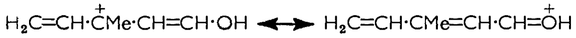
## 467. *The Stereoisomeric Penta-2,4-dienals and 3-Methylpenta-2,4-dienals.*

By E. E. Boehm and M. C. Whiting.

In our synthetical work on " tagetone "[1] we prepared the two stereoisomers of 3-methylpent-2-en-4-ynal (I) and encountered their ready conversion into a *ca.* 98 : 2 *cis–trans*-equilibrium mixture. The known stereoisomeric 3-methylpenta-2,4-dienols[2] were also

$HC{\equiv}C{\cdot}CMe{=}CH{\cdot}CHO$ (I)

$H_2C{=}CH{\cdot}CMe{=}CH{\cdot}CHO$ (II)



$H_2C{=}CH{\cdot}\overset{+}{C}Me{\cdot}CH{=}CH{\cdot}OH \longleftrightarrow H_2C{=}CH{\cdot}CMe{=}CH{\cdot}CH{=}\overset{+}{O}H$

(III)

$H_2C{=}CH{\cdot}C({=}CH_2){\cdot}CH{=}CH{\cdot}OH$ (IV)

oxidised by manganese dioxide, the *cis*-alcohol giving the *cis*-aldehyde and the *trans*-alcohol a 4 : 1 mixture of *trans*- and *cis*-isomers. The latter result was probably a consequence of adventitious acid-catalysed equilibration during isolation; however, the pure *trans*-aldehyde was readily obtained by semihydrogenation of *trans*-3-methylpent-2-en-4-ynal. Both isomers underwent gas–liquid chromatography without decomposition, and this could be used as an analytical method. As with the 3-methylpentenynals,[1] the *trans*-isomer had higher refractive index, $\lambda_{max.}$ and $\varepsilon_{max.}$ values, and formed a higher-melting 2,4-dinitrophenylhydrazone; and, again, nuclear magnetic resonance measurements[3] showed that the methyl group *cis* to CHO in the *trans*-isomer was deshielded by 0·18 p.p.m. relative to that in the *cis*-aldehyde.

On treatment with 5% sulphuric acid each isomer was converted (almost completely in 3·5 hr. at 20°) into a 21 : 79 *cis–trans*-equilibrium mixture. Evidently a vinyl group is effectively larger than methyl, whereas ethynyl is much smaller. The order (H) $<$ $HC{\equiv}C{-}$ $<$ $H_3C$ $<$ $H_2C{=}CH$, implied by our experiments, is of course readily predicted from a study of models, if the vinyl group is assumed to be coplanar with the αβ-ethylenic linkage.

An attempt was made to equilibrate the *cis*- and *trans*-penta-2,4-dienals themselves. The *trans*-compound is well known.[4] *cis*-Penta-2,4-dien-1-ol was prepared by semihydrogenation of pent-4-en-2-yn-1-ol. In agreement with Crombie, Harper, and Thompson[5a] and Crombie, Harper, and Newman[5b] we found that overhydrogenated products were formed even at less than 1 mol. uptake, but rigorous fractionation removed these. Freedom from *trans*-penta-2,4-dien-1-ol could not be demonstrated by gas–liquid chromatography in this case, as the isomers could not be separated, but infrared spectra proved that hydrogenation gave essentially the *cis*-product. Physical constants for our product differed appreciably from earlier data.[5b] Oxidation gave the corresponding *cis*-dienal, also inseparable from the *trans*-isomer but readily distinguished by its infrared spectrum. Treatment with 10% sulphuric acid for 12 hr. at 20° resulted in a 70% recovery without equilibration, in sharp contrast to the easy isomerisation of some other *cis*-αβ-ethylenic carbonyl compounds;[6] under more severe conditions general decomposition ensued. Presumably the interconversion of the 3-methylpentadienals involves either the oxonium cation (III)[7] or the enol (IV). Removal of the methyl

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[1] Boehm, Thaller, and Whiting, preceding paper.

[2] Oroshnik, *J. Amer. Chem. Soc.*, 1956, **78**, 4667.

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

[4] Woods and Sanders, *J. Amer. Chem. Soc.*, 1946, **68**, 2483.

[5] (*a*) Crombie, Harper, and Thompson, *J.*, 1951, 2908; (*b*) Crombie, Harper, and Newman, *J.*, 1956, 3963.

[6] Theus, Surber, Colombi, and Schinz, *Helv. Chim. Acta*, 1955, **38**, 239.

[7] Raphael and Sondheimer, *J.*, 1951, 2693.

group would render the latter non-existent and the former much less stable, and the decreased mobility of the simpler system is no surprise. The original preparation of *trans*-penta-2,4-dienal from 2-ethoxy-2,5-dihydrofuran, involving steam-distillation from 25% phosphoric acid,[4] must, however, almost certainly have proceeded *via* the *cis*-dienal and, presumably, a cation analogous to (III); this reaction certainly proves [5a] that the *cis*-form is not the more stable.

*Experimental.*—cis-3-*Methylpenta*-2,4-*dienal.* *cis*-3-Methylpenta-2,4-dien-1-ol [2] (2·3 g.), manganese dioxide (23 g.), and methylene dichloride (100 c.c.) were stirred together for 18 hr. at 20° with the exclusion of light. The mixture was filtered and the manganese dioxide washed with more solvent; evaporation of the solvent and distillation gave the *aldehyde* (1·45 g., 63%), b. p. 51—52°/10 mm., $n_D^{21}$ 1·5180 (Found: C, 74·7; H, 8·8. $C_6H_8O$ requires C, 75·0; H, 8·4%), which had $\lambda_{max.}$ (in EtOH) 2650 ($\varepsilon$ 14,500), (in hexane) 2575 Å ($\varepsilon$ 19,100), $\nu_{max.}$ (in $CS_2$) 3030w, 2920w, 2778m, 2703w, 2667w, 1835w, 1667vs, 1205m, 1120s, 976s, 921s, and 844w cm.$^{-1}$, $\tau$ 7·92, 2·59, and −0·12. Its 2,4-*dinitrophenylhydrazone* formed needles, m. p. 135—136° (from ethanol) (Found: C, 52·4; H, 4·4. $C_{12}H_{12}N_4O_4$ requires C, 52·2; H, 4·4%), $\lambda_{max.}$ (in (EtOH) 3850 ($\varepsilon$ 26,000), 2975 ($\varepsilon$ 10,100), and 2625 Å ($\varepsilon$ 14,300).

trans-3-*Methylpenta*-2,4-*dienal.* (*a*) *trans*-3-Methylpent-2-en-4-ynal (8·1 g.), ethyl acetate (150 c.c.), partially poisoned palladium catalyst (1·5 g.), and quinoline (300 mg.) were shaken in hydrogen with the exclusion of light. After the absorption of 1 mol., filtration, evaporation, and distillation gave the *aldehyde* (4·1 g.), b. p. 50—51°/12 mm., $n_D^{18}$ 1·5220, $\nu_{max.}$ 3030w, 2920m, 2700w, 2667m, 1835w, 1667vs, 1196s, 1104s, 985s, 917s, and 863m cm.$^{-1}$. Its 2,4-*dinitrophenylhydrazone* formed needles, m. p. 141—142° (from ethanol) (Found: C, 52·2; H, 4·7. $C_{12}H_{12}N_4O_4$ requires C, 52·2; H, 4·4%), $\lambda_{max.}$ (in EtOH) 3875 ($\varepsilon$ 30,200), 3000 ($\varepsilon$ 10,400), and 2625 Å ($\varepsilon$ 14,000). A mixture with the derivative of the *cis*-aldehyde had m. p. 130—132° (Heilbron, Jones, and Julia [8] give m. p. 131—132° for a dinitrophenylhydrazone prepared from the acetal of 3-methylpenta-2,4-dienal, configurational composition unknown).

(*b*) Oxidation of *trans*-3-methylpenta-2,4-dien-1-ol as described for the *cis*-isomer gave, in one experiment, a product, b. p. 62—63°/20 mm., $n_D^{24}$ 1·5190 (Found: C, 74·6; H, 8·8%), $\lambda_{max.}$ (in EtOH) 2680 ($\varepsilon$ 15,000), (in hexane) 2585 Å ($\varepsilon$ 24,000). Gas chromatography indicated that *trans*- and *cis*-components were present, ratio about 4 : 1, and the infrared spectrum was consistent with this possibility, while the nuclear magnetic resonance spectrum included bands at $\tau$ = 7·74, 3·49, and −0·10 in addition to weak bands of the *cis*-isomer. This result may well have followed adventitious acid-catalysis in, perhaps, the final distillation.

*Equilibration.* The *cis*- and *trans*-aldehyde were treated with 5% sulphuric acid at 20°; the products were chromatographed on (*a*) dinonyl phthalate (20%) on Embacel at 97° or (*b*) tritolyl phosphate (20%) on Embacel at 120°, retention times (*a*) 20·8 and 23·2, (*b*) 7·7 and 8·6 min., respectively. Both gave after 24 hr. an equilibrium mixture containing 21% of the *cis*-isomer.

cis-*Penta*-2,4-*dien*-1-*ol.* Pent-4-en-2-yn-1-ol (45 g.), ethyl acetate (150 c.c.), partially poisoned palladium catalyst (15 g.), and quinoline (6 g.) were shaken in hydrogen in the absence of light. After 10 hr. absorption ceased (uptake 0·8 mol.). Filtration and removal of the solvent below 50° gave a residue which was distilled through a 50 × 1·4 cm. Dixon column equipped with a reflux meter, total condensation still-head, and magnetically controlled bucket (cf. ref. 9); a manostat was set at 38 mm. Boil-up and take-off rates were 360 and 5 c.c./hr., respectively, and the 20 fractions were grouped as follows: (i) b. p. 75·5—81·5°, $n_D^{18}$ 1·4730—1·4780 (11·5 g.) (mainly pentenols ?); (ii) b. p. 81·5—82·5°, $n_D^{18}$ 1·4800—1·4860 (6·2 g.); and (iii) b. p. 82·5—83°, $n_D^{18}$ 1·4870—1·4890 (11·4 g.). Refractionation of fraction (iii) gave penta-2,4-dien-1-ol, essentially *cis*, b. p. 79—80°/35 mm., $n_D^{18}$ 1·4883 ± 1 (Found: C, 70·9; H, 9·7. $C_5H_8O$ requires C, 71·4; H, 9·6%), $\lambda_{max.}$ (in EtOH) 2230 Å ($\varepsilon$ 19,100), $\nu_{max.}$ (in $CS_2$) 3546m, 2857m, 1818w, 1026m, 1000s, 962s, 939s, 905s, and 778m cm.$^{-1}$. Gas chromatography on dinonyl phthalate showed it to be free from the pentenols which were present in the lower-boiling fractions, but no separation was observed when it was compared with the *trans*-penta-2,4-dienol, so that the absence of this alcohol is deducible only from the infrared spectrum, which is insensitive to small quantities. The α-*naphthylurethane* formed needles, m. p. 84—85°, from

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[8] Heilbron, Jones, and Julia, *J.*, 1949, 1430.

[9] Allan and Whiting, *J.*, 1953, 3314.

light petroleum, depressed to 75—79° on admixture with that of *trans*-penta-2,4-dienol, m. p. 89—90° (Found: C, 75·6; H, 6·1. $C_{16}H_{15}NO_2$ requires C, 75·9; H, 6·0%).

For *trans*-penta-2,4-dien-1-ol, prepared by reduction of penta-2,4-dienoic acid with lithium aluminium hydride at —30°, we observed b. p. 61—62°/19 mm., $n_{\mathrm{D}}^{19}$ 1·4903, in agreement with earlier data. Our specimen had $\lambda_{\max.}$ (in EtOH) 2230 Å ($\varepsilon$ 30,800) (cf. ref. 5*a*), $\nu_{\max.}$ 3552m, 2855m, 1802w, 1081s, 1000vs, 966s, 948s, and 892s cm.$^{-1}$. Its $\alpha$-naphthylurethane formed needles, m. p. 89—90°, in poor agreement with the quoted [10] value of 97·5°, but in agreement with m. p. 89° and 99·5° (dimorphic) quoted by Crombie *et al.*[5a] (Found: C, 75·5; H, 5·7; N, 5·4. Calc. for $C_{16}H_{15}NO_2$ C, 75·9; H, 6·0; N, 5·5%).

cis-*Penta*-2,4-*dienal*. *cis*-Penta-2,4-dien-1-ol (4 g.), methylene chloride (250 c.c.), and manganese dioxide (40 g.) were shaken in the dark for 26 hr. at 20°. Filtration, evaporation, and distillation gave the *aldehyde* (2·65 g., 60%), b. p. 29—30°/10 mm., $n_{\mathrm{D}}^{19}$ 1·5115 (Found, C, 72·9; H, 7·3. $C_5H_6O$ requires C, 73·2; H, 7·4%), $\lambda_{\max.}$ (in EtOH) 2595 ($\varepsilon$ 19,100), (in hexane) 2550 Å ($\varepsilon$ 25,300), $\nu_{\max.}$ (in $CS_2$) 2778m, 2703w, 2667m, 1835w, 1681vs, 1667vs, 1156s, 1002s, 923s, and 797m cm.$^{-1}$, and (in $CCl_4$) at 1681vs, 1667vs, and 1621w. Its 2,4-*dinitrophenylhydrazone* formed orange-red needles, m. p. 150—151° (Found: N, 21·1. $C_{11}H_{10}N_4O_4$ requires N, 21·3%).

*trans*-Penta-2,4-dienol, prepared similarly, had b. p. 30°/10 mm., $n_{\mathrm{D}}^{19}$ 1·5185—1·5190, in agreement with earlier values [4] (but cf. ref. 5), $\lambda_{\max.}$ (in hexane) 2500 Å ($\varepsilon$ 34,400), and lacked the infrared band at 797 cm.$^{-1}$ of the *cis*-isomer. Its 2,4-dinitrophenylhydrazone had m. p. 176—177° in agreement with that given earlier,[4] depressed to 147—149° on admixture with the *cis*-analogue. The two pentadienals were inseparable when chromatographed on any liquid phase examined.

One of us (E. E. B.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, October 4th,* 1962.]

[10] Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84.

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## 468. *Improved Synthetic Routes to Pyrrole-2-carboxylic Acid and its Derivatives.*

By P. HODGE and R. W. RICKARDS.

ODDO and MOSCHINI [1] described the preparation of methyl pyrrole-2-carboxylate in 90% yield by reaction of pyrrylmagnesium bromide with methyl chloroformate. Other workers [2,3] failed to duplicate this result, and we obtained varying yields of the required ester (maximum 15%) and dimethyl pyrrole-1,2-dicarboxylate. Treibs and Dietl [4] prepared ethyl pyrrole-2-carboxylate in 29% yield from pyrryl-lithium and ethyl chloroformate, but in our hands use of methyl chloroformate in this reaction gave only the carbamic ester (48%). It is clear that even if Oddo and Moschini's preparation [1] was not a mixture, these reactions are very sensitive to experimental conditions. Direct carboxylation of pyrrole [5] or its metal derivatives [6] gives only moderate yields and is not a satisfactory alternative route. In view of the synthetic value of pyrrole-2-carboxylic acid and its derivatives, we describe here two reliable, efficient routes to these compounds.

Reaction of pyrrylmagnesium bromide with methyl chloroformate by Signaigo and Adkins's method [4] gave, on distillation, methyl pyrrole-1-carboxylate (20%), and a

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[1] Oddo and Moschini, *Gazzetta*, 1912, **42**, II, 244.

[2] Andrews and McElvain, *J. Amer. Chem. Soc.*, 1929, **51**, 887; Reichstein, *Helv. Chim. Acta*, 1930, **13**, 349; Takeda, *Bull. Agric. Chem. Soc., Japan*, 1959, **23**, 169.

[3] Signaigo and Adkins, *J. Amer. Chem. Soc.*, 1936, **58**, 1122.

[4] Treibs and Dietl, *Annalen*, 1958, **619**, 80.

[5] Ciamician and Silber, *Ber.*, 1884, **17**, 1150; Smissman, Graber, and Winzler, *J. Amer. Pharmaceut. Assoc.* (*Sci. Edn.*), 1956, **45**, 509.

[6] (*a*) Letellier and Bouthillier, *Canad. J. Biochem. Physiol.*, 1957, **35**, 811 and references cited therein; (*b*) Doyle, Mehta, Sach, and Pearson, *J.*, 1958, 4458.

mixture containing mainly the 1,2-diester together with a little of the 2-ester. Mild alkaline hydrolysis of this mixture, with concomitant decarboxylation of the carbamic acid, afforded very pure pyrrole-2-carboxylic acid in 68% overall yield from pyrrole. Alternatively, pyrrole-2-aldehyde, readily available (83—89%) by formylation of pyrrole with phosphorus oxychloride–dimethylformamide,[7] was oxidised with alkaline silver oxide to pyrrole-2-carboxylic acid in 82% overall yield from pyrrole.

Methyl pyrrole-2-carboxylate was best (94%) prepared from the acid with diazomethane. Methyl iodide and silver oxide gave a less readily purified product; methyl iodide and potassium carbonate afforded either the required ester or its *N*-methyl derivative depending on reaction conditions.

*Experimental.*—Infrared spectra were recorded on a Unicam S.P. 200 spectrophotometer. Ultraviolet spectra were measured for ethanol solutions.

*Dimethyl pyrrole*-1,2-*dicarboxylate*. Reaction of pyrrylmagnesium bromide with methyl chloroformate (cf. ref. 1) yielded *dimethyl pyrrole*-1,2-*dicarboxylate* (13%), b. p. 145°/28 mm., m. p. 37—40° (from hexane), $\nu_{\text{max.}}$ (in $CCl_4$) 1758 (carbamic ester), 1728 cm.$^{-1}$ (ester), $\lambda_{\text{max.}}$ 235, 263 mμ (log ε 3·61, 3·61) (Found: C, 52·8; H, 4·5. $C_8H_9NO_4$ requires C, 52·5; H, 4·9%).

*Methyl pyrrole*-1-*carboxylate*. To ethereal butyl-lithium [8] (0·5 mole), stirred at 0° under nitrogen, was added dropwise pyrrole (33·5 g., 0·5 mole) in ether (30 ml.). To the resulting white suspension methyl chloroformate (47 g., 0·5 mole) in ether (30 ml.) was added, and the mixture was refluxed for 2 hr. After filtration from lithium chloride, the residue was washed with aqueous potassium hydrogen carbonate, dried, and distilled. The methyl pyrrole-1-carboxylate (29·7 g., 48%) obtained had b. p. 50·0—50·5°/12 mm., $n_D^{22}$ 1·4882, $\nu_{\text{max.}}$ (in $CCl_4$) 1757 cm.$^{-1}$ (carbamic ester), $\lambda_{\text{max.}}$ 228 mμ (log ε 3·85) (Found: C, 57·8; H, 5·5. Calc. for $C_6H_7NO_2$: C, 57·6; H, 5·6%). Acheson and Vernon [9] report b. p. 168—170°.

Acidification of the aqueous washings and extraction with ethyl acetate gave pyrrole-1-carboxylic acid (2·5 g.), m. p. 123—125° [from light petroleum (b. p. 60—80°)] (lit., m. p. 95° [10] and 118—118·5° [11]), $\nu_{\text{max.}}$ (in $CCl_4$) 3300—2450, 1709 cm.$^{-1}$, $\lambda_{\text{max.}}$ 224 mμ (log ε 3·68) (Found: C, 54·6; H, 4·3. Calc. for $C_5H_5NO_2$: C, 54·1; H, 4·5%). The acid was identified by conversion with diazomethane into its methyl ester, which had the correct infrared spectrum.

*Pyrrole*-2-*carboxylic acid*. (i) Distillation of the product [3] from methyl chloroformate and pyrrylmagnesium bromide gave methyl pyrrole-1-carboxylate (20%), b. p. 53—58°/20 mm., and a mixture, b. p. 116—124°/10 mm., of methyl pyrrole-2-carboxylate (5·6%) and dimethyl pyrrole-1,2-dicarboxylate (64%) (analysed by infrared spectroscopy and gas–liquid chromatography on a silicone column). This mixture, when kept in aqueous-methanolic potassium hydroxide at room temperature for 2 days, gave pyrrole-2-carboxylic acid (98%), m. p. 207—208° (from ether) (lit.,[6a] 208·5°), $\nu_{\text{max.}}$ (in Nujol) 3330, 3200—2100, 1662 cm.$^{-1}$.

(ii) To a suspension of silver oxide [prepared [12] by adding, with stirring, silver nitrate (3·4 g.) in water (25 ml.) to sodium hydroxide (1·7 g.) in water (25 ml.)] was added pyrrole-2-aldehyde (1·04 g.; b. p. 108—109°/13 mm.) in 1 : 1 aqueous methanol (10 ml.). After vigorous stirring for 1 hr. at room temperature, the precipitate was filtered off and washed with hot water. The combined filtrate and washings were extracted with ether, and then acidified at 0° with concentrated hydrochloric acid. Extraction four times with ether, drying ($MgSO_4$), and removal of ether under a vacuum afforded pyrrole-2-carboxylic acid (1·15 g., 95%), crystals, m. p. 198—200° raised to 207—209° by sublimation at 170°/0·05 mm., identified by mixed m. p. and infrared spectrum.

*Methyl pyrrole*-2-*carboxylate*. (i) The acid with ethereal diazomethane (cf. ref. 6*b*) overnight gave methyl pyrrole-2-carboxylate (94%), m. p. 72—73° (from hexane, after chromatography in ether on neutral alumina), $\nu_{\text{max.}}$ (in $CCl_4$) 3420, 3280 (NH), 1710, 1700 cm.$^{-1}$ (ester), $\lambda_{\text{max.}}$ 238 (infl.), 263 mμ (log ε 3·62, 4·14). (ii) The acid with silver oxide and methyl iodide in

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[7] Smith, *J.*, 1954, 3842; Silverstein, Ryskiewicz, Willard, and Kochler, *J. Org. Chem.*, 1955, **20**, 668.

[8] Gilman, Beel, Brannen, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499; Gilman and Haubein, *ibid.*, 1944, **66**, 1515.

[9] Acheson and Vernon, *J.*, 1961, 457.

[10] Tschelinzeff and Maxoroff, *Ber.*, 1927, **60**, 194.

[11] Shirley, Gross, and Roussel, *J. Org. Chem.*, 1955, **20**, 225.

[12] Cf. Campaigne and Le Suer, *Org. Synth.*, 1953, **33**, 94.

refluxing chloroform (7 hr.) afforded the ester (74%, purified as above). (iii) The acid with methyl iodide and anhydrous potassium carbonate in boiling acetone (3 hr.) gave the ester (75%).

*Methyl* 1-*methylpyrrole*-2-*carboxylate.* Pyrrole-2-carboxylic acid (8·1 g.), potassium carbonate (40 g.), and methyl iodide (20 ml.) were refluxed in dry acetone (180 ml.) for 40 hr. with stirring. Distillation gave methyl 1-methylpyrrole-2-carboxylate (7·3 g., 72%), b. p. 86·5—87·0°/13 mm. (lit., b. p. 95—98°/28 mm.,[11] 62°/1 mm.[6b]), $\nu_{\text{max.}}$ (in $CCl_4$) 1707 cm.$^{-1}$, $\lambda_{\text{max.}}$ 240 (infl.), 265 mμ (log ε 3·84, 4·18) (Found: C, 60·4; H, 6·1. Calc. for $C_7H_9NO_2$: C, 60·4; H, 6·5%).

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# 469. 7- *and* 8-*Ethyloctahydroindolizines.*

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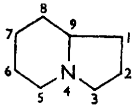
The perhydro-base B obtained from strychnine by Clemo[1] contains the tertiary nitrogen atom of the alkaloid, and its analysis and possible modes of derivation suggest that it is an ethyl derivative of octahydroindolizine (I). 1-, 2-, 3-, 5-, and 6-Ethyloctahydroindolizine have already been synthesised in these laboratories,[2] and we now report the preparation of 7- and 8-ethyloctahydroindolizine. None of these bases is identical with that obtained by Clemo. Each should, however, occur in two geometrically isomeric externally compensated forms, but only in the case of the 6-ethyl base, which gave two picrates, has any indication of the presence of more than one form been found.



(I)

Lions and Willison[3] obtained octahydro-7-oxoindolizine by the condensation of γ-aminobutyraldehyde, formaldehyde, and diethyl acetone-1,3-dicarboxylate, followed by hydrolysis and decarboxylation. We have obtained this ketone by condensing potassium pyrrole with ethyl β-bromopropionate and treating the resulting ethyl β-pyrrol-1-ylpropionate with ethyl diazoacetate,[4] giving ethyl β-(2-ethoxycarbonylmethylpyrrol-1-yl)-propionate, which, after catalytic reduction to the corresponding pyrrolidinyl compound, was cyclised, hydrolysed, and decarboxylated. The ketone was then treated with ethylmagnesium bromide and the resulting 7-ethyl-7-hydroxyoctahydroindolizine dehydrated to 7-ethylhexahydroindolizine, catalytic reduction of which yielded 7-ethyloctahydroindolizine.

8-Ethyloctahydroindolizine was prepared in a similar manner from octahydro-8-oxoindolizine.[5]

*Experimental.—Ethyl* β-(2-*ethoxycarbonylpyrrol*-1-*yl*)*propionate.* A paste of potassium pyrrole (42·5 g.) and toluene (20 ml.) was mixed slowly with ethyl β-bromopropionate (70 ml.). The solvent was removed from the filtered liquid in a vacuum, crude ethyl β-pyrrol-1-ylpropionate (26 g.) remaining. Ethereal ethyl diazoacetate, freshly prepared from glycine ester hydrochloride (30 g.), was slowly added to this ester (62 g.) and copper bronze (2·5 g.) at 0° with stirring, the mixture was heated for 30 min. on the steam-bath, the solvent was removed, and the residue distilled, giving unchanged propionate (35 g.) and the diester (12·5 g.), b. p. 158°/9 mm. The substance gave inconsistent analyses, and no crystalline derivatives could be obtained.

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[1] Clemo, *J.*, 1936, 1695.

[2] Clemo and Metcalfe, *J.*, 1937, 1518; Clemo, Fletcher, Fulton, and Raper, *J.*, 1950, 1140; Raper and Prasad, *J.*, 1956, 217.

[3] Lions and Willison, *J. Proc. Roy. Soc. New South Wales*, 1940, **73**, 240.

[4] Nenitzescu, *Ber.*, 1931, **64**, 1928.

[5] Leonard, Swan, and Figuersis, *J. Amer. Chem. Soc.*, 1952, **74**, 4620.

*Ethyl* β-(2-*ethoxycarbonylpyrrolidin*-1-*yl*)*propionate*. The above ester (12·4 g.) in glacial acetic acid (25 ml.) and ethanol (20 ml.) was shaken with platinum oxide (750 mg.) in hydrogen at 100 lb./in.$^2$ for 12 hr. Platinum oxide (750 mg.) was added and shaking continued for 24 hr. After filtration and removal of solvents the diethyl ester (10·3 g.), b. p. 138°/18 mm., 84°/2·5 mm., was obtained. It gave no crystalline derivatives.

*Octahydro*-7-*oxoindolizine*. The pyrrolidinyl ester (8·7 g.) and powdered potassium (12 g.) were heated in toluene (100 ml.) for 4 hr. on the steam-bath. Ethanol (20 ml.), water (50 ml.), and concentrated hydrochloric acid (45 ml.) were successively added, and, after 12 hours' heating on the steam-bath the mixture was evaporated in a vacuum, the residue basified with 50% potassium hydroxide solution and extracted with ether, and the ethereal extract was dried; on removal of the solvent, it gave octahydro-7-oxoindolizine (4·2 g.), b. p. 110°/18 mm. (Found: C, 69·1; H, 9·6. Calc. for $C_8H_{13}NO$: C, 69·1; H, 9·3%). Its picrate had m. p. 198—200°. Lions and Willison record the same m. p.

7-*Ethyloctahydro*-7-*hydroxyindolizine*. A Grignard reagent from magnesium (4 g.), ethyl iodide (36 g.), and ether (40 ml.) was added slowly at 0° to octahydro-7-oxoindolizine (3 g.) in ether (10 ml.). After 16 hr. damp ether, water, and 30% hydrochloric acid were added successively, the aqueous layer was separated, and the ether layer was extracted three times with 30% hydrochloric acid. The combined aqueous layers were evaporated in a vacuum, and the residue was basified with 50% potassium hydroxide solution, and distilled in a current of steam. The distillate (1·5 l.) was acidified and evaporated to dryness, and the residue was basified with aqueous potassium hydroxide, and the liberated 7-*ethyloctahydro*-7-*hydroxyindolizine* was extracted with ether and distilled; it (1·4 g.) had b. p. 92°/2 mm. (Found: C, 71·2; H, 11·4. $C_{10}H_{19}NO$ requires C, 71·0; H, 11·25%). The *methiodide* crystallised from acetone in needles, m. p. 110° (Found: C, 42·2; H, 6·9. $C_{10}H_{19}NO,CH_3I$ requires C, 42·4; H, 7·1%). The *picrolonate* forms yellow needles, m. p. 136°, from ethanol (Found: C, 55·6; H, 6·3. $C_{10}H_{19}NO,C_{10}H_8N_4O_5$ requires C, 55·4; H, 6·2%).

7-*Ethylhexahydroindolizine*. The above alcohol (0·6 g.) was treated with an excess of phosphorus pentachloride in small lumps at 0°. The mixture was heated to 100° for 15 min., cooled, treated with glacial acetic acid (9 ml.), and refluxed for 1 hr. Concentrated hydrochloric acid (1·5 ml.) was added, the whole evaporated to dryness, and the residue basified with 50% potassium hydroxide and distilled in a current of steam. Potassium hydroxide (0·5 g.) was added to the distillate (100 ml.), from which ether then extracted 7-*ethylhexahydroindolizine* (0·22 g.), b. p. 73°/0·9 mm. (Found: C, 79·3; H, 11·5. $C_{10}H_{17}N$ requires C, 79·5; H, 11·3%). The *picrolonate* formed deep yellow needles, m. p. 175°, from dilute ethanol (Found: C, 57·4; H, 6·1. $C_{10}H_{17}N,C_{10}H_8N_4O_5$ requires C, 57·8; H, 6·0%), and the *picrate* yellow needles, m. p. 156° (decomp.) from ethanol–dipentyl ether (Found: C, 50·7; H, 5·4. $C_{10}H_{17}N,C_6H_3N_3O_7$ requires C, 50·5; H, 5·3%).

7-*Ethyloctahydroindolizine*. The above base (0·25 g.) and platinum oxide (40 mg.) were shaken in glacial acetic acid (10 ml.) and ethanol (5 ml.) in hydrogen at 100 lb./in.$^2$ for 12 hr. After filtration dilute hydrochloric acid (2 ml.) was added and, after evaporation and basification with 50% potassium hydroxide, ether extracted 7-*ethyloctahydroindolizine* (0·16 g.), b. p. 65°/18 mm. (Found: C, 78·7; H, 12·8. $C_{10}H_{19}N$ requires C, 78·4; H, 12·5%). Its *picrolonate* formed orange needles, m. p. 146°, from ethanol (Found: C, 57·6; H, 6·6. $C_{10}H_{19}N,C_{10}H_8N_4O_5$ requires C, 57·55; H, 6·5%).

8-*Ethyl*-8-*hydroxyindolizine*. A Grignard reagent prepared from magnesium (4 g.), ethyl iodide (24 g.), and ether (25 ml.) was added to octahydro-8-oxoindolizine (Found: C, 69·4; H, 9·2%) (2·1 g.) in ether (10 ml.) at 0°. After being kept overnight at room temperature the mixture was worked up in the same way as for the 7-ethyl compound, giving 8-ethyl-8-hydroxyindolizine (1·1 g.), b. p. 109°/0·8 mm. The *picrate* formed yellow needles, m. p. 192°, from ethanol–dipentyl ether (Found: C, 48·0; H, 5·6. $C_{10}H_{19}NO,C_6H_3N_3O_7$ requires C, 48·1; H, 5·5%), and the *picrolonate* deep yellow needles, m. p. 175°, from ethanol (Found: C, 55·7; H, 6·0. $C_{10}H_{19}NO,C_{10}H_8N_4O_5$ requires C, 55·4; H, 6·2%).

8-*Ethylhexahydroindolizine*, prepared from the above alcohol (0·9 g.) in the same way as the 7-ethyl compound, was a colourless oil (0·21 g.) b. p. 61°/2 mm. (Found: C, 79·5; H, 11·3%). Its *picrolonate* formed orange needles, m. p. 164°, from ethanol (Found: C, 57·3; H, 6·0%).

8-*Ethyloctahydroindolizine* (0·13 g.), b. p. 41°/2 mm., was obtained by catalytic reduction of the above hexahydro-compound (0·18 g.) (Found: C, 78·7; H, 12·9%). Its *picrate* forms yellow needles, m. p. 185°, from ethanol–dipentyl ether (Found: C, 50·2; H, 5·5.

$C_{10}H_{19}N,C_6H_3N_3O_7$ requires C, 50·3; H, 5·8%). The derivatives of perhydrobase B are recorded [1] as follows: picrate, m. p. 147—148°; picrolonate, m. p. 243—244° (decomp.); methiodide, m. p. 263—264°.

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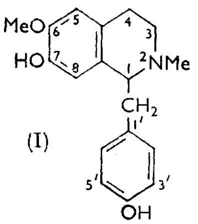
## 470. (—)-N-*Methylcoclaurine from* Phylica rogersii *Pillans.*

### By R. R. Arndt.

An alkaloid, $C_{18}H_{21}NO_3$, has been isolated from *Phylica rogersii* Pillans (family, Rhamnaceae) in two isomorphic forms, m. p. 154—155° and 184—185°. The alkaloid was shown, by chemical degradation and finally by direct comparison with an authentic sample, to be identical with (—)-*N*-methylcoclaurine (I), a sodium–liquid ammonia fission product of bisbenzylisoquinoline alkaloids.[1]

The alkaloid has two phenolic groups (green colour with ferric chloride; $\nu_{max.}$ 3440 cm.$^{-1}$; dimethyl and diacetyl derivatives), and one methoxyl and one *N*-methyl group. The tertiary nature of the nitrogen is evident from the preparation of a methiodide and methopicrate.



(I)

The nuclear magnetic resonance spectrum (in trifluoroacetic acid with tetramethylsilane as internal standard $\delta = 0{\cdot}00$) [2] showed a peak at $\delta = 4{\cdot}00$ (OMe), a doublet ($J = 5$ c./sec.) at $\delta = 3{\cdot}10$, and a quartet ($J = 5$ c./sec.) centred at $\delta = 4{\cdot}78$ due to the system $\geqslant$NMe$^+$H formed in the trifluoroacetic acid. The dimethyl and the diacetyl derivative (in deuterochloroform) showed the *N*-methyl peak at the expected position ($\delta = 2{\cdot}53$).[3]

Zinc-dust distillation gave *p*-cresol, and Hofmann degradation of the fully methylated base afforded a trimethoxyvinylstilbene.[4]

The nuclear magnetic resonance spectrum of the dimethyl derivative of the akaloid showed two single peaks at $\delta = 6{\cdot}60$ and $6{\cdot}03$ of two *para*-protons [positions 5 and 8 in (I)] with no adjacent hydrogen atoms.

The picrate of the quaternary base of the alkaloid was identical with authentic (—)-magnocurarine picrate.[1]

This is the first record of the occurrence of (—)-*N*-methylcoclaurine in a plant.

*Experimental.*—Samples were dried *in vacuo* at 60° for analyses. Samples which still retained solvent of crystallisation under these conditions decomposed when dried at higher temperatures.

*Isolation of* (—)-N-*methylcoclaurine.* Ground, air-dried branches and leaves (40 kg.) of *Phylica rogersii* were soaked with aqueous ammonia and exhaustively extracted with chloroform. The extract was concentrated and shaken with 2% aqueous tartaric acid, the acid solution was made alkaline, and the crude alkaloid (55 g.) was isolated with chloroform. The pH of a solution of the crude product in 5% aqueous sulphuric acid (200 ml.) was adjusted to 8 with sodium carbonate; extraction with chloroform then yielded a crude weakly basic fraction (10·6 g.). The aqueous solution was adjusted to pH 10 and again extracted with chloroform. Concentration of the latter extract yielded crystalline (—)-*N*-methylcoclaurine (26 g., 0·06%) which, when crystallised from aqueous methanol and benzene, had m. p. 154—155° or 184—185°, respectively (both unaltered on sublimation *in vacuo* at 130°), $[\alpha]_D^{21}$ $-96°$ (*c* 0·6 in EtOH), $pK_a$ 8·0 (toluene-*p*-sulphonic acid in 50% EtOH), $\lambda_{max.}$ (in EtOH) 226 and 286 mμ (ε 20,600 and 7100, respectively) or (in 0·20N-KOH–EtOH) $\lambda_{max.}$ 246 and 302 mμ (ε 24,800 and 9540, respectively), $\nu_{max.}$ (in KBr; Perkin-Elmer Infrared Spectrophotomer) 3440 (OH), 1620, 1515 cm.$^{-1}$ (aromatic) [Found: C, 72·1; H, 7·0; N, 4·6; OMe, 10·3; *N*-Me, 4·7%; Equiv., 297

[1] Kidd and Walker, *J.*, 1954, 669.

[2] Djerassi, *J. Org. Chem.*, 1961, **26**, 1192.

[3] Edwards and Handa, *Canad. J. Chem.*, 1961, **39**, 1801.

[4] Marion, Lemay, and Portelance, *J. Org. Chem.*, 1950, **15**, 216.

(non-aqueous acid titration). Calc. for $C_{18}H_{21}NO_3$: C, 72·2; H, 7·1; N, 4·7; OMe, 10·4; *N*-Me, 5·0%; *M*, 299], identical in m. p., mixed m. p., and ultraviolet spectrum with authentic (—)-*N*-methylcoclaurine.

The *hydrochloride* crystallised from methanol–ether as colourless plates, m. p. 252—254° (decomp.) (Found: C, 64·3; H, 6·3; N, 4·4. $C_{18}H_{21}NO_3,HCl$ requires C, 64·5; H, 6·6; N, 4·2%). The *perchlorate*, prepared in the usual manner, crystallised from methanol–ether as colourless needles, m. p. 232—234° (Found: C, 54·25; H, 5·55; N, 3·5; Cl, 9·2. $C_{18}H_{21}NO_3,HClO_4$ requires C, 54·2; H, 5·5; N, 3·5; Cl, 8·9%). The *hydrobromide* crystallised from methanol–ether as colourless plates, m. p. 235—238° (Found: C, 55·4; H, 5·8; N, 3·9. $C_{18}H_{21}NO_3,HBr,0{\cdot}5H_2O$ requires C, 55·5; H, 5·9; N, 3·6%). The *methiodide* was precipitated from a chloroform solution of the alkaloid on addition of an excess of methyl iodide and crystallised from methanol–acetone as colourless needles, m. p. 200—202° (Found: C, 49·7; H, 5·4; N, 3·2. $C_{19}H_{24}NIO_3,H_2O$ requires C, 49·8; H, 5·7; N, 3·1%); the *methopicrate* had m. p. 177—178° (from methanol–ether) (Found: C, 55·5; H, 5·0; N, 9·6. $C_{25}H_{26}N_4O_{10},H_2O$ requires C, 55·4; H, 4·8; N, 10·3%).

The free base (150 mg.) with acetic anhydride and pyridine (2 : 1) gave a syrup (184 mg.) which afforded crystals, m. p. 70—73°, on trituration with ether, but could not be recrystallised; this diacetate had $\nu_{max.}$ (in $CHCl_3$) 1770 and 1200 cm.$^{-1}$ (phenolic acetate). The *hydrochloride* crystallised from methanol–ether as needles, m. p. 133—135° (Found: C, 61·6; H, 6·1. $C_{22}H_{25}NO_5,HCl,0{\cdot}5H_2O$ requires C, 61·6; H, 6·2%).

The alkaloid (500 mg.) in methanol (20 ml.) was treated with ethereal diazomethane (from 5 g. of methylnitrosourea) for 6 days at 0°. The product in chloroform was extracted with 2N-sodium hydroxide, dried ($Na_2SO_4$), and passed through a column of alumina. A crystalline dimethyl derivative (300 mg.) was obtained which could not be recrystallised; it had m. p. 58·5 —61°, $[\alpha]_D^{21}$ —84·0° (*c* 1·36, $CHCl_3$) [lit.,[1] for (—)-*O*-methylarmepavine, m. p. 60—61°, $[\alpha]_D^{21}$ —82·4° (in $CHCl_3$)]. The *hydrochloride*, crystallised from methanol–ether, had m. p. 234—235·5° (Found: C, 65·9; H, 7·3; OMe, 25·3. $C_{20}H_{25}NO_3,HCl$ requires C, 65·9; H, 7·15; 3OMe, 25·6%).

*Zinc-dust distillation of the alkaloid.* The alkaloid (300 mg.) and zinc (8 g.) were heated at 300° under hydrogen for 30 min. The volatile product was dissolved in ether, dried ($Na_2SO_4$), and recovered on evaporation as a light yellow residue (69 mg.). This was chromatographed in the gas phase (2% of SE 30 on Celite at 80°), behaving as *p*-cresol. The 3,5-dinitrobenzoate was identical (m. p., mixed m. p.) with *p*-tolyl 3,5-dinitrobenzoate.

*Hofmann degradation of the* OO-*dimethyl derivative.* The *OO*-dimethyl derivative (688 mg.) was refluxed for 3 hr. with methyl iodide (5 ml.) in methanol (5 ml.). After evaporation, the residue separated from methanol as cream-coloured needles (771 mg.), m. p. 136—137° (sintered at 127°) [lit.,[1] for (—)-*O*-methylarmepavine methiodide, m. p. 136—137°] (Found: C, 51·9; H, 6·0; N, 2·6. Calc. for $C_{21}H_{28}INO_3,H_2O$: C, 51·7; H, 6·2; N, 2·9%).

This methiodide (700 mg.) and sodium hydroxide (2·8 g.) were refluxed in methanol (40 ml.) for 2 hr., the solution was evaporated to dryness, water added, and the product isolated with ether. The methine (367 mg.), on crystallisation from hexane, had m. p. 86° (lit.,[4] for de-*ON*-dimethylarmepavine, m. p. 87°) (Found: C, 73·6; H, 8·0; N, 3·7. Calc. for $C_{21}H_{27}NO_3$: C, 73·9; H, 8·0; N, 4·1%).

The methine (230 mg.) in methanol (10 ml.) was refluxed with methyl iodide (5 ml.) for 80 min. The solution was concentrated, affording crystals (272 mg.) which on recrystallisation from methanol had m. p. 235° (lit.,[4] for de-*ON*-dimethylarmepavine methiodide, m. p. 233—234°) (Found: C, 54·6; H, 6·4; N, 2·7. Calc. for $C_{22}H_{30}NO_3I$: C, 54·7; H, 6·2; N, 2·9%).

That methiodide (220 mg.) was refluxed for 2 hr. in methanol (10 ml.) with sodium hydroxide (1·2 g.). The *N*-trimethyl derivative formed during the reaction was characterised as its picrate. After evaporation, the residue was distributed between water and ether, and the ether extract was washed with 6N-hydrochloric acid and water, and dried (KOH). On evaporation to dryness, an oil (157 mg.) was obtained which crystallised from hexane in colourless needles, m. p. 79°, $\lambda_{max.}$ (in 96% EtOH) 231, 268, and 325 mμ (ε 16,300, 21,150, and 27,600, respectively) (lit.,[4] for 4,4′,5-trimethoxy-2-vinylstilbene, m. p. 79—79·5°) (Found: C, 76·8; H, 6·6; OMe, 30·9. Calc. for $C_{19}H_{20}O_3$: C, 77·0; H, 6·8; 3OMe, 30·9%).

*Conversion of the alkaloid into* (—)-*magnocurarine.* The methiodide of the alkaloid (500 mg.) was converted into the methochloride by refluxing it for 1 hr. in methanol (50 ml.) saturated with hydrogen chloride. On evaporation, a yellow syrup (184 mg.) was obtained which was dissolved in methanol. The solution was adjusted to pH 9 with methanolic potassium hydroxide. The crude product which separated recrystallised from methanol–water, to yield colourless prisms (192 mg.), m. p. 199—200°, $[\alpha]_D^{21}$ $-86°$ ($c$ 1·05, $H_2O$), $\lambda_{max.}$ (in $H_2O$) 224 and 284 mμ (ε 14,450 and 3980, respectively) [lit.,[1,5,6] m. p. 200°, $[\alpha]_D^{29}$ $-91°$, $\lambda_{max.}$ (in $H_2O$) 225 and 282 mμ (ε 13,490 and 4190, respectively)] (Found: C, 65·3; H, 8·0. Calc. for $C_{19}H_{25}NO_4,H_2O$: C, 65·3; H, 7·8%).

The picrate of the quaternary base, crystallised from acetone, had m. p. 183°, identical (m. p., mixed m. p.) with authentic (—)-magnocurarine picrate.

The author thanks Dr. A. Malera (Varian A.G. Zürich) for recording the nuclear magnetic resonance spectra, and Professor Masao Tomita (Kyoto University, Japan) for samples of (—)-*N*-methylcoclaurine and (—)-magnocurarine picrate. The work is supported by Messrs. Smith, Kline, and French, Philadelphia, U.S.A.

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[5] Tomita, Imbushi, and Yomogata, *J. Pharm. Soc. Japan*, 1951 69.
[6] McKenzie and Price, *Austral. J. Chem.*, 1953, **6**, 180.

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# **471.** *The Reactivity of Organophosphorus Compounds. Part XVI.*[1] *Photo-oxidation of Trialkyl Phosphites.*

By J. I. G. CADOGAN, M. CAMERON-WOOD, and W. R. FOSTER.

TRIALKYL phosphites are excellent deoxygenating agents.[2] Thus they reduce, for example, epoxides,[3] diaroyl peroxides,[1] amine *N*-oxides,[4] and *C*-nitroso-compounds [5] to the corresponding olefins, anhydrides, amines, and azenes, respectively, and are themselves converted thereby into the corresponding trialkyl phosphates. Despite the large variety of such reactions, there are few convenient methods for the anhydrous conversion of phosphites into phosphates. Formally, the simplest of such reactions might be expected to be direct oxidation by oxygen and it has indeed been reported that the related dialkyl alkylphosphonites $[R{\cdot}P(OR)_2]$ are converted into the phosphonates by exposure to oxygen,[6] but a thin film of the phosphonite on filter paper inflames in air.[7] Direct oxidation of tri-(1-cyano-1-methylethyl) phosphite [8] is moderately successful but the reaction fails with the simpler triethyl phosphite.[9] Monothiophosphites, $(RO)_2P{\cdot}SR$, on the other hand, react vigorously in air to give unidentified products.[10]

Recently there have been many reports of reactions of trialkyl phosphites with free radicals, which have involved the formation of a quadricovalent phosphoranyl radical in which the phosphorus octet is expanded to nine electrons. It is noteworthy in this connection that triethyl phosphite reacts with smaller amounts of alkyl peroxides in the

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[1] Part XV, Bunyan, Burn, and Cadogan, *J.*, 1963, 1527.
[2] Cadogan, *Quart. Rev.*, 1962, **16**, 208.
[3] Scott, *J. Org. Chem.*, 1957, **22**, 1118.
[4] Ramirez and Aguair, Amer. Chem. Soc., 134th Meeting, 1958, Abs., p. 42N.
[5] Bunyan and Cadogan, *J.*, 1963, 42.
[6] Razumov, Mukhacheva, and Sim-Do-Khan, *Bull. Acad. Sci. U.S.S.R.*, 1952, 797; see also *Chem. Abs.*, 1953, **47**, 10,466.
[7] Arbusov and Rizpolozhenskii, *Doklady Akad. Nauk S.S.S.R.*, 1952, **83**, 581; *Chem. Abs.*, 1953, **47**, 3226.
[8] Kuznetzov and Valetdinov, *Trudy Kazan. Khim. Tekhnol. im S.M. Kirova*, 1956, **21**, 167; *Chem. Abs.*, 1957, **51**, 11,985.
[9] Cox and Westheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5441.
[10] Arbusov and Nikonorov, *Doklady Akad. Nauk S.S.S.R.*, 1948, **62**, 75; *Chem. Abs.*, 1949, **43**, 1004.

presence of air, to give more than an equivalent of triethyl phosphate based on peroxide, a process attributed [11] to autoxidation involving recycling of alkyl radicals:

$$\begin{aligned} &\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{RO{\cdot}O\cdot} \\ &\mathrm{RO{\cdot}O\cdot} + \mathrm{(EtO)_3P} \longrightarrow \mathrm{(EtO)_3\dot{P}O{\cdot}OR} \longrightarrow \mathrm{(EtO)_3PO} + \mathrm{RO\cdot} \\ &\mathrm{RO\cdot} + \mathrm{(EtO)_3P} \longrightarrow \mathrm{(EtO)_3\dot{P}{\cdot}OR} \longrightarrow \mathrm{(EtO)_3PO} + \mathrm{R\cdot}\text{, etc.} \qquad \text{(i)} \end{aligned}$$

In view of this and of similar reactions involving oxygen and phosphorus trichloride,[12] it seemed reasonable to expect that suitable irradiation of a mixture of triethyl phosphite and oxygen or air would lead to the formation of triethyl phosphate. It has now been shown that irradiation of trialkyl phosphites $(RO)_3P$ (where R = Et, $Bu^n$, allyl, $Cl{\cdot}CH_2{\cdot}CH_2$, and $Cl{\cdot}CHMe{\cdot}CH_2$) and of benzyl diethyl phosphite in dry air or oxygen readily gives the corresponding phosphates in quantitative yield. Polymerisation of triallyl phosphite occurred at 253 mμ but oxidation proceeded smoothly at 280 mμ. Triphenyl phosphite was only partially oxidised under the standard conditions of reaction and attempts to sensitise this oxidation by the inclusion of triethyl phosphite were unsuccessful. In view of the wavelength of the radiation used and the fact that one-half of an equivalent of oxygen was absorbed in the reaction, the participation of ozone in the reaction can be excluded.[13] The process probably involves homolysis of otherwise stable unidentified impurities followed by reactions similar to (i). Regardless of mechanistic detail this method appears to be the simplest one-step oxidation of trialkyl phosphites yet recorded.

*Experimental.*—Benzyl diethyl phosphite was prepared as described by Cadogan and Foster.[14] Other phosphites were commercial samples and were purified by distillation.

*Photo-oxidation of phosphites.* The method is illustrated by the following examples:

(i) Dry oxygen was passed through tri-(2-chloropropyl) phosphite (10 ml.) in a silica vessel (200-ml. capacity) which was irradiated (12″) by a 500-w mercury-vapour source (Hanovia U.V. S. 500). The flask was air-cooled so that the temperature of the contents was $<50°$. After 8 hr. infrared analysis indicated that oxidation to tri-(2-chloropropyl) phosphate was complete ($>96\%$).

(ii) Triethyl phosphite was placed in a shallow dish in air and exposed to radiation ($_{\text{min.}}$ 2800 Å; Philips Medicinal lamp; 300 w; $d = 4{\cdot}5''$) for 2·5 hr., giving triethyl phosphate (correct infrared spectrum; $n_D^{24}$ 1·4040). This method is suitable only for small quantities (10 ml.) since larger quantities require longer exposure which in turn leads to hydrolysis.

(iii) Triethyl phosphite (1 mol.) in a silica test-tube attached to a gas-burette containing oxygen, was irradiated with the Hanovia lamp. After 2 hr. 0·465 mol. (93%) of oxygen had been taken up and the product was almost pure triethyl phosphate (infrared spectrum). The reaction was 69% complete after 1 hr. Use of a longer wavelength (2800 Å) resulted in a slower uptake of oxygen in this apparatus (63% after 4 hr.).

(iv) In the apparatus of experiment (iii) and with the longer wavelength (2800 Å), triallyl phosphite was oxidised smoothly to pure triallyl phosphate (97·5%) (correct infrared spectrum). Use of a shorter wavelength (Hanovia lamp) caused an exothermic reaction which gave a black polymer.

(v) Tri-(2-chloroethyl) phosphite, tri-n-butyl phosphite, and benzyl diethyl phosphite were also oxidised to the corresponding phosphates (correct infrared spectra). Triphenyl phosphite was only partially oxidised to the phosphate (*ca.* 5% by infrared spectrum) after prolonged (18 hr.) irradiation with the mercury-vapour source. Oxidation was not sensitised by triethyl phosphite.

The addition of diethyl phosphite (10%) to tri-(2-chloroethyl) phosphite did not increase the rate of oxidation of the latter.

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[11] Walling and Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243.

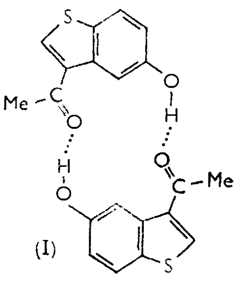
[12] Mayo and Durham, Amer. Chem. Soc. Meeting, Sept. 1961, Abs., p. 41Q.

[13] Cf. Thompson, *J. Amer. Chem. Soc.*, 1961, **83**, 845.

[14] Cadogan and Foster, *J.*, 1961, 3071.

# **472.** *Sixteen-membered Hydrogen-bonded Dimers.*

By Ivor Brown, G. Eglinton, and M. Martin-Smith.


(I)

The existence, in solution, of stable dimers involving 12-membered rings closed by hydrogen bonds is well established, examples being afforded by compounds of the dimedone type [1] and certain steroidal β-diketones.[2] An analogous situation pertains in certain heterocyclic phenols in the solid state [3] and a related instance of ring formation has been postulated to occur intramolecularly in the anticoagulant drug dicoumarol.[4] Recently the first examples of hydrogen-bonded dimer formation involving 14-membered rings were reported for certain *m*-nitrophenols and *m*-methoxycarbonylphenols in solution [5] and we now present infrared evidence to support the existence of dimers (*e.g.*, I) involving 16-membered rings whose association persists at dilutions in carbon tetrachloride and chloroform well below those normally known to permit intermolecular hydrogen-bonding (*ca.* 50mM for phenols).

Dimer formation was initially observed in the case of 3-acetyl-5-hydroxybenzo[*b*]thiophen (I), but it was also seen with the 3-methoxycarbonyl, the 3-cyano-, and to a small extent with the 3-nitro-derivative. The infrared data are given in the Table and for compound (I) in the Figure. In the case of 4-bromo-5-hydroxy-3-nitrobenzo[*b*]thiophen,[6] only the intramolecular OH · · · Br bond is observed at the concentration examined.[7] The dimerisation persists in chloroform although this solvent always tends to reduce the proportion of dimeric species in solution by preferential solvation of the more polar monomer.

Hydroxyl and carbonyl absorptions of 5-hydroxybenzo[*b*]thiophens in $CCl_4$ and $CHCl_3$.

| | Concn. | | Monomer | | Dimer | | | |
|---|---|---|---|---|---|---|---|---|
| Deriv. | (mM) | Solvent | ν(OH) | ν(C=O) | ν(OH) | ν(C=O) | $\frac{\varepsilon(\text{mOH})}{\varepsilon(\text{dOH})}$ | $\frac{\varepsilon(\text{mC=O})}{\varepsilon(\text{dC=O})}$ |
| 3-Ac (I) ............... | <0·24 (S) | $CCl_4$ | 3602 | 1673 | 3295 | 1652 | 3 | 2·5 |
| 3-$CO_2$Me ............ | <0·37 (S) | ,, | 3605 | 1719 | 3395 | 1695 | 12 | 6 |
| 3-CN .................. | <0·275 (S) | ,, | 3602 | — | 3395 | — | 4 | — |
| 3-$NO_2$ .................. | 0·48 | ,, | 3601 | — | 3420 | — | 18 | — |
| 4-Br-3-$NO_2$ ......... | 5·0 | ,, | 3507 | — | — | — | — | — |
| 3-Ac .................. | (S) | $CHCl_3$ | 3596 | 1666 | 3275 | 1650 | 1·5 | 1 |
| ,, .................. | Dil. | ,, | 3598 | 1666 † | 3275 | * | 3 | * |
| 3-$CO_2$Me ........... | (S) | ,, | 3597 | 1712 † | 3390 | * | 6 | * |
| ,, .............. | Dil. | ,, | 3598 | 1712 † | 3390 | * | 18 | * |
| 3-CN .................. | (S) | ,, | 3595 | — | 3380 | — | 6 | — |
| ,, .................. | Dil. | ,, | 3595 | — | 3380 | — | 9 | — |

Values for ν(OH) of the dimer are approximate, to the nearest 5 cm.$^{-1}$. * Not measured. — No band present. † Band has shoulder on low-frequency side. ε(m)/ε(d) = Ratio of apparent extinction coefficients of monomer to that of dimer. (S) = Saturated solution. Dil. = 1 : 4 dilution of saturated solution.

The principal requirement for relatively stable dimer formation must be the presence of suitably disposed acidic and basic centres within the individual molecule and it is to be expected that dimerisation will also occur, for example, in suitable di-terminally-substituted aromatic systems, steroids, triterpenes, and alkaloids. In many such cases, however, bulky substituents projecting from the face of the molecule might be expected to hinder dimerisation. However, even in relatively flexible systems such as the di- and tri-nuclear

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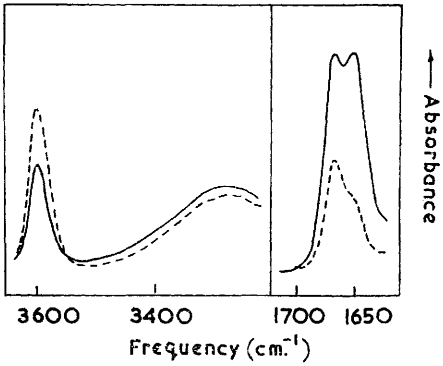
[1] Bellamy and Rogasch, *Proc. Roy. Soc.*, 1960, *A*, **257**, 98.
[2] Tamm and Albrecht, *Helv. Chim. Acta*, 1960, **43**, 769.
[3] Cairns-Smith, *J.*, 1961, 182.
[4] Knobloch and Prochâzka, *Chem. Listy*, 1953, **47**, 1285; *Coll. Czech. Chem. Comm.*, 1954, **19**, 744.
[5] Anet and Muchowski, *Proc. Chem. Soc.*, 1962, 219.
[6] Martin-Smith and Reid, *J.*, 1960, 938.
[7] Brown, Eglinton, and Martin Smith, *Spectrochim. Acta*, 1962, **18**, 1593.

novolaks, the existence of well-defined conformations where dimerisation permits closure of a ring of hydrogen bonds has been demonstrated.[8]

Although the position in polar media such as biological fluids is certainly different from that in organic solvents the recognition of the existence of 14- and 16-membered hydrogen-bonded dimers in the latter make it conceivable that similar macrocyclic hydrogen-bonded rings between drug molecules and tissue proteins play a hitherto unsuspected role in drug action.

*Experimental.*—Spectra were measured with a Unicam S.P. 100 double-beam spectrophotometer equipped with an S.P. 130 sodium chloride prism-grating double monochromator operated under vacuum-conditions by the general procedure described previously.[9] Carbon tetrachloride ("AnalaR") was used without purification. Chloroform ("AnalaR") was freed from ethanol by two successive passages through blue silica gel immediately before use.



Hydroxyl and carbonyl absorptions of 3-acetyl-5-hydroxybenzo[*b*]thiophen (I) in $CHCl_3$.

—— saturated solution; - - - - 1 : 4 dilution of saturated solution.

5-Hydroxy-3-nitrobenzo[*b*]thiophen was prepared as previously described.[6] The preparation of the other compounds will be described elsewhere.

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[*Received, October 11th*, 1962.]

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[8] Cairns and Eglinton, *Nature*, 1962, **196**, 535.

[9] Bellamy, Eglinton, and Morman, *J.*, 1961, 4762.

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## 473. *Square-planar Bisethylenediamine–Metal Complexes.*

By A. B. P. Lever, J. Lewis, and R. S. Nyholm.

As part of our studies of the chemistry of nickel, we noted the report [1-4] that nickel forms certain diamagnetic amine complexes, *e.g.*, the bisethylenediamine complex, Ni $en_2(AgIBr)_2$, whereas with these ligands nickel generally forms octahedral and paramagnetic derivatives. We set out to investigate the structure of this cation and to see whether the stereochemistry of the anion was a critical factor in determining this.

The complex, Ni $en_2(AgI_2)_2$, and the corresponding palladium and platinum complexes have now been prepared and shown to be isomorphous with it. Since there can be little doubt of the square-planarity of the cations of the palladium and platinum derivatives,

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[1] Harris, *J. Roy. Soc. N.S.W.*, 1951, **85**, 142.

[2] Harris and Schafer, *J. Roy. Soc. N.S.W.*, 1951, **85**, 147.

[3] Spacu and Spacu, *Bull. Soc. Stiinte Cluj.*, 1931, **5**, 387, 473; *Z. analyt. Chem.*, 1932, **90**, 182.

[4] Nyholm, *Chem. Rev.*, 1953, **53**, 263; Ballhausen and Jørgensen, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1955, **29**, No. 14.

it is evident that the nickel complex is also square-planar. A series of diamagnetic compounds with other linear anions, of the type Ni $en_2X_2$, where X = $CuI_2^-$, $AgI_2^-$, $AuI_2^-$, and $I_3^-$ has been prepared. The diffuse reflectance spectra (see Table 1) and infrared spectra (see Table 2) of these complexes are essentially independent of the anion, indicating that the conformation of the ethylenediamine is similar in all cases. A corresponding bisethylenediaminecopper(II) complex, first prepared by Harris,[1] has an *X*-ray powder pattern closely similar to the patterns given by this series and is evidently isostructural with them. The magnetic moment of this cupric complex (see Table 1) is normal, which suggests that the cations are not stacked on top of one another but are held apart, perhaps in the manner found [5] for $Cs_2(AuCl_2)(AuCl_4)$.

TABLE 1.

| Complex | Colour | $\mu_{eff.}$ (293°K) | Diffuse reflectance spectra $\lambda_{max.}$ (mμ) | Complex | Colour | $\mu_{eff}$ (293°K) | Diffuse reflectance spectra $\lambda_{max.}$ (mμ) |
|---|---|---|---|---|---|---|---|
| * Ni $en_2(AgI_2)_2$ | Pink | 0 | 462 | * Pt $en_2(AgI_2)_2$ | White | 0 | |
| * Ni $en_2(CuI_2)_2$ | Orange | 0 | 466 | † Cu $en_2(AgI_2)_2$ | Violet | 1·88 | 517, 540 |
| * Ni $en_2(AuI_2)_2$ | Orange | 0 | 462 | Ni $en_2(HgI_4)$ | Pink | 0 | 472 |
| Ni $en_2(I_3)_2$ | Black | 0 | | ‡ Ni $en_2(PbI_3)_2$ | Bright red | 0 | 380, 450sh, 545 |
| † Co $en_2(AgI_2)_2$ | Pink | 2·46 | 440sh | ‡ Cu $en_2(PbI_3)_2$ | Bright red | 1·91 | 380, 460sh, 545 |
| * Pd $en_2(AgI_2)_2$ | Lemon | 0 | | | | | |

*†‡ Isomorphous groups.

TABLE 2.

Infrared absorption frequencies ($cm.^{-1}$) (in Nujol).

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ni $en_2(AgI_2)_2$ | | 1570s | 1304w | 1281w | 1260m | 1205s | 1106s | 1090w |
| Ni $en_2(CuI_2)_2$ | | 1560s | 1300w | 1276w | 1256w | 1205s | 1106s | 1083w |
| Ni $en_2(AuI_2)_2$ | | 1560s | 1300w | 1276w | 1256w | 1193m | 1101s | 1086w |
| Ni $en_2HgI_4$ | | 1560s | 1311m | 1281w | 1260w | 1206s | 1106s | 1091w |
| Ni $en_2(I_3)_2$ | | 1560s | 1312w | 1278w | — | 1200m | 1111s | — |
| Ni $en_2(PbI_3)_2$ | 1575m | 1565s | 1302w | 1278w | — | 1196m | 1111s | 1091w |
| Pd $en_2(AgI_2)_2$ | | 1563s | 1304m | 1281m | 1256m | 1188s | 1106s | 1082w |
| Pt $en_2(AgI_2)_2$ | | 1563s | 1304m | 1288m | 1256m | — | 1136s | 1099m |
| Co $en_2(AgI_2)_2$ | | 1582s | 1309w | 1282m | 1266s | 1192s | 1099s | 1082w |
| Cu $en_2(AgI_2)_2$ | | 1568s | 1309w | 1274w | 1256m | 1171s | 1085s | 1072w |
| Cu $en_2(PbI_3)_2$ | 1575w | 1563s | 1309m | 1273w | — | 1156s | 1116w | 1088m |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni $en_2(AgI_2)_2$ | 1048s | 1000m | 984m | 891w | 740s | 722w | |
| Ni $en_2(CuI_2)_2$ | 1046s | 1000m | 982s | 893m | 743s | 722w | |
| Ni $en_2(AuI_2)_2$ | 1046s | 996m | 979s | 886m | 739s | 722w | |
| Ni $en_2HgI_4$ | 1048s | 1000m | 984m | 890w | 740s | 722w | |
| Ni $en_2(I_3)_2$ | 1054s | 1007w | 990w | — | 740s | 722m | |
| Ni $en_2(PbI_3)_2$ | 1054s | 1001w | 980w | — | 738s | 723s | |
| Pd $en_2(AgI_2)_2$ | 1052s | — | 989s | 892w | 752s | 722w | |
| Pt $en_2(AgI_2)_2$ | 1047s | 1000s | 989w | 893m | 789s | 723s | |
| Co $en_2(AgI_2)_2$ | 1042s | 999s | 975s | 885w | 728s | — | |
| Cu $en_2(AgI_2)_2$ | 1041s | 1005m | 976s | — | — | 722m | 689s |
| Cu $en_2(PbI_3)_2$ | 1042s | 1005w | 970w | 890w | 740m | 727s | 682s |

Cobalt(II) forms similar, presumably square-planar, complexes. The compound, Co $en_2(AgI_2)_2$, is isomorphous with the copper derivative and has a magnetic moment typical of low-spin square-planar cobalt.[6]

Irrespective of the stereochemistry of the anion, one expects that with copper and ethylenediamine one will obtain a square-planar cation. With nickel we were able to obtain square-planar complexes with non-linear anions such as the presumably pyramidal $PbI_3^-$ and the tetrahedral $HgI_4^{2-}$. In the same experimental conditions, *i.e.*, a deficiency of ethylenediamine, cobalt invariably gave a trisethylenediamine complex with these non-linear anions.

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[5] Elliott and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 1846.

[6] Figgis and Nyholm, *J.*, 1954, 12.

The complex, Ni en$_2$(HgI$_4$), has a diffuse reflectance spectrum showing its similarity to the series with linear anions, but the intensely coloured tri-iodoplumbate(II) complex is different. The visible spectrum of this is virtually identical with that of the corresponding copper compound, Cu en$_2$(PbI$_3$)$_2$, both compounds being bright red, whereas the pyridinium tri-iodoplumbate(II) is pale yellow.[2] It is possible that the intense colour arises from the presence of nickel–lead and copper–lead bonds, respectively.

No corresponding complexes could be obtained with chloride or bromide anions and it seems likely that the high polarisability of the iodide atoms, present in all the complexes described, is an important factor.

In support of this view, the visible spectra of all the nickel complexes, with the exception of the tri-iodide and tri-iodoplumbate(II), are similar to that [7] of the diamagnetic Ni(Diarsine)$_2$I$_2$ where a tetragonal distortion [8] is believed to be present.

With cobalt and nickel, ethylenediamine does not readily form square-planar complexes in solution, so that we must regard these tetragonal complexes as examples of lattice stabilisation of otherwise unknown complex cations. As may be expected, therefore, heating these materials with solvents, particularly water, usually results in decomposition.

We conclude that a lattice favourable for formation of a square-planar cation is produced when the anion is linear and/or highly polarisable and that the complexes so formed are probably tetragonal. Elements which readily form square complexes such as copper(II) and nickel(II) will form tetragonal lattices with heavy polarisable non-linear anions, but those elements which rarely form square-planar complexes, such as cobalt(II), are no longer stabilised in this form.

*Experimental.*—*Bisethylenediaminenickel*(II) *bisdi-iodoargentate*(I). Ethylenediamine (0·51 g., 1 mol.) was added to an aqueous solution of nickel acetate (1·5 g., 1 mol., in 50 ml. of water). This solution was added, with stirring, to silver nitrate (2·9 g., 2 mol.) dissolved in an excess of lithium iodide solution (5 g. in 25 ml.). The pale red *salt* that was precipitated was washed with aqueous lithium iodide and water and dried in a desiccator (Found: C, 5·5; H, 1·9; Ag, 23·7; N, 6·1; Ni, 6·1. $C_4H_{16}Ag_2I_4N_4Ni$ requires C, 5·3; H, 1·8; Ag, 23·9; N, 6·2; Ni, 6·5%).

The following complexes were prepared by the same general method—a stoicheiometric ratio of metal acetate (or chloride) : ethylenediamine : anion of 1 : 1 : 2. A deficiency of ethylenediamine was used to minimise the formation of trisethylenediamine cations.

*Bisethylenediaminenickel*(II) *bisdi-iodocuprate*(I) (the anion solution was prepared by dissolving the calculated amount of cuprous iodide in lithium iodide solution) (Found: C, 6·2; H, 2·2. $C_4H_{16}Cu_2I_4N_4Ni$ requires C, 5·9; H, 2·0%).

*Bisethylenediaminenickel*(II) *bisdi-iodoaurate*(I) (the anion solution was prepared by reducing chloroauric acid with sulphur dioxide in the presence of an excess of potassium iodide) (Found: C, 4·4; H, 1·4. $C_4H_{16}Au_2I_4N_4Ni$ requires C, 4·4; H, 1·5%).

*Bisethylenediaminenickel*(II) *bistri-iodide* (the anion solution was prepared by addition of iodine to potassium iodide solution) (Found: C, 5·5; H, 1·8; N, 6·1; Ni, 6·1. $C_4H_{16}I_6N_4Ni$ requires C, 5·1; H, 1·7; N, 6·0; Ni, 6·3%).

*Bisethylenediaminenickel*(II) *bistri-iodoplumbate*(II) (Found: C, 3·8; H, 1·4; Ni, 4·1; Pb, 30·1. $C_4H_{16}I_6N_4NiPb_2$ requires C, 3·5; H, 1·2; Ni, 4·3; Pb, 30·5%).

*Bisethylenediaminenickel*(II) *tetraiodomercurate*(II) (Found: C, 5·9; H, 2·1; Hg, 22·8. $C_4H_{16}HgI_4N_4Ni$ requires C, 5·4; H, 1·8; Hg, 22·6%).

*Bisethylenediaminepalladium*(II) *bisdi-iodoargentate*(I) [a hot solution of potassium chloropalladite(II) and ethylenediamine was employed] (Found: C, 5·2; H, 1·8; Ag, 22·8; N, 5·8. $C_4H_{16}Ag_2I_4N_4Pd$ requires C, 5·1; H, 1·7; Ag, 22·7; N, 5·9%).

*Bisethylenediamineplatinum*(II) *bisdi-iodoargentate*(I) [a hot solution of potassium chloroplatinite(II) and ethylenediamine was employed] (Found: C, 4·5; H, 1·7; Ag, 20·9. $C_4H_{16}Ag_2I_4N_4Pt$ requires C, 4·6; H, 1·5; Ag, 20·8%).

*Bisethylenediaminecobalt*(II) *bisdi-iodoargentate*(I) [the reaction was carried out in an inert

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[7] Nyholm, *J.*, 1950, 2061; Harris, Nyholm, and Phillips, *J.*, 1960, 4379.

[8] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

atmosphere (nitrogen) with out-gassed solutions] (Found: C, 5·7; H, 1·9; N, 6·1. $C_4H_{16}Ag_2CoI_4N_4$ requires C, 5·3; H, 1·8; N, 6·2%).

Bisethylenediaminecopper(II) bisdi-iodoargentate(I) (cf. ref. 3) (Found: C, 5·6; H, 1·9; N, 6·3. Calc. for $C_4H_{16}Ag_2CuI_4N_4$: C, 5·3; H, 1·8; N, 6·2%).

*Bisethylenediaminecopper*(II) *bistri-iodoplumbate*(II) (Found: Cu, 4·8; Pb, 30·3. $C_4H_{16}CuI_6N_4Pb_2$ requires Cu, 4·7; Pb, 30·4%).

We are indebted to the Wyandotte Chemical Corporation, Michigan, U.S.A., for financial assistance.

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## **474.** *The Reaction of Disulphur Dichloride with Ammonia in Dimethylformamide.*

By P. Tavs, H-J. Schulze-Steinen, and J. E. Colchester.

Heptasulphur imide, $S_7NH$, and hexasulphur di-imide, $S_6(NH)_2$, have been found[1,2] among the reaction products of disulphur dichloride, $S_2Cl_2$, with ammonia in dimethylformamide at low temperatures. Both imides are analogous to $S_8$, and consist of eight-membered rings in which one or two sulphur atoms are replaced by NH groups.

We have isolated heptasulphur imide and three hexasulphur di-imides from the products of this reaction by repeated chromatography on aluminium oxide (see Table).

|  | M. p.* | Approx. yield (%) based on $S_2Cl_2$ | $R_F$ † in 49 : 1 $C_6H_6$–EtAc | $R_F$ † in 1 : 1 v/v $CCl_4$–Hexane |
|---|---|---|---|---|
| $S_6N_2H_2$, I | 129—130° | 1·5 | 0·92 | 0·34 |
| $S_6N_2H_2$, II | 152—154 | 0·1 | 0·76 | 0·07 |
| $S_6N_2H_2$, III | 122—124 | 0·1 | 0·68 | 0·07 |
| $S_7NH$ | 113 | 19 | 0·96 | 0·54 |

* Determined on a Kofler hot-stage microscope. † On Merck aluminium oxide for thin-layer chromatography. In both solvent mixtures sulphur moves with the solvent front.

The three isomers are colourless and crystalline. Their infrared absorption spectra are similar to that of heptasulphur imide. Isomers II and III show a split NH band (KCl pellet).

The isomers I, II, and III represent probably the 1,5-, 1,4-, and 1,3-hexasulphur di-imide, respectively. However, this requires confirmation by *X*-ray diffraction analysis.

*Experimental.*—Column-chromatographic procedures were checked by thin-layer chromatography. Spraying with aqueous silver nitrate solution developed black or brown spots instantaneously.

*Materials.* Commercial alumina (Peter Spence Ltd., type H, 100—200 mesh) was stirred in 5% aqueous phosphoric acid (pH 2), dried, and activated for 48 hr. at 150°. Commercial silica gel (Silica Gel Ltd., 100—200 mesh) was activated for 24 hr. at 150°.

The reaction was carried out as described by Becke-Goehring *et al.*[1]. Dimethylformamide (19 l.) was cooled to $-10°$ and saturated with ammonia. Disulphur dichloride (1·9 l.) was added in 20 ml. portions during 4 hr. The crude solid product (1075 g.) was extracted with ether ($6 \times 2$ l.). The residue (545 g.) was sulphur. The residue (535 g.) obtained on evaporation of the ether was chromatographed in a column ($8 \times 350$ cm.) containing silica gel (8 kg.). Hexane eluted sulphur (85 g.) and heptasulphur imide (305 g.); carbon tetrachloride eluted hexasulphur di-imide I (19 g.), then a mixture (23 g.) of I, II, and III, and finally 9 : 1 carbon tetrachloride–methylene dichloride eluted a mixture (8 g.) of II and III. Isomers II and III

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[1] Becke-Goehring, Jenne, and Fluck, *Chem. Ber.*, 1958, **91**, 1947.

[2] Weiss, *Angew. Chem.*, 1959, **71**, 246; *Z. anorg. Chem.*, 1960, **305**, 190.

were separated by chromatography on an alumina column (4 × 200 cm.) (ratio of $Al_2O_3$ to product 300 : 1), benzene and 99·5 : 0·5 benzene–ethyl acetate being used as eluents.

Thus were obtained heptasulphur imide (305 g.) and *hexasulphur di-imide* I (29 g.) [Found: S, 85·9; N, 12·5; active H, 0·9%; *M* (ebullioscopic in PhCl), 235. $H_2N_2S_6$ requires C, 86·5; N, 12·6; H, 0·9%; *M*, 222], II (4·9 g.) (Found: S, 86·9; N, 12·2; H, 0·9%; *M*, 251), and III (5·1 g.) (Found: S, 85·5; N, 12·6; H, 0·9%; *M*, 227).

We acknowledge the interest of Dr. R. A. Shaw, Birkbeck College, London, in this work.

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# 475. *The Use of Density Measurements to Follow the Thermal Decomposition of Cobalt Oxalate.*

By N. ARMSTRONG, P. CAMPION, J. L. DAWSON, D. DOLLIMORE, and C. E. WOOD.

DOLLIMORE and NICHOLSON [1] have shown that in the thermal decomposition of a number of oxalates to oxide in air, the resultant solid residue has a maximum surface area at a particular temperature. This was due to an increase in the number of particles, with a decrease in particle radius and an increase in their surface area.

The equation, $V_1/V_2 = (S_1/S_2)^{1 \cdot 5} n^{0 \cdot 5}$, should describe the process, where $n$ is the number of product particles formed from a single particle of original oxalate, $V_1$ is the molar volume of the oxalate, $V_2$ is the volume of an equivalent amount of the oxide, $S_1$ is the surface area of the oxalate, and $S_2$ is the surface area of the oxide (both the surface areas being quoted per g. of oxide). This equation could be applied in the above form only to give the value of $n$ for conversion of the anhydrous oxalate into the oxide. To use the equation over the whole range of decomposition, the term $V_2$ must be redefined as the equivalent volume of partially decomposed material. Now $V_1 = M_1/\rho_1$ where $M_1$ is the molecular weight of the oxalate and $\rho_1$ its density. Similarly $V_2 = M_2/\rho_2$, where $M_2$ is the effective molecular weight of the partially decomposed material which is a mixture of oxalate (mol. wt. $M_1$) and oxide (mol. wt. $M_0$), and $\rho_2$ is the density of the solid residue. If the fraction decomposed is $\alpha$, then $M_2 = (1 - \alpha)M_1 + \alpha M_0$. In this investigation the above equations are used to give $n$, both during the decomposition and in the subsequent sintering of the oxide produced by the thermal decomposition in air of cobalt oxalate dihydrate.

*Experimental.*—The samples studied in this investigation were all outgassed at 25° to a pressure of $< 10^{-4}$ mm. Hg before the density determinations. Carbon tetrachloride was used as the displacement fluid in the density determinations. A specific gravity bottle with a B10 joint was used so that the sample could be degassed *in situ*. The apparatus was so arranged that the carbon tetrachloride could be run into the specific gravity bottle while the sample was still under a vacuum.

The density of the cobalt oxalate dihydrate was found to be 2·3 g./c.c. The density of the anhydrous cobalt oxalate prepared by heating it at 190° for 90 mins. was 2·81; a sample of the oxide ($Co_3O_4$) prepared by heating the cobalt oxalate dihydrate for 15 hr. between 200° and 250° had a density of 5·67 g./c.c. To study the thermal decomposition of cobalt oxalate the dihydrate was heated for 30 min. at various temperatures; the density results are shown in the Figure. It will be seen that the density changes record the decomposition from the cobalt oxalate dihydrate, through the anhydrous salt, to the final oxide ($Co_3O_4$). The density of this oxide

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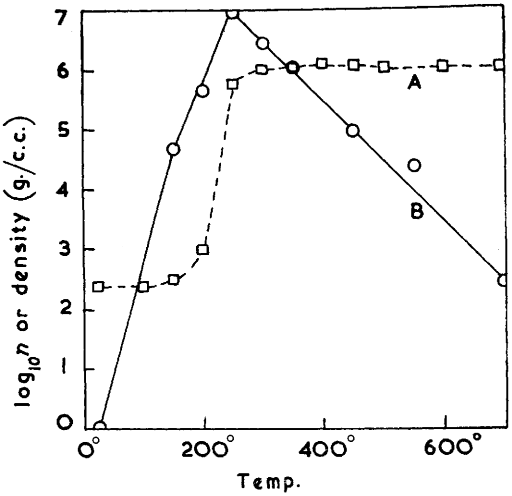
[1] Dollimore and Nicholson, *J.*, 1962, 960.

increased progressively from samples heated at 250° to 1300°, and samples heated at temperatures beyond 400° showed densities higher than that quoted in the literature.[2] Thus the oxide prepared at 350° had a density of 6·03 g./c.c. which had increased linearly to 6·25 g./c.c. for a sample heated at 1300°. The surface area and weight loss of these heat-treated samples of cobalt oxalate have been recorded elsewhere [1] and may be used with the density values to show the variation in *n* as given by the above equations (Figure).



Variation of (A) density and (B) no. of particles, *n*, with temperature of heating, for cobalt oxalate.

*Discussion.*—The values of *n* in the Figure are higher than the single value previously reported [1] because the reaction was previously followed from the anhydrous oxalate to the oxide, whilst in the Figure the values refer to the complete reaction, starting with the dihydrate and ending with the sintered oxide. Previously the density values used were those quoted in the literature,[2] but in the Figure we were able to use experimental values of the density recorded, and this also made a significant contribution to the difference in the value of *n* noted above. In the earlier paper [1] it was pointed out that the average number of micelles formed from each crystallite of starting material should increase as the difference in specific volume increases. The results for samples heated above 300° are affected by sintering but below this temperature this prediction seems to hold. The Figure shows that the greatest number of product particles are formed at the temperature which just produces a change in density values from those associated with salts (between 2 and 3) to those associated with oxides (above 5). The sintering obeys a log law, *viz.*, $\log n = kT + c$ ($k$ and $c$ are constants and $T$ the temperature). It is not known if this is characteristic of other oxide systems on sintering, but Dollimore and Nicholson [1] observed a logarithmic relation between the surface area and temperature of treatment of various sintered oxides. A more detailed study of the density changes accompanying the thermal decomposition of metal oxalates will be presented later.

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[*Received, October 29th,* 1962.]

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[2] " Handbook of Chemistry and Physics," Chemical Publ. Co., 39th edn., 1957—58, p. 518.

# 476. *The Formation of an Alkyl Fluoride from Silicon Tetrafluoride.*

By K. G. Mason, J. A. Sperry, and E. S. Stern.

The few known organic reactions of silicon tetrafluoride involve either the elimination of the fluorine as anionic fluoride and up-grading of the silicon present into alkyl- or alkoxy-silanes [1,2] or complex formation, *e.g.*, with ethylenediamine,[3] ethylene oxide,[4] or dimethylformamide,[5] when subsequent decomposition of the complex may lead to further reaction in which the silicon tetrafluoride does not participate directly.

Silicon tetrafluoride is an abundant by-product of fertiliser manufacture and may therefore be a suitable starting material for the preparation of organic fluorides. We here report the preparation of ethyl fluoride from silicon tetrafluoride and ethyl orthoformate, a reaction which not only appears to be the first transfer of fluorine from silicon tetrafluoride into an organic molecule, but also provides a relatively convenient preparation of ethyl fluoride. Under suitable conditions about 0·9 mole of ethyl fluoride was obtained per mole of orthoformate.

The reaction proceeded exothermically in presence of aluminium chloride as catalyst; other compounds with catalytic activity were aluminium trifluoride, boron trifluoride (etherate), stannic chloride, and titanium tetrachloride. Of these, stannic chloride appeared to be the most active, and also the one to produce most diethyl ether. Cobaltous fluoride had little or no catalytic activity. In the absence of catalyst no ethyl fluoride was formed and the starting materials were unchanged.

Besides ethyl fluoride, the reaction products were ethyl formate and ether (separable by fractional distillation) and silicon-containing materials which were readily removed by washing with water. The organic reaction products were identified and analysed by gas chromatography, the identifications being confirmed by infrared spectrophotometry.

Attempts to extend the reaction to alkoxy- and other polyalkoxy-compounds, *e.g.*, to ether, acetal, butyraldehyde or benzaldehyde diethyl acetal, or diethyl carbonate were unsuccessful, no low-boiling gaseous products being evolved.

*Experimental.*—*Preparation of ethyl fluoride from ethyl orthoformate.* In a typical experiment, gaseous silicon tetrafluoride was slowly passed into a boiling solution of anhydrous aluminium chloride (2 g.) in ethyl orthoformate (100 g.). The outgoing gas passed through a water

Effect of various catalysts (2 g.) in ethyl chloroformate (100 g.).

| | | Products | | |
|---|---|---|---|---|
| Catalyst | Reaction rate | Ethyl fluoride (1 equiv. = 26 g.) | Diethyl ether (1 equiv. = 50 g.) | Ethyl formate (1 equiv. = 50 g.) |
| $SnCl_4$ | Fast | 6 g. | 35 g. | 31 g. |
| $TiCl_4$ | Moderate | 16 g. | 20 g. | 25 g. |
| $AlF_3$ * | Moderate | 1 g. | Nil | *ca.* 40 g. |
| $BF_3$ (etherate) | Moderate | 15 g. | *ca.* 15 g. | *ca.* 40 g. |
| $AlCl_3$ | Moderate | 23 g. | 9 g. | 29 g. |
| $CoF_2$ | No reaction | — | — | — |

* A further (unidentified) product was obtained.

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[1] Cf. Medoks and Soshentsveskaya, *Zhur. obshchei Khim.*, 1956, **26**, 116, 3310.

[2] Kali-Chemie A.G., B.P. 756,612, D.R.P. 946,893.

[3] Schumb and Cook, *J. Amer. Chem. Soc.*, 1953, **75**, 5133.

[4] Schmeisser and Jenkner, *Z. Naturforsch.*, 1952, **7**b, 583.

[5] Piper and Rochow, *J. Amer. Chem. Soc.*, 1954, **76**, 4318.

condenser, a water-scrubber, a drying tower ($CaCl_2$), and a cold trap (acetone–$CO_2$) to the atmosphere.

In the course (24 hr.) of the experiment, material (25 g.) collected in the cold trap and the boiling point of the reaction mixture fell. The lower-boiling material (39 g.) was therefore continuously removed at a point before the water condenser. Silica was precipitated in the water-scrubber (but the aqueous solution was not examined). Fractional distillation of the low-boiling material collected gave diethyl ether (9 g.), b. p. 35—36°, and ethyl formate (29 g.), b. p. 52—54°; the material in the cold trap gave pure ethyl fluoride (23 g.), b. p. −30 to −40°, and the reaction flask contained some high-boiling residue.

When other catalysts were examined the relative proportions of the reaction product varied as indicated in the Table.

The authors are grateful to Mr. A. P. Lowes for his interest and encouragement.

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Loughborough, Leicestershire.

[*Received, October* 30*th*, 1962.]

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## 477. *A Novel Oxidation of Triethyl Phosphite.*

By P. C. Crofts and I. M. Downie.

Triethyl phosphite is known to react with an excess of carbon tetrachloride under reflux, to give diethyl trichloromethylphosphonate in high yield.[1] The temperature at which this occurs is lower than that usually necessary for Arbusov reactions, although carbon tetrachloride would not be expected to be susceptible to the bimolecular nucleophilic attack which is apparently involved in most of these.[2]

Kamai and Kharrasova[3] suggested that the reaction of triethyl phosphite with carbon tetrachloride proceeded by a radical-chain mechanism. Evidence in support of this was provided by Griffin[4] and by Cadogan and Foster,[5] who showed that trichloromethyl radicals rather than ethyl radicals are involved:

$$(EtO)_3P + \cdot CCl_3 \longrightarrow (EtO)_3\overset{\bullet}{P}\cdot CCl_3 \ (I)$$

$$(I) + CCl_4 \longrightarrow [(EtO)_3P\cdot CCl_3]^+Cl^- \ (II) + \cdot CCl_3$$

the quasi-phosphonium cation (II) then breaks down by nucleophilic attack of chloride ion on one of the ethyl groups, as in the second stage of a normal Arbusov reaction:

$$(II) + Cl^- \longrightarrow (EtO)_2P(O)\cdot CCl_3 + EtCl$$

We attempted to prepare diethyl tribromomethylphosphonate from triethyl phosphite and carbon tetrabromide. The reaction was violent at room temperature in the absence of a solvent but in light petroleum at −20° a white suspension was formed which decomposed to give a clear yellow solution above room temperature. Although no products were identified it appeared possible that the quasi-phosphonium intermediate analogous to (II) had been formed and that it might undergo the usual type of breakdown in a more polar solvent, such as ethanol. Reaction in ethanol at −20° gave a white suspension, as before, but this dissolved completely on slight warming, giving an almost

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[1] Kamai and Egorova, *Zhur. obshchei Khim.*, 1946, **16**, 1521; Kosolapoff, *J. Amer. Chem. Soc.* 1947, **69**, 1002.

[2] Crofts, *Quart. Rev.*, 1958, **12**, 347.

[3] Kamai and Kharrasova, *Zhur. obshchei Khim.*, 1957, **27**, 953.

[4] Griffin, *Chem. and Ind.*, 1958, 415.

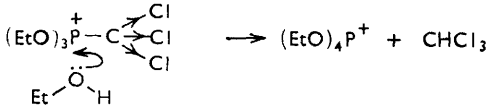
[5] Cadogan and Foster, *J.*, 1961, 3071.

colourless solution from which bromoform and triethyl phosphate were isolated by distillation. These products had apparently been formed by the reaction (Hal = Br):

$$(EtO)_3P + CHal_4 + EtOH \longrightarrow (EtO)_3PO + CHHal_3 + EtHal$$

A similar reaction (Hal = Cl) was found when a mixture of triethyl phosphite, carbon tetrachloride and ethanol was refluxed and gave high yields of triethyl phosphate and chloroform.

Diethyl trichloromethylphosphonate was recovered unchanged after being boiled in ethanol for four hours. The oxidation therefore apparently involves reaction of ethanol either with the phosphoranyl radical (I) or with the quasi-phosphonium cation (II). The latter appears more probable since the low electron density in the carbon–phosphorus



$$(III) + Cl^- \longrightarrow (EtO)_3PO + EtCl$$

bond would make it susceptible to nucleophilic attack, the second quasi-phosphonium cation (III) then undergoing normal Arbusov-type breakdown to give triethyl phosphate and ethyl chloride.

*Experimental.—Reaction of triethyl phosphite with carbon tetrabromide.* (*a*) Triethyl phosphite (16·6 g.) in light petroleum (50 ml.; b. p. 40—60°) was added dropwise with stirring to carbon tetrabromide (33·2 g.) in light petroleum (200 ml.) at −20°. A white suspension was formed without evolution of heat. When the mixture was warmed to 40° the solid dissolved, giving a clear yellow solution which formed two liquid layers on cooling to −30°. The light petroleum was distilled off and the residue (37·6 g.) was distilled under reduced pressure, giving carbon tetrabromide (11·6 g.) and a series of liquid fractions (total 14·3 g.), b. p. 40—105°/0·1 mm., $n_D^{25}$ 1·5280 to 1·4140. The residue weighed 6·4 g.

(*b*) Triethyl phosphite (16·6 g.) in dry ethanol (50 ml.) was added dropwise with stirring to carbon tetrabromide (33·2 g.) in dry ethanol (200 ml.) at −20°. A white suspension was formed; at −10° this dissolved, giving a clear, almost colourless solution. The ethanol was distilled off and the residue (38·0 g.) was distilled, giving bromoform (8·0 g.), b. p. 42—49°/12 mm. (Found, after redistillation: Br, 94·5. Calc. for $CHBr_3$: Br, 94·9%), and a series of liquid fractions (total 19·6 g.), b. p. 43—57°/0·02 mm., from which triethyl phosphate, $n_D^{25}$ 1·4048, was obtained by fractional distillation.

*Reaction of triethyl phosphite with carbon tetrachloride and ethanol.* Triethyl phosphite (33·2 g.), carbon tetrachloride (30·8 g.), and ethanol (9·2 g.) were boiled together under reflux for 6 hr. After cooling, the mixture was shaken with calcium chloride to remove ethanol, filtered, and distilled, giving chloroform (16·6 g., 70%), b. p. 60—61·5°, $n_D^{20}$ 1·4445, and triethyl phosphate (26·5 g., 73%), b. p. 94—102°/15 mm., $n_D^{20}$ 1·4061.

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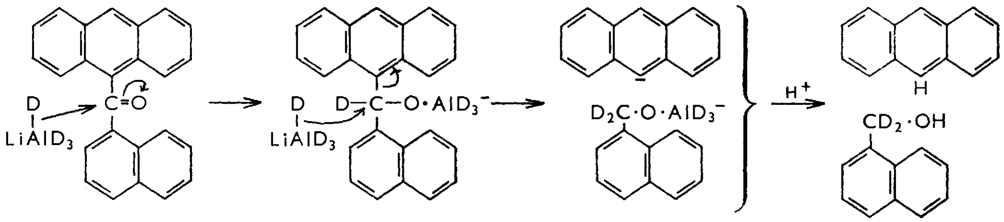
[*Received, October* 31*st*, 1962.]

# 478. *Mechanism of Carbon–Carbon Cleavage in the Reduction of 9-1′-Naphthoylanthracene by Lithium Aluminium Hydride.*

By R. Bar-Shai and David Ginsburg.

Rona and Feldman [1] have shown that reduction of 9-benzoylanthracene and of 9-1′-naphthoylanthracene with lithium aluminium hydride affords 9-benzyl- and 9-1′-naphthylmethyl-anthracene, respectively. However, in each case, hydrogenolysis is accompanied by another reaction involving cleavage of a carbon–carbon single bond: anthracene is formed in each case, accompanied by benzyl alcohol and 1-naphthylmethanol, respectively.

Lansbury [2] has shown that tetra-arylpinacolones are similarly cleaved by lithium aluminium hydride in pyridine, to give triarylmethanes and benzyl alcohols. Several additional examples of such cleavages have been reported.[3]

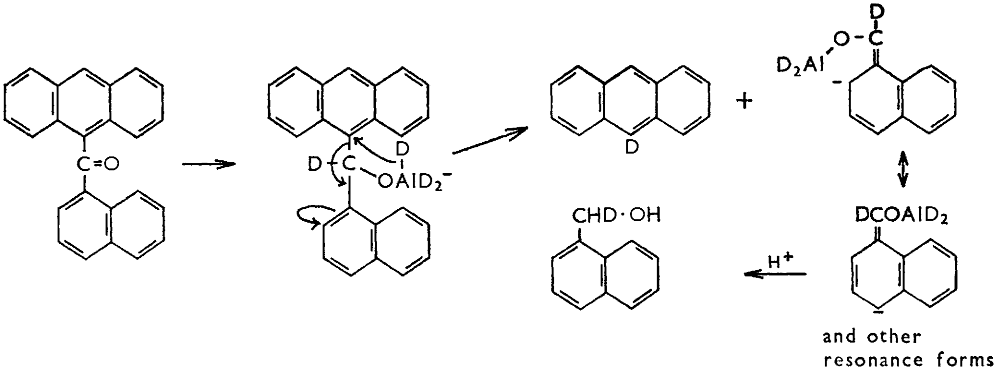


The mechanism of the cleavage has now been studied in the case of 9-1′-naphthoylanthracene by using lithium aluminium deuteride as reducing agent.

Any mechanism involves first attack on the carbonyl group by hydride (or deuteride) ion. The next stage might be further, possibly intermolecular, attack by deuteride ion on the same carbon atom, with concomitant cleavage of its bond to the anthracene nucleus. This is reasonable because of the relative stability of the anthryl anion and would require isolation of undeuterated anthracene and dideutero-1-naphthylmethanol.

When reduction of 9-1′-naphthoylanthracene was in fact carried out with lithium aluminium deuteride under the conditions reported for the analogous reduction with lithium aluminium hydride,[1] the anthracene isolated contained one atom of deuterium and the 1-naphthylmethanol contained only one atom of deuterium.

These results may be explained by the accompanying reaction scheme.



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[1] Rona and Feldman, *J.*, 1958, 1737.

[2] Lansbury, *J. Amer. Chem. Soc.*, 1961, **83**, 429.

[3] Reynaud, *Bull. Soc. chim. France*, 1951, 612; Dornow and Fust, *Chem. Ber.*, 1957, **90**, 1774; Johns and Markham, *J.*, 1962, 3712.

The first stage in this mechanism is again attack on the carbonyl-carbon atom by deuteride ion. Next, it is reasonable to postulate, on steric grounds, intramolecular attack by deuteride ion on the 9-carbon atom in the anthracene nucleus, with concomitant cleavage of the bond to the adjacent, deuterium-bearing carbon atom. The species thus obtained is a resonance-stabilised carbanion. Additional stabilisation is conferred upon this species by co-ordination with the aluminium atom so as to complete its sextet to a full electron shell. Protonation then permits isolation of monodeuteroanthracene and monodeutero-1-naphthylmethanol, in accord with the experimental results.

*Experimental.*—9-1′-Naphthoylanthracene [1] was purified by chromatography on alumina (Fisher). It had m. p. 211—212° as reported [1] (from acetic acid).

*Reduction.* To a solution of the ketone (1·5 g.) in tetrahydrofuran (40 ml.) was added a suspension of lithium aluminium deuteride (Merck; 1 g.) in tetrahydrofuran (20 ml.). The mixture was heated under reflux for 3 hr. in an inert atmosphere and set aside overnight. Decomposition was effected by ethyl acetate and Rochelle salt solution. The solvent was removed at reduced pressure and water, ether, and benzene were added to the residue. The organic phase was separated, dried ($MgSO_4$), and evaporated at reduced pressure. The residue was triturated with benzene, and the solid anthracene obtained (0·5 g.) was removed. The mother-liquor was passed through a column of alumina (Fisher). Elution with benzene–hexane (1 : 1) gave more anthracene (0·1 g.). Elution with benzene–chloroform (1 : 1) then gave 1-naphthylmethanol (0·35 g.). The anthracene, purified by recrystallisation from benzene followed by sublimation, had m. p. 212°. The 1-naphthylmethanol, purified by several distillations, had b. p. 100°/0·5 mm., m. p. 59—60°.

*Isotopic analyses.* The deutero-compounds were diluted with the respective unlabelled substances to bring the isotopic abundance of deuterium within the range 0—3 atom % of D. The combustion water from each sample was reduced with zinc, and the deuterium content of the hydrogen gas was determined mass-spectrometrically. Found: Anthracene, 0·9 atom of D per molecule. 1-Naphthylmethanol, 1·0 atom of D per molecule. The overall accuracy of the (duplicate) analyses was ±5%.

We are indebted to Mr. R. Levy for mass-spectrometric analyses and to Professors E. A. Halevi and D. Ben-Ishai for stimulating discussion.

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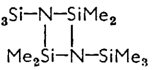
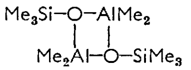
## 479. *The Structure of Tetramethyl*-OO′-*bistrimethylsilylcyclodialumoxane.*

By P. J. Wheatley.

The structure of tetramethyl-*NN*′-bistrimethylsilylcyclodisilazane (I) has been established by two-dimensional *X*-ray diffraction methods.[1] Recently the isoelectronic molecule tetramethyl-*OO*′-bistrimethylsilylcyclodialumoxane (II) has been prepared and characterized.[2] The annexed Table compares the crystallographic and some of the physical constants [2,3] of these two compounds.


(I)
$$\begin{array}{l} Me_3Si-N-SiMe_2 \\ \qquad\quad | \quad\; | \\ Me_2Si-N-SiMe_3 \end{array}$$


(II)
$$\begin{array}{l} Me_3Si-O-AlMe_2 \\ \qquad\quad | \quad\; | \\ Me_2Al-O-SiMe_3 \end{array}$$

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[1] Wheatley, *J.*, 1962, 1721.

[2] Schmidbaur and Schmidt, *J. Amer. Chem. Soc.*, 1962, **84**, 1069.

[3] Fink, *Angew. Chem.*, 1961, **73**, 736.

Examination of the diffracted *X*-ray spectra shows that, whereas there are some differences between corresponding reflexions from the two crystals, these differences are in all cases small. Thus not only are the molecules isoelectronic, but also the crystals are truly isomorphous. It is concluded that the molecules are isostructural.

| | (I) | (II) | | (I) | (II) |
|---|---|---|---|---|---|
| M. p. | 38·5° | 45·5° | $\beta$ | 104° 23′ | 104° 49′ |
| B. p. | 85°/7 mm. | 81·5°/10 mm. | $U$ (Å$^3$) | 968·7 | 987·0 |
| $M$ | 290·7 | 292·5 | $D_x$ | 0·997 | 0·984 |
| $a$ (Å) | $6{\cdot}75_9$ | $7{\cdot}00_8$ | $D_m$ | 0·998 | 0·98 |
| $b$ (Å) | $13{\cdot}18_1$ | $13{\cdot}22_0$ | $Z$ | 2 | 2 |
| $c$ (Å) | $11{\cdot}22_5$ | $11{\cdot}02_2$ | Space group | $P2_1/n$ | $P2_1/n$ |

It follows that the three valencies to the oxygen atom are coplanar within approximately the same limits of error as the three valencies to the nitrogen atom.[1]

I thank Dr. H. Schmidbaur and Professor M. Schmidt of the University of Marburg for bringing this compound to my attention and for providing the sample.

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[*Received, November 6th,* 1962.]

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## **480.** *An Improved Synthesis of* DL-[1-$^{14}$C]*Glyceric Acid.*

By J. M. ASHWORTH.

THE synthesis[1] of calcium DL-[1-$^{14}$C]glycerate from glycollaldehyde and sodium [$^{14}$C]-cyanide involves condensation of liquid hydrogen [$^{14}$C]cyanide with glycollaldehyde and subsequent hydrolysis of the [$^{14}$C]cyanohydrin compound, which is not isolated. However, the yield of 33% reported[1] for the overall synthesis of calcium DL-[1-$^{14}$C]glycerate was not reproducibly attainable in our hands and was considered to be unsatisfactorily low for an isotopic synthesis.

We here describe an alternative route to DL-[1-$^{14}$C]glyceric acid which results in an improved yield:

$$\mathrm{HO{\cdot}CH_2{\cdot}CHO + Na^{14}CN} \xrightarrow{1} \underset{\text{(I)}}{\mathrm{BzO{\cdot}CH_2{\cdot}CH(OBz){\cdot}^{14}CN}} \xrightarrow{2} \underset{\text{(II)}}{\mathrm{HO{\cdot}CH_2{\cdot}CH(OH){\cdot}^{14}CO_2H}}$$

Reagents: 1, BzCl–NaOH. 2, 50% HCl.

The route involves the initial formation of the nitrile (I), which occurs in a yield of >68%, as described by Dyer and his co-workers[2] and confirmed by us. The nitrile (I) is insoluble in the reaction mixture and is thus readily isolated. Hydrolysis of the crude nitrile and elution of the hydrolysate from a Dowex 1 (OH$^-$) column gives essentially pure glyceric acid (II) in 70% overall yield.

The use of benzoyl chloride instead of the more usual hydrochloric acid (which gives an overall yield of DL-glyceric acid of 41%) results in a greatly increased yield, suggesting that by benzoylating the initial condensation product the equilibrium of the cyanohydrin reaction is shifted in favour of the products. It is possible that this procedure may therefore be generally useful in obtaining higher yields in cyanohydrin condensations.

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[1] Sallach, *J. Amer. Chem. Soc.*, 1952, **74**, 2415.
[2] Dyer, Pickett, Strause, and Worrell, *J. Amer. Chem. Soc.*, 1956, **78**, 3384.

*Experimental.*—[1-$^{14}$C]*Dibenzoylglyceronitrile* (I). Glycollaldehyde (34 mg.) (obtained in dimeric form from Fluka A.G., Zurich) was dissolved in water (0·2 ml.) and left at room temperature for 24 hr. before use.[3] Sodium cyanide (5 mg.) was dissolved in 0·1N-sodium hydroxide (2 ml.), mixed with alkaline sodium [$^{14}$C]cyanide (15 mg.) (obtained from the Radiochemical Centre, Amersham), and placed in a stoppered test-tube with a drop of phenolphthalein. The glycollaldehyde solution and benzoyl chloride (0·15 ml.) were then added alternately and dropwise; the test-tube was shaken vigorously before each set of additions. A drop of N-sodium hydroxide was added, when necessary, to keep the reaction mixture alkaline. When addition was complete (10 min.), the white solid was allowed to settle and the major portion of the supernatant solution was drawn off. This solution contained $<15\%$ of the radioactivity of the initial solution: further addition of glycollaldehyde and benzoyl chloride did not result in the formation of any more of the white solid (I). The solid was then washed with water (2 × 2 ml. portions) and dried *in vacuo.*

In a similar synthesis with glycollaldehyde (700 mg.) and sodium [$^{12}$C]cyanide (540 mg.), the white solid was recrystallised from ethanol; it had m. p. 93—94° (lit.,[2] 94·5—95°) (65%) (Found: C, 69·3; H, 4·4; N, 4·8. Calc. for $C_{17}H_{13}NO_4$: C, 69·2; H, 4·4; N, 4·75%).

[1-$^{14}$C]*Glyceric acid* (II). 50% v/v Hydrochloric acid (10 ml.) was added to the test-tube containing the crude nitrile (I), and the mixture was boiled under reflux for 4 hr. The hydrolysate was cooled to 0° and the dirty-white precipitate was filtered off. This solid, which was not radioactive, after rerystallisation from water had m. p. 122° alone or mixed with authentic benzoic acid.

The filtrate was then poured on to a water-jacketed column of Dowex 1 resin (OH-form) and the column was washed with water (200 ml.). The washings contained $<1\%$ of the radioactivity of the starting material. The column was then washed with N-hydrochloric acid, and the first 30 ml. of acid effluent were collected. This fraction, which contained all the glyceric acid and 96% of the radioactivity in the hydrolysate, was freeze-dried. The residue was dissolved in water and assayed for periodate-oxidisable material.[4] Co-chromatography of a portion of this solution with authentic glyceric acid [5] in Kornberg's two-dimensional system,[6] and co-electrophoresis of a similar mixture by Gross's method,[7] showed that the radioactive area (detected by autoradiography) was, in both cases, indistinguishable from the acid-reacting area (detected by spraying the paper with Bromophenol Blue [6]). The yield of DL-[1-$^{14}$C]glyceric acid, assayed as periodate-oxidizable material,[4] was 70%.

In the similar synthesis from [$^{12}$C]cyanide the solution of glyceric acid obtained after freeze-drying was neutralized with calcium carbonate and the calcium DL-glycerate was precipitated by the addition of 4—5 vol. of ethanol. After recrystallization from water, the dihydrate of this salt (65%) was obtained; it had m. p. 137—138° (decomp.) and was identical (chromatographic behaviour, mixed m. p.) with an authentic sample [5] [Found: C, 25·2; H, 5·1; Ca, 13·9. Calc. for $(C_3H_8O_4)_2Ca,2H_2O$: C, 25·3; H, 4·9; Ca, 14·0%].

I thank Professor H. L. Kornberg for his interest and encouragement. This work was supported in part by the U.S. Air Force through the European Office, Office of Aerospace Research.

DEPARTMENT OF BIOCHEMISTRY, THE UNIVERSITY,
LEICESTER.

[*Received, November 20th,* 1962.]

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[3] McCleland, *J.*, 1911, 1829.
[4] Frisell, Meech, MacKenzie, *J. Biol. Chem.*, 1954, **207**, 709.
[5] Kiliani, *Ber.*, 1921, **54**, 465.
[6] Kornberg, *Biochem. J.*, 1958, **68**, 535.
[7] Gross, *Nature*, 1955, **176**, 72.

## 481. *Improved Preparation of Indole-2-aldehyde and 2-Indol-2′-ylethylamine.*

By JOHN HARLEY-MASON and EDDIE H. PAVRI.

INDOLE-2-ALDEHYDE has been obtained [1] in rather poor yield by oxidation of 2-hydroxymethylindole with potassium permanganate. We have now found that by use of activated manganese dioxide in ether the yield of aldehyde is substantially increased. The aldehyde condensed readily with nitromethane to give 2-2′-nitrovinylindole, which with lithium aluminium hydride gave 2-indol-2′-ylethylamine (isotryptamine). This compound had earlier been obtained by Schindler [2] using a longer preparative sequence.

*Experimental.—Indole-2-aldehyde.* To a solution of 2-hydroxymethylindole [3] (1·0 g.) in dry ether (200 ml.), manganese dioxide B [4] (6 g.) was added and the mixture was shaken at room temperature for 24 hr. After filtration, the residual manganese dioxide was thoroughly extracted with ether, and the combined extract and filtrate were evaporated, giving the crude aldehyde (0·667 g.) as a pale brown solid. Two recystallisations from aqueous methanol gave pure indole-2-aldehyde (0·645 g., 65%) as plates, m. p. 140—142° (lit.,[1] 141—142°).

*2-2′-Nitrovinylindole.* A solution of indole-2-aldehyde (2 g.) and nitromethane (3 g.) in methanol (50 ml.) was cooled to −5° and 50% aqueous sodium hydroxide (15 ml.) was added dropwise with stirring, at 0°. A bulky white precipitate rapidly separated. After 1 hr. at 0°, ice–water (50 ml.) was added and the resulting solution added slowly to a stirred mixture of concentrated hydrochloric acid (65 ml.) and water (240 ml.) at 0°. The crude product separated as a brownish-orange solid, which was collected and dried. Two recrystallisations from benzene–light petroleum gave *2-2′-nitrovinylindole* (1·86 g., 72%) as brownish-orange needles, m. p. 150—151° (decomp.) (Found: C, 64·1; H, 4·0; N, 14·6. $C_{10}H_8N_2O_2$ requires C, 63·9; H, 4·25; N, 14·9%), $\lambda_{max.}$ (in EtOH) 258 ($\varepsilon$ 8260), 395 m$\mu$ ($\varepsilon$ 24,300).

*2-Indol-2′-ylethylamine.* A solution of 2-2′-nitrovinylindole (2 g.) in dry ether (150 ml.) was added dropwise to a stirred suspension of lithium aluminium hydride (3 g,.) in ether (30 ml.). The mixture was then heated under reflux for 6 hr. After cooling, the excess of lithium aluminium hydride was decomposed by cautious addition of water, and the ethereal layer was then separated, dried, and evaporated, leaving the crude product as a buff solid. Sublimation at $115°/2 \times 10^{-2}$ mm. gave 2-indol-2′-ylethylamine (1·4 g., 73%) as white needles, m. p. 99—101° (lit.,[2] 100—101°) (Found: C, 75·2; H, 7·3; N, 17·1. Calc. for $C_{10}H_{12}N_2$: C, 75·1; H, 7·6; N, 17·5%).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 21st, 1962.*]

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[1] Taylor, *Helv. Chim. Acta*, 1950, **33**, 164; Doyle, Ferrier, Holland, Mehta, and Nayler, *J.*, 1956, 2853; Millich and Becker, *J. Org. Chem.*, 1958, **23**, 1096.
[2] Schindler, *Helv. Chim. Acta*, 1957, **40**, 2156.
[3] Brehm, *J. Amer. Chem. Soc.*, 1949, **71**, 3541.
[4] Harfenist, Bavley, and Lazier, *J. Org. Chem.*, 1954, **19**, 1608.

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## 482. $^{13}$C–H *Spin–Spin Splitting in the Nuclear Magnetic Resonance Spectra of the Methyl Esters of Some Inorganic Oxyacids.*

By P. R. HAMMOND.

A STUDY of the physical properties of the esters of inorganic oxyacids may help to elucidate the bonding in these compounds and explain their acid strength and alkylating properties.[1] An earlier paper [2] related the position of proton nuclear magnetic resonance of the methyl

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[1] Anbar, Dostrovsky, Samuel, and Yoffe, *J.*, 1954, 3603.
[2] Hammond, *J.*, 1962, 1370.

esters of nine oxyacids of the first- and second-row elements to electronegativity of the central atom. This Note concerns $^{13}$C–H spin–spin splitting in these spectra.

Measurements have been made on homogeneous samples and 1 : 3 v/v solutions in carbon tetrachloride where possible. Only for the phosphate and sulphate were variations greater than the experimental accuracy (about 0·2 cycle) on change of solvent. For these two a small increase in coupling occurred with solvents of greater dielectric constant; it must arise from small changes in bonding of the esters in these solvents.

TABLE 1.

| | | | | |
|---|---|---|---|---|
| Borate<br>142·8 | Carbonate<br>148·2 | Nitrate<br>150·6 | — | — |
| — | — | Nitrite<br>147·3 | — | — |
| — | Silicate<br>144·1 | Phosphate<br>149·4 *<br>149·2 †<br>150·2 ‡ | Sulphate<br>152·5 §<br>152·9 †<br>153·2 ¶ | Perchlorate<br>152·5 |
| — | — | Phosphite<br>145·8 | Sulphite<br>149·9 | — |

Solvents: * Dioxan, † homogeneous, ‡ deuterium oxide, § carbon tetrachloride, ¶ trifluoroacetic acid.

TABLE 2.

| | | | | |
|---|---|---|---|---|
| Borate<br>0·143 | Carbonate<br>0·111 | Nitrate<br>0·096 | — | — |
| — | — | Nitrite<br>0·116 | — | — |
| — | Silicate<br>0·135 | Phosphate<br>0·105 | Sulphate<br>0·085 | Perchlorate<br>0·085 |
| — | — | Phosphite<br>0·125 | Sulphite<br>0·101 | — |

The coupling constants tend to increase with decreasing chemical shifts [2] or increasing electronegativity of the central atom, although the lack of any simple relation between $J_{\mathrm{CH}}$ and $\tau$ across a series suggests [3] that anistropy effects contribute unequally to the latter.

The work of several investigators [4] indicates that $^{13}$C–H couplings provide a direct and fairly reliable measure of the *s*-character in the carbon bonding orbital, that is, of hybridisation. It is thus possible to estimate an orbital-hybridisation parameter, here defined by $\alpha^2_{\mathrm{C-O}} = 1 - (3J_{\mathrm{C-H}}/500)$, representing the *s*-character of the carbon atom in the C–O bonds of the esters. The values of $\alpha^2_{\mathrm{C-O}}$ in Table 2 are markedly low in all cases, particularly for the sulphate and perchlorate (strong alkylating agents), for which they are close to the values expected for $sp^2$-hybridisation in the $CH_3$ bonds.

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[3] Goldstein and Reddy, *J. Chem. Phys.*, 1962, **36**, 2644.

[4] Lauterbur, *J. Chem. Phys.*, 1957, **26**, 217; Muller and Pritchard, *ibid.*, 1959, **31**, 768, 1471; Malinowski, *J. Amer. Chem. Soc.*, 1961, **83**, 4479; Gutowsky and Juan, *ibid.*, 1962, **84**, 307.

# **483.** *The Interaction between Olefins and the Hexafluoroplatinate*(IV) *Ion.*

By R. D. W. KEMMITT and D. W. A. SHARP.

ALTHOUGH the hexafluoroplatinate(IV) ion is thermodynamically unstable with respect to hydrolysis and substitution it is kinetically a relatively stable entity, and salts containing the ion may be recrystallised from water, and displacement of fluoride ion by other halide ions will occur only in acid solution.[1,2] It has now been found that passage of ethylene through an aqueous solution of sodium hexafluoroplatinate(IV) results in rapid precipitation of hydrated platinum(IV) oxide, reduction of some of the platinum(IV) to an unidentified platinum(II) species, and formation of acetaldehyde. Cyclohexene, butadiene, propene, pent-1-ene, pent-2-ene, and oct-1-ene induce hydrolysis and precipitation of hydrated platinum(IV) oxide in a similar manner; so do acetylene and oct-1-yne. Cyclohexene gives cyclohexanone in a 34% yield based on the sodium hexafluoroplatinate(IV), and some cyclohexyl fluoride was also found. Butadiene gives crotonaldehyde as one product but owing to small yields it was not possible to identify positively the organic products of reaction between aqueous sodium hexafluoroplatinate(IV) and other olefins or acetylenes: ketonic or aldehydic groups were, however, detected in all cases.

The conversion of olefins into aldehydes or ketones is very similar to the corresponding reaction in the presence of aqueous palladium(II) chloride.[3] This reaction is assumed to proceed through an intermediate complex in which the olefin is $\pi$-bonded to the metal. The bound olefin is attacked by hydroxyl ion and there is subsequent migration of hydrogen in the organic residue; the palladium is reduced from the dipositive state to metallic palladium. By analogy it is postulated that the present reactions proceed through an intermediate olefin–platinum fluoride complex. The adduct can then be attacked by hydroxyl ion in two ways; by attack on the olefin with rearrangement to ketone and formation of a platinum(II) species; or by attack on the metal and hydrolysis of the Pt–F bonds, the olefin being lost from the co-ordination sphere during this process. The first stage of either of these processes could be common, as a co-ordinated hydroxyl group could attack a co-ordinated olefin. The overall reaction is thus:

$$\mathrm{R{\cdot}CH{=}CHR' + PtF_6{}^{2-} + H_2O \longrightarrow R{\cdot}CO{\cdot}CH_2R' + Pt^{2+} + 4F^- + 2HF}$$

Olefins would react with hydrofluoric acid to give alkyl fluorides—the addition of hydrogen fluoride to cyclohexene to give cyclohexyl fluoride has been shown to occur at or below room temperature[4]—and there will undoubtedly be some polymerisation of the olefins.

No olefin–metal fluoride complex has yet been isolated although carbonyl–metal fluoride, *e.g.*, $[\mathrm{RhF_3(CO)_2}]_2$,[5] and phosphine–metal fluoride complexes, *e.g.*, $\mathrm{(Ph_3P)_2PtF_2}$,[6] in which both fluorine and a $\pi$-bonding ligand are bound to the same metal atom, are known. It has not yet proved possible to isolate the platinum(II) species which is formed in solution, although this could be a further olefin–metal fluoride complex. It is of interest to consider why a $\pi$-bonding ligand such as an olefin can induce reaction of the hexafluoroplatinate(IV), ion whereas $\sigma$-bonding ligands do not appear to co-ordinate or react readily with this ion. The electronic configuration of the hexafluoroplatinate ion is $d^6$, with all the $d_\epsilon$-orbitals filled. Thus electrons donated to the ion can go only into orbitals of higher energy but, after the stereochemical rearrangement which would accompany increase of co-ordination

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[1] Sharpe, *J.*, 1950, 3444.
[2] Schlesinger and Tapley, *J. Amer. Chem. Soc.*, 1924, **46**, 276.
[3] Smidt, *Chem. and Ind.*, 1962, 54.
[4] McElvaine and Langston, *J. Amer. Chem. Soc.*, 1944, **66**, 1759.
[5] Sharp, *Proc. Chem. Soc.*, 1960, 317.
[6] Moss and Sharp, unpublished results.

to seven, what was formerly a $d_\epsilon$-orbital could be in a position to donate electrons to the anti-bonding orbitals of the olefin whilst a vacant orbital might now be available to accept electrons. It is thus suggested that it is the initial π-bonding which facilitates the attack by the olefin.

*Experimental.*—Sodium hexafluoroplatinate(IV) was prepared by the action of bromine trifluoride on sodium hexabromoplatinate and recrystallised from water and ethanol.[1] Gaseous olefins and acetylene were used from cylinders; liquid olefins and acetylenes were stored over molecular sieves and redistilled before use.

An aqueous solution of sodium hexafluoroplatinate(IV) was shaken in an atmosphere of ethylene in an apparatus similar to that described for the preparation of Zeise's salt.[7] A yellow precipitate was formed immediately and after being left overnight was filtered off and dried (Found: Pt, 67·5; H, 2·6. Calc. for $PtO_2,3H_2O$: Pt, 69·5; H, 2·2%). The precipitate dissolved in dilute hydrochloric acid to give a solution from which potassium hexachloroplatinate could be precipitated. The original solution smelt strongly of acetaldehyde and on addition of hydrochloric acid and bis(ethylenediamine)platinum(II) dichloride gave a violet precipitate of $[Pt\ en_2][PtCl_4]$ indicating the presence of a platinum(II) species. Acetylene also gave the precipitate $PtO_2,3H_2O$ (Found: Pt, 69·8; H, 2·9%). Cyclohexene behaved similarly, and cyclohexanone was distilled from the solution (m. p. of 2,4-dinitrophenylhydrazone 160°; lit., 160°). In a typical experiment, cyclohexene (10·4 g.) and sodium hexafluoroplatinate (0·42 g.) in water (10 ml.) gave cyclohexanone (0·04 g., 34% based on $Na_2PtF_6$). Cyclohexyl fluoride was detected by nuclear magnetic resonance spectroscopy. Butadiene was treated with aqueous sodium hexafluoroplatinate in a bomb overnight; crotonaldehyde was distilled from the solution (m. p. of 2,4-dinitrophenylhydrazone, 190°; lit., 190°). Other olefins gave immediate yellow precipitates ($PtO_2,3H_2O$) and solutions containing carbonyl compounds.

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[7] Chatt and Searle, *Inorg. Synth.* 1957, **5**, 210.