·9; H, 3·9; Pd, 32·9. $C_4H_{12}Cl_2N_4O_2Pd$ requires C, 14·8; H, 3·7; Pd, 32·7%).

The other complexes were similarly prepared, though the sodium tetrachloropalladate(II) need not be in concentrated solution. trans-*Dichlorobisdiethylnitrosaminepalladium*(II), obtained in 95% yield, formed yellow needles (from hot water), m. p. 163° (decomp.) (Found: C, 25·2, 25·3; H, 5·5, 5·4; Pd, 27·7. $C_8H_{20}Cl_2N_4O_2Pd$ requires C, 25·2; H, 5·3; Pd, 27·9%). trans-*Dichlorobisdi-n-butylnitrosaminepalladium*(II) formed yellow prisms (from methanol), m. p. 125° (decomp. from 150°) (Found: C, 39·0; H, 7·5; Pd, 22·0%; *M*, cryoscopically in benzene, 359, 363, 384; in nitrobenzene, 544, 541. $C_{16}H_{36}Cl_2N_4O_2Pd_2$ requires C, 38·9; H, 7·35; Pd, 21·6%; *M*, 494).

Though the cryoscopic results in benzene suggest there may be some dissociation of the type, $2(Bu_2N_2O)_2PdCl_2 \rightleftharpoons (Bu_2N_2O)_2Pd_2Cl_4 + 2Bu_2N_2O$, attempts to prepare a binuclear complex were not successful.

The principal bands in the infrared spectrum of the dimethylnitrosamine complex, at frequencies less than 2000 cm.$^{-1}$, are at 1490vs, 1437s, 1412s, 1400s, 1348s, 1277s, 1163w, 1106s, 1044m, 866m, 686s, 609s, 447m, 391m, 362s, 292m.

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916. *Preparation of Tritiobutane by the Reaction of Tritiated Water with n-Butylmagnesium Bromide.*

By R. ITÔ, N. MORIKAWA, and O. SIMAMURA.

TRITIOBUTANE was introduced by Glascock [1] as a satisfactory counting gas for the radioactivity assay of tritium. He observed that reaction of tritiated water with a thin layer of solid butylmagnesium bromide at 120° gave rise to one mole of tritiobutane per mole of water.[2] We have searched for a more efficient preparation and have now found that water and excess of butylmagnesium bromide in bis-2-ethoxyethyl ether produce two moles of butane per mole of water at 110° in about two hours. The table shows change in yield of butane with reaction time, and also that fractionation of tritium was not observed when more than 75% of the theoretical amount of butane had been collected.

Tritiobutane produced by reaction of tritiated water with n-butylmagnesium bromide in bis-2-ethoxyethyl ether at 110°.

Expt.	1	2	3	4	5	6
^3H_2O reacting (mmole)	0·97	0·88	0·96	0·97	0·96	1·01
Reaction time (min.)	15	30	50	80	130	130
Bu^3H liberated (mmole)	1·51	1·28	1·61	1·78	1·87	2·01
$Bu^3H/^3H_2O$	1·56	1·46	1·68	1·83	1·95	1·99
Relative radioactivity of Bu^3H	100	101	99	99	99	100

Our result that one mole of water gives two moles of butane apparently is at variance with Glascock's observation. In spite of Zerewitinoff's finding [3] that methylmagnesium

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[1] Glascock, " Isotopic Gas Analysis for Biochemists," Academic Press Inc., New York, 1954, p. 180.

[2] Glascock, *Nature*, 1951, **168**, 121.

[3] Zerewitinoff, *Ber.*, 1907, **40**, 2023.

iodide reacts with one mole of water to produce two moles of methane in pyridine at room temperature, results of a number of preparations[4] of deutero- or tritio-hydrocarbons by the Grignard reaction with deuterium oxide or tritiated water all indicate liberation of one mole of hydrocarbon from one mole of water. More recently, Klass and Jensen[5] have concluded that water and methylmagnesium iodide react with evolution of one mole of methane under the usual conditions of the Zerewitinoff determination. The complete conversion of hydrogen in water into butane in our experiments is undoubtedly due to the use of an adequately high temperature; at lower temperatures we obtained lower yields and slight isotopic fractionation; *e.g.*, 1·28 moles of butane, the radioactivity of which was 90·4% of theory, was obtained in 3 hours at 26° under otherwise the same experimental conditions.

Downes and Till[6] showed that Glascock's method might give unreliable results owing to exchange between the hydrogen atoms of tritiated water and the magnesium hydroxide bromide which has been formed from the Grignard reagent by the action of moisture before the tritiated water reacts. No such exchange takes place in our case, because in our procedure any magnesium hydroxide bromide formed had been converted into Mg_2OBr_2 before tritiated water is introduced.

Experimental.—A vessel containing n-butyl bromide (1·37 g., 10·0 mmoles), magnesium (0·25 g., 10·3 mg.-atoms), and bis-2-ethoxyethyl ether (dried on Na; 8 ml.) was attached, through a cold finger type reflux condenser kept at about −10°, to a vacuum line with necessary arrangements for manipulation of gaseous materials.[7] The flask was slightly evacuated and warmed. After reaction was complete, butane was introduced to a pressure of 5 cm., and the Grignard solution was refluxed to destroy any moisture. The gas which was formed was removed, as evolved, so that the pressure was kept at 5 cm. This pressure maintained the boiling point of the solution at about 110°. When gas evolution was no longer observed, the heating was stopped, and the flask was evacuated, cooled with liquid air, and evacuated thoroughly. About one millimole of tritiated water was condensed into the flask, which was gently heated. After the initial vigorous reaction had subsided, the mixture was refluxed under the liberated butane, the pressure of which was maintained at 5 cm. by removing excess, as evolved, to the second flask cooled with liquid air. When the reaction was over, the whole of the butane was collected in the second flask, distilled into the third flask of a known volume and evaporated, and the pressure and temperature were then measured. The purity of butane thus obtained was shown to be better than 99·5% by mass-spectrometry. Radioactivity measurements were made by counting tritiated butane at a pressure of 20 cm. in a gold-cathode gas counter in the Geiger region.[7]

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[4] Ginsburg and Barker, *J. Chem. Phys.*, 1935, **3**, 668; Childs and Jahn, *Proc. Roy. Soc.*, 1939, *A*, **169**, 428; Posey and Barker, *J. Chem. Phys.*, 1949, **17**, 182; Hurd and Azorlosa, *J. Amer. Chem. Soc.*, 1951, **73**, 33; Robinson, *Rev. Sci. Instr.*, 1951, **22**, 353; Armstrong, Brickwedde, and Scott, *J. Chem. Phys.*, 1953, **21**, 1297.

[5] Klass and Jensen, *J. Org. Chem.*, 1961, **26**, 2110.

[6] Downes and Till, *Internat. J. Appl. Radiation Isotopes*, 1961, **11**, 154.

[7] Itô, Nozaki, Nakamura, Morikawa, and Simamura, *Radioisotopes (Tokyo)*, 1961, **10**, 302.

917. *The Interaction of Pyridine with Hydrogen Chloride and Hydrogen Bromide in Nitrobenzene.*

By I. R. Beattie and G. J. Leigh.

In agreement with the related results of Schnell and Wersin,[1] we *initially* found that addition of pyridine to a solution of silicon tetrachloride in nitrobenzene produced a large increase in the conductivity of the solution. However, within limits, the curve obtained was independent of the initial concentration of silicon tetrachloride, suggesting the presence of water in the solvent. On repeating the above experiments in a vacuum-system we found that the conductivity of nitrobenzene was virtually unaffected by the addition of silicon tetrachloride and pyridine, separately or together.

If water were the impurity in our system, then the results obtained could be due to the interaction of hydrogen chloride with pyridine. Fig. 1 (curve b) shows the effect of adding pyridine to an approximately 0·01M-solution of hydrogen chloride in nitrobenzene, and is of the same form as the initial curve obtained by using silicon tetrachloride in "impure" nitrobenzene. A similar result for 2,6-lutidine and 0·05M-hydrogen chloride is shown in Fig. 1 (curve a). In both cases at a composition approaching 1 mol. of base to 2 mols. of acid there is a broad maximum where the conductivity is about ten times that of the corresponding hydrochloride (mole. ratio 1·0).

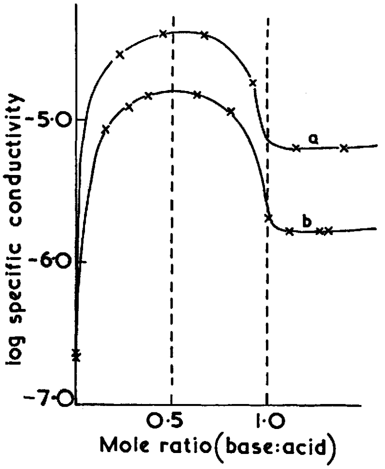

Fig. 1. (a) Titration of 2,6-lutidine with M/20-hydrogen chloride in nitrobenzene. (b) Titration of pyridine with M/100-hydrogen chloride in nitrobenzene.

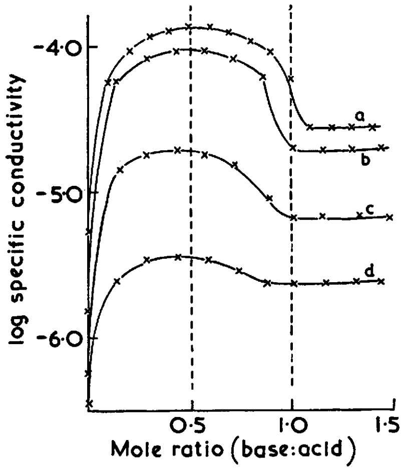

Fig. 2. Titration of pyridine with hydrogen bromide in nitrobenzene: [HBr] = (a) M/25, (b) M/60, (c) M/300, (d) M/1500.

We can only account for these results by assuming that they are due to the change from a relatively strong electrolyte (mole ratio 0·5) to a relatively weak electrolyte (mole ratio 1·0). Thus in pyridinium chloride there is strong hydrogen bonding between the anion and the cation.[2] With the symmetrical HCl_2^- ion [3] this interaction is likely to be greatly reduced. The situation is in many ways similar to that found in acetonitrile where even tetramethylammonium chloride (with a symmetrical cation which cannot form a

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[1] Schnell and Wersin, *Monatsh.*, 1961, **92**, 1055.

[2] See, *e.g.*, Cook, *Canad. J. Chem.*, 1961, **39**, 2009.

[3] Waddington, *J.*, 1958, 1708.

hydrogen bond) is considerably more associated than the strong electrolyte tetramethylammonium dibromoiodide.[4] The presence of the HCl_2^- ion in nitrobenzene solutions of tetraethylammonium chloride containing hydrogen chloride is well established from the work of Herbrandson, Dickerson, and Weinstein.[5] The equilibrium constant for the reaction $Cl^- + HCl \rightleftharpoons HCl_2^-$ has been estimated to be 5×10^2 mole^{-1} l. at 25° in nitrobenzene, suggesting about 35% dissociation of HCl_2^- to HCl and Cl^- at initial concentrations of HCl_2^- of ~0·01M. The HCl_2^- ion has been shown to exist in the solid state and in certain solutions in liquid hydrogen chloride.[6]

As there is no evidence for the HBr_2^- ion, analogous titrations between pyridine and hydrogen bromide were undertaken. The results are shown in Fig. 2. We are unable to interpret these results without recourse to the presence of the HBr_2^- ion.

Experimental.—Reagents. Nitrobenzene and pyridine were prepared as described previously.[7] Hydrogen chloride was obtained from sodium chloride and concentrated sulphuric acid, and hydrogen bromide from tetrahydronaphthalene and bromine.

Techniques. Initial experiments were carried out in a dry-box, and subsequent measurements with silicon tetrachloride were made in a vacuum-apparatus; the nitrobenzene used had been dried with silicon tetrachloride and distilled *in vacuo*. Certain of the hydrogen chloride reactions with pyridine were also carried out in a vacuum-apparatus. Final measurements on the reaction between hydrogen chloride or hydrogen bromide and pyridine were made by using a dry-box.

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[4] Popov and Skelly, *J. Amer. Chem. Soc.*, 1954, **76**, 5309.
[5] Herbrandson, Dickerson, and Weinstein, *J. Amer. Chem. Soc.*, 1954, **76**, 4046.
[6] See, *e.g.*, West, *J. Amer. Chem. Soc.*, 1957, **79**, 4568; Waddington and Klanberg, *J.*, 1960, 2332.
[7] Beattie and Leigh, *J. Inorg. Nuclear Chem.*, 1961, **23**, 55.

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918. *Butylcellosolve Ester of Gibberellic Acid.*

By J. MacMillan and J. S. Moffatt.

Moffatt and Radley[1] prepared a series of alkyl esters of gibberellic acid none of which showed significant plant growth-promoting activity. Recently the following growth-promoting effects of a butylcellosolve ester of gibberellic acid have been reported: promotion of lettuce-seed germination, of tomato-ovary growth, and of elongation of bean epicotyl,[2] stimulation of internode extension and the production of staminate flowers in a species of gynoecious cucumber,[3] and promotion of growth of cucumber seedlings;[4,5] but the preparation of this ester has not been described.

We have prepared the n-butylcellosolve ester by the action of n-butylcellosolve on gibberellic anhydride, which, in turn, was obtained from gibberellic acid and *NN'*-dicyclohexylcarbodi-imide. Like the simple alkyl esters, our preparation showed no significant promotion of lettuce-seed germination, of cucumber- and lettuce-hypocotyl extension, or of internode extension of Meteor pea seedlings.

Gibberellic anhydride which retained one molecule of water of crystallisation was as active as gibberellic acid (cf. ref. 6) in promoting extension of lettuce and cucumber

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[1] Moffatt and Radley, *J. Sci. Food Agric.*, 1960, 386.
[2] Bukovac and Wittwer, in Proc. 4th Internat. Conf. on Plant Growth Regulation, ed. R. Klein, Iowa State College Press, Ames, Iowa, 1961, p. 505.
[3] Bukovac and Wittwer, *Advances in Chemistry Series*, 1961, **28**, 80.
[4] Cathey, Stuart, Toole, and Asen, *Advances in Chemistry Series*, 1961, **28**, 135.
[5] Halevy and Cathey, *Botan. Gaz.*, 1960, **122**, 63.
[6] Brian, *Nature*, 1962, **193**, 946.

hypocotyl, of the internodes of Meteor pea, and of leaf sheaths of mutants d_1, d_3, and d_5 of maize.

Experimental.—*Gibberellic anhydride.* Powdered gibberellic acid (865 mg.; m. p. 233—235°) and *NN'*-dicyclohexylcarbodi-imide (257·5 mg.) in dry dioxan (7·5 ml.) were kept overnight at 18°. Dicyclohexylurea (218 mg.; m. p. 235°) was collected; the residue obtained on evaporation of the mother-liquors crystallised from acetone–light petroleum (b. p. 60—80°), giving the *anhydride monohydrate* as needles, m. p. 185—187° (decomp.) (Found: C, 65·6; H, 6·4; H_2O, 2·4, 3·1. $C_{38}H_{42}O_{11},H_2O$ requires C, 65·9; H, 6·4; H_2O, 2·6%), $\nu_{max.}$ (Nujol) 3501, 3410, 1812, 1776, 1757, 1660, 1655, 1634 cm.$^{-1}$.

Butylcellosolve ester of gibberellic acid. Gibberellic anhydride hydrate (110 mg.) and 2-butoxyethanol (1 ml.) were heated at 100° for 6 hr. The solution was evaporated under reduced pressure. The residue, in ethyl acetate, was separated into acidic and neutral products by extraction with sodium hydrogen carbonate solution. The acidic product consisted of gibberellic acid (40 mg.), identified by its infrared spectrum. The neutral product, in benzene, was chromatographed on acid alumina (Woelm II; 3 g.). Elution with benzene–methanol (200 : 1) afforded the *ester* (55 mg.) which crystallised from benzene in needles, m. p. 171° (Found: C, 67·5; H, 7·7. $C_{25}H_{34}O_7$ requires C, 67·2; H, 7·7%), $\nu_{max.}$ (in Nujol) 3265, 1770, and 1735 cm.$^{-1}$.

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919. *Intracrystalline Behaviour in the Fibrous Zeolite, Laumontite.*

By W. E. ADDISON, J. PLUMMER, and ANNE WALTON.

IT has been shown [1] that the oxidation of hydrogen sulphide is catalysed by the three-dimensional zeolites known as molecular sieves. Some experiments, in which the fibrous zeolite laumontite was used, indicate that it is the zeolitic environment which is responsible for the catalysis rather than the specific structure of the molecular sieves. Laumontite has a much lower sorptive power than the molecular sieves, and because of this limitation has not been studied extensively. A brief account of the sorption behaviour is here given since little previous work is available.[2,3]

The laumontite was obtained from Shap blue quarry, Westmorland.[4] Its identity was confirmed by *X*-ray powder photography and by chemical analysis; its composition is similar to that given by previous analyses.[5] An outgassing temperature of 110° was used, since more vigorous conditions were found to impair sorptive capacity. The purity of the gases used was verified spectroscopically. The experimental methods used are those described in ref. 1.

Isotherms for the gases listed below were of type I; the volume of gas sorbed is always small compared with the corresponding figures for the molecular sieves. These volumes, expressed in c.c./g. at 70 cm. pressure, are: at —183°, argon 7 c.c. and oxygen 7 c.c.; at 0°, ammonia 5 c.c., carbon dioxide 3 c.c., and nitrous oxide 1 c.c. Sorption of the first two was completely reversible, whereas after sorption of the more polar gases little or no gas could be desorbed even when the pressure was reduced to 1 cm.

The sorption of oxygen by laumontite containing presorbed hydrogen sulphide showed

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[1] Addison and Walton, *J.*, 1961, 4741.
[2] Sameshima, *Bull. Chem. Soc. Japan*, 1930, **5**, 303.
[3] Sameshima and Henni, *Bull. Chem. Soc. Japan*, 1934, **9**, 27.
[4] Firman, *Quart. J. Geol. Soc. London*, 1957, **113**, 205.
[5] Coombs, *Amer. Min.*, 1952, **37**, 812.

the same features as were reported previously for molecular sieves. Sulphur dioxide was detected spectroscopically in the desorbate obtained at an elevated temperature, after unchanged oxygen had been removed from the system. The results are shown in the Table for the highest concentration of hydrogen sulphide possible. Corresponding results

H_2S sorbed per g. of laumontite (c.c. at N.T.P.)	Temp.	V_{O_2}/V_{H_2S}	V_{O_2}/V_{H_2S} for max. concn. of H_2S at same temperature	
			Sieve 4A	Sieve Cal3X
0·18	0°	0·58	1·01	0·58
0·15	100	1·57	1·70	0·65

for the molecular sieves are included for comparison. It can be said that laumontite, which contains both univalent and bivalent cations, is intermediate between the sodium-containing sieve 4A and sieve Cal3X in the degree to which hydrogen sulphide is oxidised.

Sorption of the isoelectronic carbon dioxide and nitrous oxide at 0° by laumontite containing presorbed ammonia was also measured. Whereas nitrous oxide can be desorbed reversibly, in contrast to the behaviour in the absence of presorbed ammonia, carbon dioxide cannot. It is probable that ammonia and carbon dioxide undergo intracrystalline interaction although this is difficult to prove since the reaction product, ammonium carbamate, dissociates readily. Comparable behaviour was observed with the molecular sieves.

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920. *Compounds Related to the Steroid Hormones. Part X.*[1] *Recovery of 3-Oxo-steroids from their 2,4-Dinitrophenylhydrazones.*

By J. ELKS and J. F. OUGHTON.

ATTEMPTS to overcome the difficulty of recovery of carbonyl compounds from their 2,4-dinitrophenylhydrazones include exchange with pyruvic and lævulic acid which afford a favourable equilibrium in the presence of mineral acid;[2] though these methods are successful in some instances,[3] the severe conditions required preclude their use with sensitive structures. Exchange with acetone[4] and reduction of the nitro-groups with stannous chloride are normally successful only with simpler and more rugged structures. The range of these procedures would be extended provided the strongly acidic conditions could be dispensed with, and this should be possible by prior reduction of the electron-attracting nitro-groups to the electron-donating amino-groups. Casnati and Cavalleri[5] have illustrated this by using lithium aluminium hydride as the reducing agent, but unfortunately the reagent places limitations on the type of other reactive groupings permissible in the molecule.

The limited success of these methods of hydrolysis with derivatives of cortical steroids led us to experiment with chromous chloride as a means of reducing nitro-groups. With 2,4-dinitrophenylhydrazine in aqueous organic solution the characteristic colour of both

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[1] Part IX, *J.*, 1962, 1578.

[2] Conant and Bartlett, *J. Amer. Chem. Soc.*, 1932, **54**, 2881; DePuy and Ponder, *ibid.*, 1959, **81**, 4629.

[3] (*a*) Mattox and Kendall, *J. Amer. Chem. Soc.*, 1948, **70**, 882; but see (*b*) Djerassi, *ibid.*, 1949, **71**, 1003; (*c*) Mattox and Kendall, *J. Biol. Chem.*, 1950, **185**, 601.

[4] Demaecker and Martin, *Nature*, 1954, **173**, 266; Beereboom and Djerassi, *J. Org. Chem.*, 1954, **19**, 1196.

[5] Casnati and Cavalleri, *Gazzetta*, 1959, **89**, 615.

reagents disappeared immediately the solutions were mixed. With 4,5α-dihydrocortisone 21-acetate 3-(2,4-dinitrophenylhydrazone) in the presence of dichloromethane and an excess of chromous chloride in dilute hydrochloric acid, the colour of the derivative disappeared immediately at room temperature and after 15 minutes hydrolysis was found to be complete; the free steroid was isolated in good yield. With cortisone 21-acetate 3-(2,4-dinitrophenylhydrazone)[6] hydrolysis was complete in 3·5 hours, but with prednisone 21-acetate 3-(2,4-dinitrophenylhydrazone) and cholesta-1,4-dien-3-one 2,4-dinitrophenylhydrazone[3b] no hydrolysis was apparent even after extended times at higher temperatures.

The success of the method with 3-oxo-steroids, saturated or singly unsaturated in ring A, depends upon the maintenance of an atmosphere of inert gas in the reaction vessel. The presence of a water-immiscible solvent protects the released steroid from damage by aqueous acid, thus permitting retention of the cortical side chain.

The method may be applicable to other saturated or αβ-unsaturated ketones when other groups in the molecule are inert to the mild reducing action of chromous chloride.

Experimental.—4,5α-Dihydrocortisone 21-acetate (1·0 g.) in acetic acid was treated with 2,4-dinitrophenylhydrazine (0·55 g.) in acetic acid at 100° for 1 hr. Water was added until the solution was just cloudy and after 1 hr. at 0° the crystals (850 mg.) were filtered off and recrystallised twice from ethyl acetate, to give yellow needles of the 3-(2,4-*dinitrophenylhydrazone*) (250 mg.), m. p. 208—211°, $\lambda_{max.}$ 370 mμ (ε 24,300), $\lambda_{min.}$ 298 mμ, $\lambda_{infl.}$ 249—268 mμ (Found: C, 59·4; H, 6·4; N, 9·9. $C_{29}H_{36}N_4O_9$ requires C, 59·6; H, 6·2; N, 9·6%).

Cortisone 21-acetate 3-(2,4-dinitrophenylhydrazone) was made in a similar manner and had m. p. 238—240°, $\lambda_{max.}$ 387 mμ (ε 30,500) [lit.,[6] m. p. 240—242°, $\lambda_{max.}$ 387 mμ (ε 30,800)].

The derivatives of prednisone 21-acetate and cholesta-1,4-dien-3-one were not obtained pure.

Reduction and cleavage of 4,5α-*dihydrocortisone* 21-*acetate* 3-(2,4-*dinitrophenylhydrazone*). The derivative (1·0 g.), suspended in methylene chloride (30 ml.), was placed in a separatory funnel and covered with N-hydrochloric acid (60 ml.). Small chips of solid carbon dioxide were added and when all the air had been expelled 2·15M-chromous chloride (20 ml.) containing hydrochloric acid (2·15N) was added. The funnel was closed and the mixture shaken for 2 min. and occasionally during a further 15 min. The methylene chloride layer was then run into water and the aqueous solution extracted twice more with methylene chloride. The combined organic layers were washed twice with water, dried, and evaporated under reduced pressure, giving 4,5α-dihydrocortisone 21-acetate (0·64 g., 94%), m. p. and mixed m. p. 231—235°, $[\alpha]_D^{28}$ +104° (in $CHCl_3$), with the correct infrared spectrum.

Reduction and cleavage of cortisone 21-*acetate* 3-(2,4-*dinitrophenylhydrazone*). The derivative (0·80 g.) was treated as in the previous experiment. After 30 min. the methylene chloride layer was run off and found to contain only 100 mg. of a crystalline substance. A further quantity (25 ml.) of methylene chloride was added and the mixture agitated for 3 hr. Evaporation of the organic layer gave 395 mg. of crystals, m. p. 224—232°, $[\alpha]_D^{25}$ +215° (in $CHCl_3$). The combined product recrystallised from ethyl acetate, to give cortisone 21-acetate (60%), m. p. 242—244°, $[\alpha]_D^{24}$ +221° (in $CHCl_3$), $\lambda_{max.}$ 237 mμ (ε 15,600), with the correct infrared spectrum.

Prednisone 21-acetate 3-(2,4-dinitrophenylhydrazone) was reduced under the above conditions, but there was no hydrolysis even at 100°. Hydrolysis of the derivative of cholesta-1,4-dien-3-one also failed in similar circumstances.

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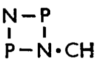
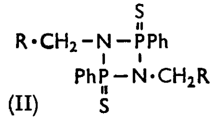
[6] Mattox and Kendall, *J. Biol. Chem.*, 1951, **188**, 287.

921. *Phosphine Imide Dimers.*

By S. TRIPPETT.

MICHAELIS[1] prepared a variety of compounds containing a potential P:N link. Many, *e.g.*, $[PhN{:}P({:}O)Ph]_2$, were dimeric and, on this basis alone, were formulated with four-membered rings containing alternate nitrogen and phosphorus atoms. Others, *e.g.*, $RN{:}P({:}O)NHR'$, appeared to be monomeric. In the proton magnetic resonance of organophosphorus compounds, phosphorus spin-spin couples with hydrogen on the carbon atom β to the phosphorus with J_{PH} 10—20 c./sec.[2] This means that, in compounds having a symmetrically substituted four-membered ring system (I), hydrogen atoms on carbon attached to the ring nitrogen atoms are coupled with two identical β-phosphorus atoms and, assuming that they are not further coupled, would be expected to lead to a 1 : 2 : 1 triplet. The presence of this feature in the proton magnetic resonance spectra of suitable molecules would constitute definitive proof of their structures. Such proof has now been obtained for the phosphine imide dimers (II; R = H, Ph).


(I)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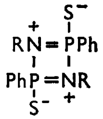
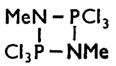

(III)


(IV)

When *NN'*-dimethylphenylphosphonothioic diamide was heated to 260°, methylamine was eliminated and the dimer $[MeN{:}P({:}S)Ph]_2$ formed. The molecular weight was determined cryoscopically in bromoform. The proton magnetic resonance spectrum showed a 1 : 2 : 1 triplet at 7·68 τ (J_{PH} 14 c./sec.), confirming the structure (II; R = H). The dimer after only two crystallisations also showed a second 1 : 2 : 1 triplet at 7·44 τ (J_{PH} 15·5 c./sec.), of about one-tenth of the intensity of the main triplet, but this feature was eliminated on repeated crystallisation. However, the corresponding dimer (II; R = Ph) showed two similar triplets in its proton magnetic resonance spectrum, at 5·86 and 6·01 τ (J_{PH} 15·0 and 18·0 c./sec.) of approximately equal intensity, and so far all attempts at separation of the dimer into isomers have failed. Presumably the two triplets in both cases arise from geometrical isomers in which the two phenyl groups attached to phosphorus are respectively on the same and opposite sides of the planar four-membered ring.

The dimers (II; R = H, Ph) showed unexpected absorption at about 280 mμ (ε ~8500), not shown by the diamides $Ph{\cdot}P({:}S)(NHR)_2$. This suggests that "cyclobutadiene" structures (*e.g.*, III) may play important parts in the final resonance picture of these molecules. A survey of compounds having potential P:N bonds reveals that, where contributions from structures analogous to (III) might be expected to be important, the compounds are dimeric. The conditions for this are (a) that the lone-pair of electrons on the nitrogen should be readily available for donation to the phosphorus, and (b) that the phosphorous should be able to stabilise a negative charge, either by passing it on to oxygen or sulphur or because of the powerful inductive effects of the substituents on the phosphorus atom. Both of these conditions are met by the structures (II; R = H, Ph), by the dimers $(Ar{\cdot}N{:}PCl_3)_2$ obtained by the action of phosphorus pentachloride on aromatic amines of high basicity,[3] and by the dimer $(MeN{:}PCl_3)_2$ from the action of phosphorus pentachloride on methylamine hydrochloride. Chapman *et al.*[4] suggested structure (IV) for the last dimer [with contributions from structures analogous to (III)]; the suggestion

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[1] Michaelis, *Annalen*, 1903, **326**, 129; 1915, **407**, 290.

[2] Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 349; Brook and Trippett, unpublished results.

[3] Zhmurova and Kirsanov, *Zhur. obshchei Khim.*, 1960, **30**, 4048.

[4] Chapman, Holmes, Paddock, and Searle, *J.*, 1961, 1825.

has now been confirmed by the presence of a 1 : 2 : 1 triplet at 7·0 τ (J_{PH} 20·0 c./sec.) in the proton magnetic resonance spectrum of this compound.

The conditions for stabilisation of the dimer by resonance as in (III) are not met by the phosphine imides $R_3P{:}NR$ (R = alkyl or aryl), $Cl_3P{:}N{\cdot}POCl_2$,[5] $Cl_3P{:}N{\cdot}SO_2Ph$,[6] and similar compounds, and by the imides $ArN{:}PCl_3$ derived from aromatic amines of weak basicity.[3] All of these exist as monomers. " Phosphazobenzochlorid " $(PhN{:}PCl{\cdot}Ph)_2$ and its derivatives, described by Michaelis and Schroeter,[7] which apparently contradict these generalisations, have been shown by Goldschmidt and Krauss [8] to be acyclic.

The dimers (II; R = H, Ph) showed strong absorption in the infrared at about 12 μ, similar to that reported [4] for the dimer (IV) and ascribed in that case to a P–N stretching vibration. The phosphenimidic amide dimer $(Ph{\cdot}CH_2{\cdot}N{:}PS{\cdot}NH{\cdot}CH_2{\cdot}Ph)_2$ [9] also showed strong absorption in this region (12·02 μ), which may be characteristic of the ring system (I).

Experimental.—Proton magnetic resonance spectra were determined for 10% solutions in chloroform or bromoform by using a Varian Associates A-60 spectrometer (60 Mc./sec.).

NN′-*Dimethylphenylphosphonothioic diamide.* A solution of phenylphosphonothioic dichloride (21 g.) in ether (20 ml.) was added slowly to a stirred solution of methylamine (12 g.) in ether (150 ml.) cooled in ice. The resulting suspension was stirred at room temperature for 3 hr., extracted twice with water, and dried, and the solvent removed under reduced pressure. Crystallisation of the residue from benzene–light petroleum gave the *diamide* (4·3 g.), m. p. 69·5—70·5° (Found: C, 47·75; H, 6·75; N, 14·25. $C_8H_{13}N_2PS$ requires C, 48·0; H, 6·5; N, 14·0%).

N-*Methylphenylthionophosphine imide dimer.* *NN*′-Dimethylphenylphosphonothioic diamide (3·5 g.) was heated to 250—260° for 12 min., then cooled, and the residue crystallised from butan-1-ol. Recrystallisation twice from butan-1-ol and four times from ethyl acetate gave the *phosphine imide dimer* (90 mg.), m. p. 216—217°, $\lambda_{max.}$ 280 mμ (ε 8850 in ethanol), 11·92 μ (Found: C, 49·5; H, 4·5; N, 8·4%; *M*, 350. $C_{14}H_{16}N_2P_2S_2$ requires C, 49·7; H, 4·7; N, 8·3%; *M*, 338).

NN′-*Dibenzylphenylphosphonothioic diamide.* A solution of phenylphosphonothioic dichloride (32 g.) in benzene (50 ml.) was added slowly to a stirred solution of benzylamine (66 g.) in benzene (300 ml.). The resulting suspension was stirred at room temperature for 3 hr., filtered, and the filtrate evaporated under reduced pressure. Crystallisation of the residue from ethanol gave the *diamide* (43 g.), m. p. 80—81° (Found: C, 67·8; H, 6·1; N, 7·8. $C_{20}H_{21}N_2PS$ requires C, 68·2; H, 6·0; N, 7·95%).

N-*Benzylthionophenylphosphine imide dimer.* *NN*′-Dibenzylphenylphosphonothioic diamide (25 g.) was heated at 270°/10 mm. for ½ hr. during which time benzylamine (10·1 g.) distilled out of the mixture. The residue crystallised from butan-1-ol (60 ml.) and was recrystallised repeatedly from this solvent and from ethyl acetate to give the *phosphine imide dimer*, m. p. 213·5—214·5°, $\lambda_{max.}$ 282 mμ (ε 8,300 in ethanol), 12·12 μ [Found: C, 63·6; H, 4·8; N, 5·9%; *M*, 475(bromoform), 482(Rast). $C_{26}H_{24}N_2P_2S_2$ requires C, 63·7; H, 4·9; N, 5·7%; *M*, 490].

THE UNIVERSITY, LEEDS, 2. [*Received, April 13th*, 1962.]

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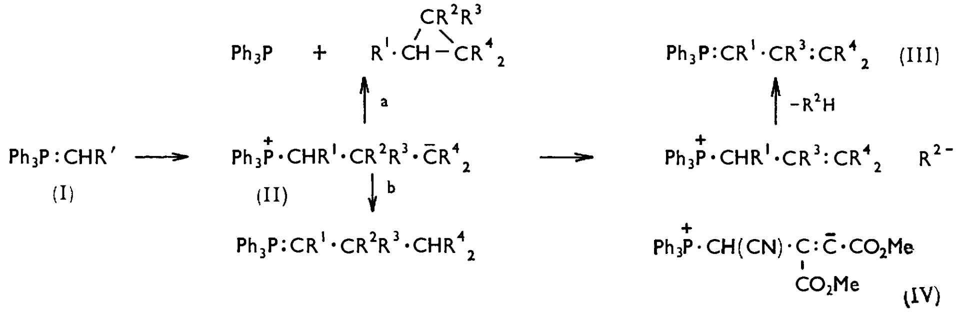
[5] Becke-Goehring, Mann, and Euler, *Chem. Ber.*, 1961, **94**, 193.
[6] Kirsanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1950, 426.
[7] Michaelis and Schroeter, *Ber.*, 1894, **27**, 490.
[8] Goldschmidt and Krauss, *Annalen*, 1955, **595**, 193.
[9] Buck, Bartleson, and Lankelma, *J. Amer. Chem. Soc.*, 1948, **70**, 745.

922. *The Addition of Wittig Reagents to Activated Carbon–Carbon Double Bonds.*

By S. Trippett.

Wittig reagents (I) add to activated carbon–carbon double bonds to give intermediates (II) which can either eliminate triphenylphosphine [reaction (a)] to give a cyclopropane,[1,2] or transfer a proton from the α- to the γ-carbon atom [reaction (b)] to form a new phosphorane.[2] Reaction (b) occurs when R^1 is an activating group, *e.g.*, methoxycarbonyl. A third way in which the intermediate (II) may react is now described.



When R^2 is capable of forming a stable anion, *e.g.*, when R^2 = OEt or CN, the intermediate (II) eliminates R^{2-} to form a phosphonium salt which then loses R^2H to give the new stable phosphorane (III). In this way, the phosphorane (I; R^2 = CN) added to diethyl ethoxymethylenemalonate to give the phosphorane (III; R^1 = CN, R^3 = H, R^4 = CO_2Et), to ethoxymethylenemalononitrile (V) to give the phosphorane (III; R^1 = R^4 = CN, R^3 = H), and to tetracyanoethylene to give the phosphorane (III; R^1 = R^3 = R^4 = CN). Similarly the ester phosphorane (I; R^1 = CO_2Et) with diethyl ethoxymethylenemalonate gave the phosphorane (III; R^1 = R^4 = CO_2Et, R^3 = H), and with ethoxymethylenemalononitrile gave the phosphorane (III; R^1 = CO_2Et, R^4 = CN, R =H).

The addition of the Wittig reagent (I; R^1 = CN) to dimethyl acetylenedicarboxylate gave the phosphorane (III; R^1 = CN, R^3 = CO_2Me, R^4 = CO_2Me, H), presumably *via* the intermediate (IV) which transferred a proton as in (b).

Experimental.—*α-Cyano-γγ-di(ethoxycarbonyl)allylidenetriphenylphosphorane.* A solution of cyanomethylenetriphenylphosphorane (3·0 g.) and diethyl ethoxymethylenemalonate (2·16 g.) in ethyl acetate (50 ml.) was refluxed for ½ hr., the solvent then evaporated, and the residue crystallised from ethyl acetate to give the *product* (3·6 g.), m. p. 183—184°, $\lambda_{max.}$ 4·55 (CN), 5·85 (conjugated CO_2Et), 6·0 μ (conjugated C⁚C) (Found: C, 71·45; H, 5·7. $C_{28}H_{26}NO_4P$ requires C, 71·3; H, 5·5%).

In a similar way cyanomethylenetriphenylphosphorane with ethoxymethylenemalononitrile gave *αγγ-tricyanoallylidenetriphenylphosphorane* (78%), m. p. 284—285° (from nitromethane), $\lambda_{max.}$ 4·49, 4·53 μ (two different CN groups) (Found: C, 76·15; H, 4·3. $C_{24}H_{16}N_3P$ requires C, 76·4; H, 4·25%), and with tetracyanoethylene gave *αβγγ-tetracyanoallylidenetriphenylphosphorane* (56%), m. p. 239—240° (from chloroform–ethyl acetate), $\lambda_{max.}$ 4·49, 4·53 μ (Found: N, 14·0. $C_{25}H_{15}N_4P$ requires N, 13·95%).

αγγ-Tri(ethoxycarbonyl)allylidenetriphenylphosphorane. A solution of ethoxycarbonylmethylenetriphenylphosphorane (1·05 g.) and diethyl ethoxymethylenemalonate (0·65 g.) in

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[1] Mechoulam and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 4386.

[2] Bestmann and Seng, *Angew. Chem.*, 1962, **74**, 154.

nitromethane (10 ml.) was heated for ½ hr. on the steam-bath, the solvent then removed under reduced pressure, and the residue crystallised from chloroform–light petroleum (b. p. 60—80°) to give the *product* (0·9 g.), m. p. 191—192°, $\lambda_{max.}$ 5·79, 6·01 μ (Found: C, 69·2; H, 5·8. $C_{30}H_{31}O_6P$ requires C, 69·5; H, 6·0%).

γγ-Dicyano-α-ethoxycarbonylallylidenetriphenylphosphorane. A solution of ethoxycarbonylmethylenetriphenylphosphorane (1·65 g.) and ethoxymethylenemalononitrile (0·65 g.) in ethyl acetate (25 ml.) was refluxed for 1 hr., the solvent then removed under reduced pressure, and the residue crystallised from chloroform–ethyl acetate to give the *product* (1·1 g.), m. p. 216—218°, $\lambda_{max.}$ 4·5, 5·92 μ (Found: C, 73·45; H, 5·05; N, 6·45. $C_{26}H_{21}N_2O_2P$ requires C, 73·6; H, 4·95; N, 6·6%).

α-Cyano-βγ-di(methoxycarbonyl)allylidenetriphenylphosphorane. A solution of cyanomethylenetriphenylphosphorane (15 g.) and dimethyl acetylenedicarboxylate (7·1 g.) in methanol (150 ml.) was refluxed for 10 min. and set aside at room temperature overnight. Filtration gave the *product* (9·6 g.), m. p. 229—230° (from chloroform–light petroleum), $\lambda_{max.}$ 4·56, 5·73, 5·93 μ (Found: C, 70·5; H, 4·8; N, 3·25. $C_{26}H_{22}NO_4P$ requires C, 70·3; H, 5·0; N, 3·15%).

No crystalline products were obtained from the reactions of dimethyl acetylenedicarboxylate with acetonylidene-, ethoxycarbonylmethylene-, and formylmethylene-triphenylphosphoranes.

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923. *The Reaction between Methylammonium Chloride and Ethylaluminium Dichloride.*

By J. D. SMITH.

INTERACTION of methylammonium chloride and alkylaluminiums or alkylaluminium halides gives methylamine addition compounds and alkanes: $(R_nAlCl_{3-n})_2 + 2MeNH_3Cl \longrightarrow 2MeH_2N,AlR_{n-1}Cl_{4-n} + 2RH$. Methylammonium chloride and triethylaluminium in toluene react conveniently at −78°, to give a compound $MeH_2N,AlEt_2Cl$, but a higher temperature (0°) is necessary for the ready conversion of diethylaluminium chloride into the analogous adduct $MeH_2N,AlEtCl_2$.[1] We have now shown that methylammonium chloride and ethyl aluminium dichloride in *boiling* toluene give the compound $MeH_2N,AlCl_3$.

At room temperature, however, evolution of ethane is negligible and removal of the solvent leaves a white solid which does not seem to be simply a mixture of unchanged reactants. For example, its *X*-ray powder pattern does not show lines corresponding to those of methylammonium chloride. The solid is involatile at room temperature, even with prolonged pumping in the vacuum-system, and it is almost insoluble in pentane, whereas ethylaluminium dichloride is readily volatile under these conditions and is freely soluble in pentane. Analysis corresponds to that expected for a 1 : 1 addition compound and it seems reasonable to formulate this as methylammonium trichloro(ethyl)aluminate, $[MeNH_3]^+[EtAlCl_3]^-$. The infrared spectrum supports this suggestion, for it is similar to that obtained by the superposition of the spectra of methylammonium chloride[2] and potassium trichloro(ethyl)aluminate. No strong absorption was observed in the infrared region between 810 and 630 cm.$^{-1}$; compounds containing aluminium–nitrogen bonds have been reported[3] to absorb in this region, but the assignment of bands is doubtful.

[1] Laubengayer, Smith, and Ehrlich, *J. Amer. Chem. Soc.*, 1961, **83**, 542.

[2] Waldron, *J. Chem. Phys.*, 1953, **21**, 734.

[3] Brame, Margrave, and Meloche, *J. Inorg. Nuclear Chem.*, 1957, **5**, 48; Zeil, Dautel, and Honsberg, *Z. Electrochem.*, 1956, **60**, 1131; Dautel and Zeil, *ibid.*, 1960, **64**, 1234; Schomburg and Hoffmann, *ibid.*, 1957, **61**, 1110; Laubengayer and Smith, unpublished observations.

Methylammonium trichloro(ethyl)aluminate is rapidly decomposed by water with quantitative evolution of ethane; it appears to be stable in dry nitrogen at room temperature, but decomposes above about 50° to ethane and methylamine–aluminium trichloride.

The isolation of methylammonium trichloro(ethyl)aluminate seems to indicate that the reaction between methylammonium chloride and ethylaluminium dichloride proceeds in two stages. In the first, the dimeric organoaluminium compound is dissociated and a new Al–Cl bond formed. In the second, occurring only above room temperature, a proton from the methylammonium ion attacks the α-carbon of the ethyl group. The corresponding reactions of methylammonium chloride with diethylaluminium chloride or triethylaluminium may proceed similarly, but isolation at room temperature of intermediates such as $(MeNH_3)(Et_2AlCl_2)$ and $(MeNH_3)(Et_3AlCl)$ is unlikely. The alkali halide complexes $M(R_nAlCl_{4-n})$ (M = Na or K) decrease in stability as the number of alkyl groups increases.[4]

Experimental.—Manipulations were made in a vacuum-system or in a nitrogen-filled dry-box. Solvents were dried over phosphorus pentoxide, then distilled, and stored over sodium wire. Aluminium chloride was sublimed, fused with aluminium wire, and twice further sublimed. Diethylaluminium chloride was obtained by distillation from a 20% solution in methylcyclohexane. Ethylaluminium dichloride[5] was distilled (b. p. 114—115°/50 mm.), recrystallised from pentane (m. p. 31°), and sublimed into the reaction flask immediately before use. Potassium trichloro(ethyl)aluminate was made as described by Sleddon[6] (m. p. 95—96°). Methylammonium chloride was recrystallised from ethanol and dried by pumping for several days in a vacuum-desiccator over phosphorus pentoxide. For analysis, compounds were hydrolysed by 2N-sulphuric acid. Ethane was estimated in the vacuum-system, chlorine by the Volhard method, aluminium gravimetrically as oxine, and methylamine by a semimicro-Kjeldahl procedure.

Interaction of Methylammonium Chloride and Ethylaluminium Dichloride.—Ethylaluminium dichloride (2·206 g., 17·3 mmoles) in toluene (10 ml.) and methylammonium chloride (1·168 g., 17·3 mmoles) were heated for 4 hr. at 94° in a nitrogen atmosphere. Volatile material, collected in the vacuum-system, consisted of ethane (15·7 mmoles, 91%; v. p. at −111·6°, 179 mm.; lit.,[7] 178 mm.) and toluene. The residue was distilled (b. p. 114—116°/0·01 mm.) to give methylamine–aluminium trichloride (2·5 g., 88%); m. p. 57—58°; lit.,[8] 58° (Found: Al, 16·3; Cl, 64·5; $MeNH_2$, 18·9. Calc. for $MeH_2N,AlCl_3$: Al, 16·4; Cl, 64·7; $MeNH_2$, 18·9%). In another experiment, methylammonium chloride (0·45 g., 6·65 mmoles) was added slowly from a rotating side-arm to a solution of ethylaluminium dichloride (0·85 g., 6·7 mmoles) in toluene (5 ml.) at −78°. As the solution warmed, the white crystals disappeared with the formation of a glassy deposit. After 3 hr. at 16°, all the volatile material was removed in the vacuum system, to give ethane (0·24 mmole, presumably from traces of water) and toluene. The latter, shaken with water in the vacuum-system, gave no further ethane and no precipitate of hydrated alumina, and therefore did not contain any dissolved alkylaluminium. The involatile solid remaining in the reaction flask after 6 hours' pumping appeared to be *methylammonium trichloro(ethyl)aluminate*; it had m. p. 60—62° (decomp.) {Found: Et, 14·3; Cl, 54·1; Al, 13·3; $MeNH_3^+$ (as $MeNH_2$), 16·4. $[MeNH_3]^+[EtAlCl_3]^-$ requires Et, 14·9; Cl, 54·7; Al, 13·9; $MeNH_3^+$, 16·5%}. The compound was slightly soluble in toluene. A sample was treated in the vacuum system with water and gave ethane quantitatively.

Infrared spectra of mulls in Nujol were recorded on a Unicam S.P. 100 spectrometer with sodium chloride and potassium bromide optics.

$[MeNH_3]^+[EtAlCl_3]^-$: 3200bvs, 2745w, 2525w, 2430w, 1600s, 1265m, 1230vw, 1200vw, 1170vw, 1110w, 1000m, 985m, 950s, 930s, 810w, 625vs, 500s, 430vs.

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[4] Hall and Nash, *J. Inst. Petr. Tech.*, 1937, **23**, 679; Ziegler, Köster, Lehmkuhl, and Reinert, *Annalen*, 1960, **629**, 33; Köster and Kroll, *ibid.*, p. 50.

[5] Grosse and Mavity, *J. Org. Chem.*, 1940, **5**, 106.

[6] Sleddon, *Chem. and Ind.*, 1961, 1492.

[7] "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Inst. Res. Project 44, Table 1k.

[8] Goubeau and Siebert, *Z. anorg. Chem.*, 1950, **261**, 63.

$K[EtAlCl_3]$: 1270vw, 1230vw, 1200vw, 1170vw, 1100vw, 1060w, 1010m, 1000m, 960w, 930w, 910vw, 850w, 810w, 630vs, 617vs, 495vs, 437vs.

$MeNH_3Cl$: [2] 3080bvs, 2776m, 2556w, 2480w, 1580s, 1538s, 1265w, 1038m, 1003m, 958s, 883w.

The author thanks Mr. A. M. Evans for help with the powder photographs, and Imperial Chemical Industries Limited for the gift of diethylaluminium chloride.

THE UNIVERSITY, LEICESTER. [*Received, May 24th,* 1962.]

924. *Nuclear Magnetic Resonance Spectra of Some Trimethylplatinum Compounds.*

By J. A. S. SMITH.

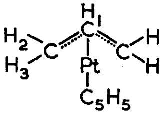
HOLMES and KAESZ[1] have shown that the spin–spin coupling constant $J(^{117}Sn\text{–}CH_3)$ of trimethyltin chloride changes from 56·0 c./sec. in 38% carbon tetrachloride solution to 65·2 c./sec. for 56% aqueous solution, both at 31°. They attribute these changes to rehybridization of the orbitals of the tin atom which occurs when the molecule ionizes in water, by analogy with the dependence of the $^{13}C\text{–}H$ coupling constant on the *s*-character of carbon orbitals.[2] It is interesting that this behaviour appears not to occur with the trimethylplatinum group; Table 1 lists spin–spin coupling constants $J(^{195}Pt\text{–}CH_3)$ for five trimethylplatinum compounds in different solvents, recorded on a high-resolution spectrometer[3] at 40·35 Mc./sec. and 35·5°. Neither variation of the solvent nor ionization of the nitrate in water appears to affect the value of J relative to $(Me_3PtI)_4$; this value seems to be more sensitive to remoter changes in groups attached to β-diketone ligands.

TABLE 1.

Compound	$J(^{195}Pt)$ (c./sec.)	Solvent	Compound	$J(^{195}Pt)$ (c./sec.)	Solvent
$(Me_3PtI)_4$	77·9 ± 1·0	C_6H_6	$(Me_3Pt{\cdot}CHAc_2)_2$	78·9	C_6H_6
$(Me_3PtI)_4$	77·7	$CHCl_3$	$[Me_3Pt{\cdot}CH(COEt)_2]_2$ ...	71·6	C_6H_6
$[Me_3Pt]NO_3$	77·3	H_2O	$[Me_3Pt{\cdot}CH(COPr)_2]_2$ ...	74·9	C_6H_6

Spin–spin coupling constants $J(^{195}Pt\text{–}CH)$ for other types of ligand are compared in Table 2. The methyl groups in trimethylplatinum iodide behave as if attached to platinum by conventional σ-bonds. The C–H vibrations in the infrared spectrum of a chloroform solution lie at 2793, 2886, and 2948 cm.$^{-1}$, compared with 2861, 2970, and 3060 cm.$^{-1}$ in methyl iodide; for a benzene solution, the τ-value is 8·27 p.p.m., which is reasonable for an organometallic compound.[5] The similarity of the J-value to that in $[CH_2]_3PtCl_2py_2$

TABLE 2.

Compound	$J(^{195}Pt\text{–}CH)$ (c./sec.)	Ref.	Compound	$J(^{195}Pt\text{–}CH)$ (c./sec.)	Ref.
$(Me_3PtI)_4$	78			$54(H_3)$ $29(H_2)$ $11(H_5)$	6
$K[C_2H_4PtCl_3]$	34	4			
$[CH_2]_3PtCl_2py_2$	83	5			

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[1] Holmes and Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 3903.
[2] Muller and Pritchard, *J. Chem. Phys.*, 1959, **31**, 768, 1471.
[3] McCann, Smith (F). Smith (J. A. S.), and Thwaites, *J. Sci. Instr.*, 1962, **39**, 349.
[4] Powell and Sheppard, *J.*, 1960, 2519.
[5] Adams, Chatt, and Guy, *Proc. Chem. Soc.*, 1960, 179.
[6] Shaw and Sheppard, *Chem. and Ind.*, 1961, 517.

supports the contention [5] that the latter contains similar σ-bonds from platinum to carbon. The values of *J* drop sharply when C_2H_4 or C_5H_5 groups are attached and have intermediate values for the allyl group. Although a quantitative explanation of these changes has not yet been advanced, it appears that the *J* value for organic derivatives of platinum might provide an empirical guide to their structure.

The author thanks Mr. K. Kite and Dr. R. C. Menzies for samples.

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925. *Some Derivatives of Isovanillin.*

By J. K. FAULKNER and D. WOODCOCK.

4-CHLORO-5-FORMYL-2-HYDROXYPHENOXYACETIC ACID was required in connection with fungal detoxication work involving 2,4-dichlorophenoxyacetic acid. Whereas direct chlorination of vanillin gives 3-chloro-4-hydroxy-5-methoxybenzaldehyde,[1] the product from isovanillin has been shown to be 2-chloro-3-hydroxy-4-methoxybenzaldehyde, identical with the product of demethylation of 2-chloroveratraldehyde.[2] Chlorination of ethyl 5-formyl-2-methoxyphenoxyacetate, obtained by the condensation of isovanillin with ethyl bromoacetate, however, gave ethyl 4-chloro-5-formyl-2-methoxyphenoxyacetate. The halogen orientation in this compound was established by an unambiguous synthesis from 6-chloroveratraldehyde,[3] which by demethylation and subsequent condensation with ethyl bromoacetate gave the same product. 4-Chloro-5-formyl-2-hydroxyphenoxyacetic acid was then obtained by demethylation of the corresponding 4-methoxyaldehyde [1] by using hydrobromic acid.

Experimental.—2-*Chloro*-3-*hydroxy*-4-*methoxybenzaldehyde*. Chlorine was passed into a stirred solution of isovanillin (7·6 g.) in chloroform (100 ml.) until the precipitate was pale yellow. Air was then passed through the solution to remove excess of chlorine and hydrogen chloride, and the solid (6·8 g.) filtered off; it crystallised from aqueous methyl alcohol in monoclinic prisms, m. p. 205—206° (Found: C, 51·1; H, 3·7. Calc. for $C_8H_7ClO_3$: C, 51·5; H, 3·75%) (Hornbaker and Burger [2] give m. p. 208—209°). The oxime, crystallised from aqueous ethyl alcohol, had m. p. 182—183° (Found: C, 47·4; H, 4·2; N, 6·7. Calc. for $C_8H_8ClNO_3$: C, 47·6; H, 4·0; N, 6·95%) (Burger and Foggio [4] give m. p. 184—186°). The methyl ether crystallised from aqueous methyl alcohol in monoclinic prisms, m. p. 69—70° (Found: C, 53·6; H, 4·55. Calc. for $C_9H_9ClO_3$: C, 53·9; H, 4·5%) (Raiford and Perry [5] give m. p. 69—70°).

Ethyl 2-*chloro*-3-*formyl*-6-*methoxyphenoxyacetate*. 2-Chloroisovanillin (1·86 g.) was dissolved in a solution from sodium (0·23 g.) in ethyl alcohol (25 ml.) and refluxed with ethyl bromoacetate (1·7 ml.) for 2 hr. The mixture was then cooled and diluted with water, and the product extracted with ether. The extract was dried (Na_2SO_4), the solvent distilled off, and the *ester* crystallised from light petroleum (b. p. 60—80°), forming needles (1·15 g.), m. p. 64—65° (Found: C, 52·6; H, 4·9. $C_{12}H_{13}ClO_5$ requires C, 52·8; H, 4·8%).

Ethyl 5-*formyl*-2-*methoxyphenoxyacetate*. Isovanillin (76 g.) was dissolved in a solution from sodium (12·5 g.) in ethyl alcohol (375 ml.) and refluxed with ethyl bromoacetate (56 g.) for 2 hr. On cooling, the crystalline product was collected, washed with ethyl alcohol and ether, and then dried (43 g.; m. p. 88—89°); dilution of the filtrate and extraction with ether gave a further 16 g. of *ester* (m. p. 87—89°). It crystallised from aqueous ethyl alcohol in needles, m. p. 88—89° (Found: C, 60·2; H, 6·0. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%).

[1] Raiford and Lichty, *J. Amer. Chem. Soc.*, 1930, **52**, 4576.

[2] Hornbaker and Burger, *J. Amer. Chem. Soc.*, 1955, **77**, 5314.

[3] Raiford and Floyd, *J. Org. Chem.*, 1943, **8**, 358.

[4] Burger and Foggio, *J. Amer. Chem. Soc.*, 1956, **78**, 4419.

[5] Raiford and Perry, *J. Org. Chem.*, 1942, **7**, 354.

2-Chloro-5-hydroxy-4-methoxybenzaldehyde. 6-Chloroveratraldehyde [3] (9·7 g.) was heated under reflux with hydrobromic acid (*d* 1·48; 50 ml.) for 20 min. The mixture was cooled, diluted with water, and extracted with ether, and the product isolated from the extract with dilute sodium hydroxide solution. The *aldehyde* crystallised from aqueous ethyl alcohol (charcoal) in rods, m. p. 114—115° (Found: C, 51·0; H, 3·9. $C_8H_7ClO_3$ requires C, 51·5; H, 3·75%). The *oxime* crystallised from aqueous ethyl alcohol in needles, m. p. 228—229° (Found: C, 47·6; H, 3·9; N, 6·7. $C_8H_8ClNO_3$ requires C, 47·6; H, 4·0; N, 6·9%).

Ethyl 4-chloro-5-formyl-2-methoxyphenoxyacetate. (*a*) Chlorine was passed through a stirred solution of ethyl 5-formyl-2-methoxyphenoxyacetate (5 g.) in chloroform (100 ml.) for 1 hr. The solvent was evaporated under reduced pressure and the residual oil, after several crystallisations from light petroleum (b. p. 60—80°), gave needles (1·9 g.) of the *chloro-ester,* m. p. 118° (Found: C, 53·0; H, 4·9. $C_{12}H_{13}ClO_5$ requires C, 52·8; H, 4·8%). The *oxime* crystallised from aqueous ethyl alcohol in clustered rods, m. p. 129—130° (Found: C, 50·4; H, 4·9; N, 5·2. $C_{12}H_{14}ClNO_5$ requires C, 50·1; H, 4·9; N, 4·9%).

(*b*) 2-Chloro-5-hydroxy-4-methoxybenzaldehyde (1·86 g.) was dissolved in a solution from sodium (0·25 g.) in ethyl alcohol (30 ml.) which was then refluxed with ethyl bromoacetate (1·12 ml.) for 2 hr. The product, isolated with ether, after cooling and dilution of the mixture with water, crystallised from light petroleum (b. p. 60—80°) (charcoal) in needles, m. p. 117° —undepressed by admixture with the product from (*a*) above.

4-Chloro-5-formyl-2-hydroxyphenoxyacetic acid. The methoxy-ester (1·36 g.) was refluxed with hydrobromic acid (*d* 1·48; 26 ml.) and water (2 ml.) for 2 hr. The solution was cooled, diluted with water, and extracted with ether. The *phenolic acid,* isolated by shaking with a solution of sodium hydrogen carbonate, crystallised from water in needles, (0·94 g.), m. p. 179—180° (Found: C, 46·7; H, 3·3. $C_9H_7ClO_5$ requires C, 46·9; H, 3·0%).

The authors thank Miss D. M. Fieldgate and Mr. D. R. Clifford for the microanalyses.

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LONG ASHTON, BRISTOL. [*Received, June 5th,* 1962.]

926. *Uranium, Plutonium, Beryllium, and Zirconium Complexes of 2-Carboxypyridine* N-*Oxide.*

By A. HELLER, R. ELSON, and Y. MARCUS.

SEVERAL complexes of pyridine *N*-oxide with uranium and transition-metal elements have been reported.[1] The observed donor properties of the *N*-oxide group indicated that the 2-carboxypyridine *N*-oxide group (A) might form stable chelates. This was found to be the case: complexes of limited solubility were precipitated on addition of 1% solutions of the acid to solutions of uranium(VI), plutonium(VI), plutonium(IV), zirconium(IV), and beryllium.

Experimental.—The uranium(VI) *complex* precipitated quantitatively at pH 2—3 has the composition $UO_2A_2,2H_2O$. This deep yellow compound loses both molecules of water at 120° and decomposes at 270°. It dissolves in mineral acids at concentrations higher than N (Found: U, 40·7. $C_{12}H_{12}N_2O_8U$ requires U, 40·8%).

The plutonium(VI) complex precipitated under similar conditions is tan-coloured. Spectrophotometric analysis indicated two acid groups per plutonium atom. It is assumed, owing to the similarity in the behaviour of uranyl and plutonyl cations, that the two compounds have analogous compositions.

In addition, spectral evidence has been obtained for the formation of an insoluble plutonium(IV) complex with four acid groups at pH 4.

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[1] Heller, *Bull. Res. Council Israel,* 1960, **9***A*, 245; Carlin, *J. Amer. Chem. Soc.,* 1961, **83**, 3773; Quagliano, Fujita, Franz, Phillips, Walesley, and Tyree, *ibid.,* p. 3770.

The colourless zirconium(IV) complex precipitated on storage or stirring from a N-hydrochloric acid solution has the composition $ZrA(OH)_3$ which suggests a polymeric structure. The *complex* is stable up to 270° where it decomposes. It is soluble in boiling acid or water whereby it can be conveniently separated from the uranyl complex (Found: Zr, 32·6. $C_6H_7NO_6Zr$ requires Zr, 32·5%).

The beryllium *complex* precipitated on addition of a concentrated solution of a beryllium salt to a 1% solution of the 2-carboxypyridine *N*-oxide has the composition BeA_2 and is soluble in mineral acids (Found: Be, 3·14; C, 50·9; H, 2·8. $C_{12}H_8BeN_2O_6$ requires Be, 3·15; C, 50·5; H, 2·9%).

Complexes of 2-carboxypyridine *N*-oxide are expected to be isostructural with complexes of 1,3-diketones and to carry the same net charge.

A possibility for application of the acid for the separation of uranium(VI) and plutonium(VI) from other metals is indicated by the fact that only their complexes are insoluble in boiling aqueous solutions at pH 2—3, while those of the alkalis, alkaline-earths, transition elements, thorium, uranium(IV), and plutonium(IV) are soluble, either in the free state or as their complexes. Iron(III) forms a deep yellow and copper(II) a turquoise-coloured complex.

One of us (R. E.) is on leave from the University of California, Lawerence Radiation Laboratory, Livermore, on an Israel Atomic Energy Commission Fellowship.

DEPARTMENT OF RADIOCHEMISTRY, ISRAEL ATOMIC ENERGY COMMISSION LABORATORIES,
SOREL RESEARCH ESTABLISHMENT, REHOVOTH, ISRAEL. [*Received, March 28th,* 1962.]

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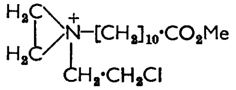
927. *Some Surface-active Alkylating Agents.*

By W. C. J. Ross.

A SUGGESTION that the tumour-growth inhibitory *p*-di-(2-chloroethyl)aminophenylbutyric acid (Chlorambucil) might owe its outstanding activity to its surface-active properties[1] has prompted the synthesis of some purely aliphatic "nitrogen mustard" derivatives which should have similar properties.

Methyl 11-aminoundecanoate hydrochloride was converted by the action of ethylene oxide in acetone into the *NN*-di-2-hydroxyethyl derivative (I; X = OH, R = Me) which afforded the *NN*-di-2-chloroethyl derivative (I; X = Cl, R = Me) when treated with thionyl chloride. Heating the last ester with concentrated hydrochloride acid yielded 11-di-(2-chloroethyl)aminoundecanoic acid (I; X = Cl, R = H).

(I) $(X\cdot CH_2\cdot CH_2)_2N\cdot[CH_2]_{10}\cdot CO_2R$



(II)

The ion from the acid (I; X = Cl, R = H) is an anionic surface-active agent and the ethyleneimmonium ion (II), which will be rapidly formed from the ester (I; X = Cl, R = Me) in solution, is a cationic agent. 11-Chloroacetamido- and 11-iodoacetamidoundecanoic acid were prepared as surface-active compounds which could react *in vivo* with thiol groups.

The ester (I; X = Cl, R = Me) produced about 75% inhibition of the growth of the transplanted Walker rat carcinoma when given daily at a dose of 5 mg./kg. (intraperitoneal) and 50% inhibition of the Crocker mouse sarcoma at a daily dose of 10 mg./kg. The chloroacetamide and iodoacetamide and *NN*-di-(2-chloroethyl)aminoundecanoic acid were inactive against the Walker tumour.

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[1] Ross, "Biological Alkylating Agents," Butterworths Scientific Publns., London, 1962, p. 126.

Experimental.—M. p.s are corrected.

Methyl 11-*di*-(2-*hydroxyethyl*)*aminoundecanoate hydrochloride.* Dry hydrogen chloride was passed through a solution of 11-aminoundecanoic acid (30 g.) in boiling methanol (200 ml.) for 4 hr. The solid remaining after removal of the solvent in a flash-evaporator was ground under dry ether and collected (Found: equiv., by Volhard Cl^- titration, 255, 253. Calc. for $C_{12}H_{26}ClNO_2$: equiv., 251·8). The ester hydrochloride (65·1 g.), ethylene oxide (38·9 ml.), and acetone (250 ml.) were heated at 50° in a pressure bottle with magnetic stirring. After 2 hr. the suspended hydrochloride had dissolved. After 16 hours' heating the solution was evaporated to dryness and the residue was dissolved in methanol (200 ml.), saturated with hydrogen chloride, and again evaporated. The residue was triturated with dry ether and then with ice-cold acetone. When crystallised from ethyl acetate *methyl* 11-*di*-(2-*hydroxyethyl*)*aminoundecanoate hydrochloride* formed very pale yellow plates (31 g.), m. p. 84—85° (Found: C, 55·8; H, 10·0; N, 4·2%; equiv., by Cl^- titration, 340. $C_{16}H_{34}ClNO_4$ requires C, 56·5; H, 10·1; N, 4·1%; equiv., 339·9).

Methyl 11-*di*-(2-*chloroethyl*)*aminoundecanoate hydrochloride.* Redistilled thionyl chloride (5 ml.), in dry chloroform (25 ml.), was added dropwise with stirring to the above hydrochloride (5 g.) in chloroform (25 ml.). After 1 hour's heating at 60° the solvent was removed under reduced pressure. A benzene solution of the residue was passed through a column of activated alumina which was washed with fresh benzene. The residue obtained by evaporating the eluates was dissolved in ether, and this solution was saturated with hydrogen chloride. The precipitated *hydrochloride* formed needles, m. p. 82—84° (depressed to 68° on admixture with an equal amount of the diol hydrochloride), from ethyl acetate (Found: C, 51·3; H, 8·6; N, 3.8%; equiv., 384. $C_{16}H_{32}Cl_3NO_2$ requires C, 51·0; H, 8·6; N, 3·7%; equiv., 376·8).

11-*Di*-(2-*chloroethyl*)*aminoundecanoic acid hydrochloride.* The last-mentioned ester hydrochloride (3 g.) in concentrated hydrochloric acid (15 ml.) was heated under reflux for 1 hr. The solution was evaporated under reduced pressure, and this was repeated twice after addition of dioxan (20 ml.). Cautious addition of dry ether to a solution of the product in dry dioxan caused slow separation of needles (3·8 g.), m. p. 40—50°, of the *acid hydrochloride.* Recrystallisation from dry chloroform–ether gave needles, m. p. 50—52° (Found, for a specimen dried at 25°/0·01 mm.; C, 49·7; H, 8·2; N, 4·0. $C_{15}H_{30}Cl_3NO_2$ requires C, 49·6; H, 8·3; N, 3·9%).

11-*Chloroacetamidoundecanoic acid.* On dropwise addition of pyridine (4 ml.) to a stirred suspension of 11-aminoundecanoic acid (10 g.) in chloroacetyl chloride (10 ml.) and acetone (25 ml.) a clear solution was obtained. This was heated for 10 min. on a steam-bath and then poured into water (150 ml.), giving a solid precipitate. The *chloroacetamido-acid* formed plates, m. p. 85—87°, from benzene (Found: C, 56·2; H, 8·7; N, 4·9. $C_{13}H_{24}ClNO_3$ requires C, 56·2; H, 8·7; N, 5·0%).

11-*Iodoacetamidoundecanoic acid.* A mixture of chloroacetamido-acid (5 g.), sodium iodide (5 g.), and acetone (50 ml.) was heated under reflux for 3 hr. Addition of water then caused the separation of the *iodoacetamido-acid* as a pale yellow solid. It formed prisms, m. p. 104—106°, from benzene (Found: C, 42·7; H, 6·5; N, 4·1. $C_{13}H_{24}INO_3$ requires C, 42·3; H, 6·6; N, 3·8%).

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928. *The Thermodynamic Properties of Furoic Acid in Aqueous and Aqueous Dioxan Solutions.*

By Donald S. Klett and Ben F. Freasier.

Experimental.—Reagents. Furoic acid, m. p. 132·0—132·8°, and 1,4-dioxan were obtained from Matheson Coleman and Bell, and potassium chloride and sodium hydroxide (Analytical Reagents grade) from Mallinckrodt Chemical Works. The furoic acid, potassium chloride, and sodium hydroxide were used without further purification.

The dioxan was purified by distillation from sodium through a 90-cm., vacuum-jacketed column packed with glass helices. The fraction of b. p. 101·0—101·4° was collected.[1]

Distilled water was produced by triple distillation ($\kappa = 1{\cdot}25 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ at 25°).

Sodium furoate was prepared by neutralising a solution of furoic acid with sodium hydroxide and precipitating the salt with dioxan. The salt was filtered off, washed with dioxan, and dried at 100°. An aqueous solution of the purified salt had pH 7·1, which indicated the absence of an excess of sodium hydroxide.

Apparatus and procedure. A Freas-type conductance cell was used. A General Radio impedance bridge of type 1650-A was employed for making the a.c. (oscillator frequency of 1000 cycles/sec.) resistance measurements of the cell. A General Radio decade resistor of type no. 1432M was used in conjunction with the bridge. A Hewlett–Packard model 130B oscilloscope was connected to the detector output of the bridge and used as a null detector. Temperature was controlled to ±0·05° by means of a Forma No. 2074-A refrigerated bath made by Forma Scientific Inc., Marietta, Ohio, U.S.A. The temperature of the conductance cell was controlled by means of an external water-jacketed copper container through which water was circulated from the thermostat-bath.

The cell constant of the conductance cell was determined by using 0·02N-potassium chloride for which the specific conductance is available from the literature.[2]

In a typical experiment, the Freas cell was filled with electrolyte solution and placed in the thermostat-bath. The cell resistance was then measured with the impedance bridge by the method of substitution.

From the literature it is known that the equivalent conductance of an electrolyte varies linearly with the square root of the concentration.[3] It will be assumed that the equivalent conductance will vary linearly with the absolute temperature and with the wt. % of dioxan. This situation is well suited to experimental design. A 3^3 factorial design was utilised.[4]

It was assumed that the negative logarithm of the apparent equilibrium constant of furoic acid (pK_c) would vary directly with the concentration. From the Clausius–Clapeyron equation, it is known that the logarithm of the equilibrium constant is a linear function of the reciprocal of the absolute temperature. Thus, for furoic acid, the concentration, wt. % of dioxan, and the reciprocal temperature were linearly spaced in the 3^3 factorial experiment used.

Discussion.—German, Jeffery, and Vogel have reported the limiting equivalent conductance for sodium furoate and furoic acid and the thermodynamic equilibrium constant at 25°.[5] The apparent equilibrium constant, measured by the pH of a half-neutralised solution of the acid, has been determined in 78·1% ethanol [6] and in aqueous solution.[7]

The equivalent conductances for sodium furoate, sodium chloride, and hydrochloric acid were calculated from resistance measurements. From these results was calculated the equivalent conductance of furoic acid, on the assumption that furoic acid was a strong

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[1] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green, and Co., London, 1956, p. 177.

[2] Daniels and Alberty, " Physical Chemistry," John Wiley and Sons, Inc., New York, 1955, p. 383.

[3] Robinson and Stokes, " Electrolyte Solutions," Academic Press, Inc., New York, 1959.

[4] Bennett and Franklin, " Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, 1954, pp. 506—512.

[5] German, Jeffery, and Vogel, *J.*, 1937, 1604.

[6] Price and Dudley, *J. Amer. Chem. Soc.*, 1956, **78**, 68.

[7] Catlin, *Iowa State Coll. J. Sci.*, 1935, **10**, 65.

TABLE 1.

$\mathrm{p}K_c$'s for the ionisation of furoic acid.

Temp.	Concn. (mmoles/l.)								
	1·050	4·885	8·720	1·050	4·885	8·720	1·050	4·885	8·720
	Dioxan, 0%			Dioxan, 10%			Dioxan, 20%		
10·0°	3·215	3·173	3·162	3·422	3·337	3·302	3·727	3·671	3·654
25·0	3·266	3·213	3·188	3·426	3·389	3·354	3·763	3·732	3·695
41·6	3·294	3·254	3·244	3·521	3·451	3·414	3·823	3·790	3·751

electrolyte. The actual equivalent conductances of furoic acid compared with its calculated equivalent conductances as a strong electrolyte were used in calculating the negative logarithms of the equilibrium constants ($\mathrm{p}K_c$'s).

TABLE 2.

Thermodynamic equilibrium constants and functions for the ionisation of furoic acid.

Temp.	$\mathrm{p}K_a$	ΔG° (kcal./mole)	$-\Delta H^\circ$ (kcal./mole)	$-\Delta S^\circ$ (cal. deg.$^{-1}$ mole^{-1})
		Dioxan, 0%		
10°	3·224 ± 0·001	4·175 ± 0·001		
25	3·272 ± 0·001	4·463 ± 0·001	1·26 ± 0·5	19·2 ± 1·8
40	3·321 ± 0·001	4·759 ± 0·001		
		Dioxan, 10%		
10	3·40 ± 0·10	4·4 ± 0·1		
25	3·45 ± 0·10	4·7 ± 0·1	1·26 ± 0·5	20·0 ± 2·3
40	3·50 ± 0·10	5·0 ± 0·1		
		Dioxan, 20%		
10	3·74 ± 0·30	4·8 ± 0·3		
25	3·78 ± 0·30	5·2 ± 0·4	1·26 ± 0·5	21·5 ± 3·0
40	3·83 ± 0·30	5·5 ± 0·4		

The empirical equation for the thermodynamic equilibrium constant of furoic acid ($\mathrm{p}K_a$) as a function of wt. % of dioxan (W) and absolute temperature (T) is:

$$\mathrm{p}K_a = 4{\cdot}198 + 1{\cdot}019 \times 10^{-2}W + 7{\cdot}683 \times 10^{-4}W^2 - 275{\cdot}9/T.$$

If this equation is combined with the Gibbs–Helmholtz equation, the results in Table 2 are obtained. The errors indicated are at the 95% confidence interval.

One value (3·272 ± 0·001) for the $\mathrm{p}K_a$ at 25° and 0% of dioxan can be compared with that reported by German, Jeffery, and Vogel (3·179).[5]

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DEPARTMENT OF CHEMISTRY, TEXAS COLLEGE OF ARTS AND INDUSTRIES,
KINGSVILLE, TEXAS, U.S.A.
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929. *The Autoxidation of Isobutyrophenone.*

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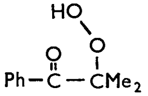
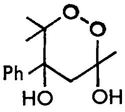
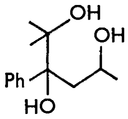
Doering and Haines[1] found that autoxidation of isobutyrophenone in t-butyl alcohol containing potassium t-butoxide afforded benzoic acid (75%) and a trace of material not soluble in heptane. In connection with a recent investigation[2] we had occasion to repeat this autoxidation. We confirm the production of benzoic acid (51%). In addition, a substantial amount of a crystalline peroxide was formed. This compound is not the expected[2] α-hydroperoxide (I). It had the composition $C_{13}H_{18}O_4$, showed three quaternary methyl groups in its nuclear magnetic resonance spectrum, and gave a crystalline triol, $C_{13}H_{20}O_3$, on reduction with lithium aluminium hydride. The triol consumed one mol. of periodate to furnish acetone and a hydroxy-ketone, $C_{10}H_{12}O_2$, which showed ultraviolet absorption indicative of the grouping Ph·CO. Oxidation of the hydroxy-ketone with chromic–sulphuric acid, or oxidation of the peroxide itself with chromium trioxide in pyridine, gave 1-phenylbutane-1,3-dione. The hydroxy-ketone must, therefore, be 3-hydroxy-1-phenylbutan-1-one, and the triol and its parent peroxide must be represented by (III) and (II), respectively.


$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{HO{-}O}{|}}{C}Me_2}$

(I)


(II)


(III)

Clearly the peroxide (II) is formed by condensation of acetone, derived from cleavage of the primary hydroperoxide (I), with the hydroperoxide (I). The fact that the rate of this condensation is greater than the rate of self-condensation of acetone is remarkable and suggests that the α-hydroperoxide plays a special role in facilitating nucleophilic attack on the adjacent, otherwise rather hindered, carbonyl group. Conceivably intramolecular protonation of the developing negative charge on carbonyl-oxygen is responsible for this effect. The phenomenon certainly deserves further study.

Experimental.—Ultraviolet absorption spectra were determined for ethanol solutions, and infrared absorption spectra for potassium chloride discs. Nuclear magnetic resonance measurements were determined by Mr. R. G. Foster on a Varian 4300 spectrometer in deuterochloroform at 56·4 mc./sec.

The peroxide (II). Isobutyrophenone (5 ml.; 4·92 g.) was autoxidised (1 mol. uptake) in the usual way.[3] Separation of the product into acidic (2·46 g.) and neutral (2·65 g.) fractions gave, in the former, benzoic acid (2·05 g., 51%) and, in the latter the peroxide 3,5-*dihydroxy*-3,6,6-*trimethyl*-5-*phenyl*-1,2-*dioxan* (II). Recrystallised from benzene–pentane the latter (1·54 g.) had m. p. 153°, $\nu_{max.}$ 3370 (OH) cm.$^{-1}$, τ 8·89, 8·71, and 8·54 (all singlets, quaternary methyl groups), 8·07 and 7·23 (AB spectrum, cyclic methylene) (Found: C, 65·7; H, 7·55; active H, 1·35. $C_{13}H_{18}O_4$ requires C, 65·55; H, 7·6; 2 active H, 1·27%). The compound gave a positive peroxide test.

Reduction with lithium aluminium hydride. The peroxide (708 mg.) in ether (50 ml.) was refluxed with lithium aluminium hydride (3·5 g.) in the same solvent (50 ml.) for 3 hr. Crystallisation of the product (621 mg.) from benzene–pentane gave 2-*methyl*-3-*phenylhexane*-2,3,5-*triol* (III) (537 mg.), m. p. 105°, $\nu_{max.}$ 3280—3450 (OH) cm.$^{-1}$, τ 9·06 and 8·74 (singlets, quaternary methyl groups) and 8·91 (doublet, J = 11 c./sec., >CHMe) (Found: C, 70·05; H, 8·8. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%). The triol consumed 1·0 mol. of sodium periodate.

Reaction of the triol (III) *with sodium periodate.* The triol (250 mg.) in water (150 ml.)

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[1] Doering and Haines, *J. Amer. Chem. Soc.*, 1954, **76**, 482.

[2] Bailey, Barton, Elks, and Templeton, *J.*, 1962, 1578.

containing sodium periodate (6·0 g.) was kept overnight at room temperature. Steam-distillation into acidic aqueous 2,4-dinitrophenylhydrazine gave acetone 2,4-dinitrophenylhydrazone (145 mg., 54%), identified by m. p. and mixed m. p. The reaction was then repeated and the product extracted into ether. Removal of the solvent gave 3-hydroxy-1-phenylbutan-1-one (170 mg., 93%) as an oil, $\lambda_{max.}$ 243 mμ (ε 11,700), $\nu_{max.}$ 3450 (OH) and 1678 (conjugated C=O) cm.$^{-1}$. The corresponding 2,4-*dinitrophenylhydrazone*, crystallised from ethanol, had m. p. 178—179°, $\lambda_{max.}$ 381 mμ (ε 31,400) (Found: C, 55·95; H, 4·55; N, 15·9. $C_{16}H_{16}N_4O_5$ requires C, 55·8; H, 4·7; N, 16·25%).

1-*Phenylbutane*-1,3-*dione*. (*a*) 3-Hydroxy-1-phenylbutan-1-one (155 mg.) in acetone (50 ml.) at 0° was oxidised with a 10% excess of chromic acid–sulphuric acid.[3] The product was treated in methanol with saturated aqueous cupric acetate. The precipitate thus formed, crystallised from aqueous ethanol, gave the copper complex, m. p. and mixed m. p. 195—197°, of 1-phenylbutane-1,3-dione.[4] (*b*) The peroxide (II) (600 mg.) in pyridine (10 ml.) was left with chromium trioxide (1·0 g.) mixed with the same solvent (100 ml.) for 24 hr. at room temperature. Crystallisation of the product from pentane gave 1-phenylbutane-1,3-dione [4] (m. p., mixed m. p., and infrared spectrum) (Found: C, 74·1; H, 6·4. Calc. for $C_{10}H_{10}O_2$: C, 74·1; H, 6·15%).

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[3] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

[4] See Hauser, Swamer, and Adams, *Organic Reactions*, 1954, **8**, 137.