NOTES.

1011. *Synthesis of Phosphoserine and Certain Phosphorylated Peptides by Transphosphorylation.*

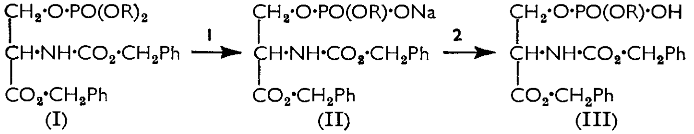
By D. THEODOROPOULOS, J. GAZOPOULOS, and I. SOUCHLERIS.

THOUGH diphenyl phosphorochloridate has been used to prepare some phosphorylated amino-hydroxy-acids and related peptides,[1] alternative methods are needed.[2] An alternative use of di-*p*-nitrobenzyl phosphorochloridate [3] has now been worked out for the synthesis of phosphoserine and certain related peptides. In preliminary experiments, benzyloxycarbonyl-DL-serine benzyl ester with di-*p*-nitrobenzyl phosphorochloridate in dry pyridine afforded the di-*p*-nitrobenzyl phosphate ester in very low yield. When pyridine was replaced by the equivalent amount of triethylamine in dry chloroform, the yield was higher (15%), but still not satisfactory.

We therefore resorted to a non-enzymic transphosphorylation involving the intermediate formation of the di-*p*-nitrobenzyl phosphoryl derivative of glyoxaline. The reactivity of phosphorylated derivatives of glyoxaline has been recently discussed.[4]

Di-*p*-nitrobenzyl phosphorochloridate was treated with glyoxaline in dry chloroform and the product, without isolation, was used directly for phosphorylation. Thus *N*-benzyloxycarbonyl-*O*-(*OO'*-di-*p*-nitrobenzylphospho)-DL-serine benzyl ester (I) and its L-isomer were prepared in crystalline form and satisfactory yield. These products, as expected,[1] suffered β-elimination in alkaline solution, as indicated by a strong light absorption at 241 mμ. They also afforded the corresponding phosphoserine on catalytic hydrogenolysis.

In a similar manner, benzyloxycarbonyl-L-seryl-L-alanine benzyl ester and benzyloxycarbonylglycyl-DL-serine benzyl ester were phosphorylated in about 45—50% yield. The products were obtained crystalline, in contrast to diphenyl phosphate esters of dipeptides which are described as oils.[1,5] Partial debenzylation [3] of ester (I) afforded the sodium s of *N*-benzyloxycarbonyl-*O*-(*O*-*p*-nitrobenzylphospho)-DL-serine benzyl ester (II), wh on acidification was converted into the corresponding acid ester (III).



$$\begin{array}{l}\text{CH}_2\cdot\text{O}\cdot\text{PO(OR)}_2\\ |\\ \text{CH}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph}\\ |\\ \text{CO}_2\cdot\text{CH}_2\text{Ph}\end{array}\xrightarrow{1}\begin{array}{l}\text{CH}_2\cdot\text{O}\cdot\text{PO(OR)}\cdot\text{ONa}\\ |\\ \text{CH}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph}\\ |\\ \text{CO}_2\cdot\text{CH}_2\text{Ph}\end{array}\xrightarrow{2}\begin{array}{l}\text{CH}_2\cdot\text{O}\cdot\text{PO(OR)}\cdot\text{OH}\\ |\\ \text{CH}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph}\\ |\\ \text{CO}_2\cdot\text{CH}_2\text{Ph}\end{array}$$

(I) (II) (III)

$R = p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$. 1, NaI–COMe$_2$. 2, HCl.

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[1] Riley, Turnbull, and Wilson, *J.*, 1957, 1373.

[2] Theodoropoulos, Gazopoulos, and Souchleris, *Nature*, 1960, **185**, 606.

[3] Zervas and Dilaris, *J. Amer. Chem. Soc.*, 1955, **77**, 5354.

[4] Baddiley, Buchanan, and Letters, *J.*, 1956, 2812; Ratlev and Rosenberg, *Arch. Biochem. Bioph* 1956, **65**, 319.

[5] Fölsch, *Acta Chem. Scand.*, 1958, **12**, 561.

In view of the doubt as to the nature of the phosphorus linkages in phosphoproteins,[6] we are exploring the possibility of using compounds (II) and (III) as essential intermediates in producing model peptides containing mixed amide ester and pyrophosphate bonds.

Experimental.—M. p.s were determined in capillary tubes when not otherwise stated. Paper chromatography was carried out in the solvent system butan-1-ol–acetic acid–water (4 : 1 : 5). Whatman No. 1 paper was used, and the phosphoserine had R_F 0·06.

N-*Benzyloxycarbonyl*-O-(-OO′-*di*-p-*nitrobenzylphospho*)-DL-*serine benzyl ester* (I). To dry chloroform (10 ml.), cooled to 0°, were added glyoxaline (0·72 g.) and di-*p*-nitrobenzyl phosphorochloridate (2·31 g.) with shaking and exclusion of moisture. One min. later a cooled solution of benzyloxycarbonyl-DL-serine benzyl ester (1·65 g.) in chloroform (5 ml.) was added, and the mixture set aside at room temperature for 24 hr. Then it was diluted with chloroform (50 ml.) and washed successively with 10% pyridine solution (twice), hydrochloric acid (to decompose *sym*-tetra-*p*-nitrobenzyl pyrophosphate, if formed [4]), pyridine again, hydrochloric acid, and water, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue solidified under ether; it was cooled, filtered off, washed with ether, and recrystallised from absolute ethanol. Complete precipitation was effected by addition of ether. The *ester* (I) (yield 50—60%) had m. p. 108—110° (corr.) (Found: C, 56·2; H, 4·2; N, 6·2. $C_{32}H_{30}O_{12}N_3P$ requires C, 56·5; H, 4·4; N, 6·1%).

N-*Benzyloxycarbonyl*-O-(OO′-*di*-p-*nitrobenzylphospho*)-L-*serine benzyl ester*. This *isomer*, prepared similarly in 40—45% yield, had m. p. 64—67° unchanged after three recrystallisations, $[\alpha]_D^{24}$ −6·9° (*c* 1 in acetic acid) (Found: C, 56·3; H, 4·2; N, 6·0; P, 4·8. $C_{32}H_{30}O_{12}N_3P$ requires C, 56·5; H, 4·4; N, 6·1; P, 4·5%).

Benzyloxycarbonyl-O-(O-p-*nitrobenzylphospho*)-DL-*serine benzyl ester and its sodium salt* (II). Compound (I) (3·39 g.) was dissolved in dry hot acetone (10 ml.), sodium iodide (0·8 g.) was then added, and the solution boiled for 45 min. The product is usually precipitated during this time but cooling and scratching may be necessary. Filtration and washing with cold acetone afford the *sodium salt* (2·4 g., 86%), m. p. 215° (Kofler block), as a white solid (Found: N, 4·7; P, 5·3. $C_{25}H_{24}O_{10}N_2PNa$ requires N, 4·9; P, 5·4%).

A solution of this salt (2·83 g.) in distilled water (the calcium or barium salt is sparingly soluble in water) (50 ml.) was acidified with hydrochloric acid to Congo Red. The resulting oil solidified slowly at 0° and was then filtered off, washed with water, and dried. For purification it was dissolved in the minimal amount of absolute ethanol and reprecipitated with ether; the *acid* (III) (2·4 g., 90%) had m. p. 83—85° (Found: N, 4·9; P, 5·4. $C_{25}H_{25}O_{10}N_2P$ requires N, 5·1; P, 5·6%).

Phosphoserine. (*a*) Hydrogenolysis of the ester (I) with 10% palladised charcoal in aqueous acetic acid afforded DL-phosphoserine (90%), m. p. 161—163° (lit., 160—161°,[1] 163—164°,[1] 165—166°, 166—167° [8]) (Found: N, 7·5; P, 16·6. Calc. for $C_3H_8O_6NP$: N, 7·5; P, 16·7%). Paper chromatography revealed a very faint spot moving in front of phosphoserine.

(*b*) Hydrogenolysis of the acid from (II) produced chromatographically pure DL-phosphoserine (91%), m. p. 166—167°.

(*c*) L-Phosphoserine, obtained by hydrogenolysis of benzyloxycarbonyl-*O*-(*OO*′-di-*p*-nitrobenzylphospho)-L-serine benzyl ester in 90% yield, had m. p. 169—170°, $[\alpha]_D^{22}$ +17·5° (*c* 0·7 in 2N-HCl) {lit., m. p. 175—176°,[1] $[\alpha]_D^{19}$ +12° (calc. from Ba salt; *c* 3·6 in N-HCl), $[\alpha]_D^{29}$ +16·2° (*c* 3 in 2N-HCl) [9]}.

Benzyloxycarbonyl-O-(OO′-*di*-p-*nitrobenzylphospho*)-L-*seryl*-L-*alanine benzyl ester*. Benzyloxycarbonyl-L-seryl-L-alanine benzyl ester (2 g.; m. p. 114°), prepared by the carbodi-imide method,[10] was treated with di-*p*-nitrobenzyl phosphorochloridate (2·9 g.) and glyoxaline (0·9 g.) as previously described. The *product* (1·8 g.), purified from ethyl acetate–light petroleum, had m. p. 81—83° (Found: C, 54·2; H, 4·4; N, 7·1; P, 4·2. $C_{35}H_{35}O_{13}N_4P$ requires C, 54·6; H, 4·6; N, 7·4; P, 4·1%). Hydrogenolysis of it produced (O-*phospho*-L-*seryl*-L-*alanine monohydrate* (86% yield), m. p. 170° (decomp.) [softening at 148—150° (Kofler block)] (Found: N, 10·1; P, 11·2. $C_6H_{13}O_7N_2P,H_2O$ requires N, 10·2; P, 11·4%).

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[6] Perlmann, *Adv. Protein Chem.*, 1955, **10**, 1; Hofmann, *Biochem. J.*, 1958, **69**, 139.

[7] Plimmer, *Biochem. J.*, 1941, **35**, 461.

[8] Plapinger and Wagner-Jauregg, *J. Amer. Chem. Soc.*, 1953, **75**, 5757.

[9] Neuhaus and Byrne, *J. Biol. Chem.*, 1959, **234**, 113.

[10] Sheehan and Hess, *J. Amer. Chem. Soc.*, 1955, **77**, 1067.

Benzyloxycarbonylglycyl-O-(OO′-*di*-p-*nitrobenzylphospho*)-DL-*serine benzyl ester*. This was similarly prepared from benzyloxycarbonylglycyl-DL-serine benzyl ester (1·93 g.; m. p. 140°; dissolved in 30 ml. of chloroform), di-*p*-nitrobenzyl phosphorochloridate (2·9 g.), and glyoxaline (0·9 g.). It was purified from absolute ethanol–ether and finally the minimal amount of ethanol. The *ester* (1·7 g.) had m. p. 116—118° (Found: C, 55·2; H, 4·5; N, 7·7; P, 4·4. $C_{34}H_{33}O_{13}N_4P$ requires C, 55·2; H, 4·5; N, 7·6; P, 4·2%). Catalytic hydrogenation afforded glycyl-*O*-phospho-DL-serine (90% yield), m. p. 198—201° (lit.,[5] m. p. 201—204°).

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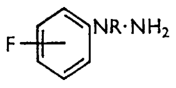
TECHNICAL UNIVERSITY OF ATHENS, GREECE. [*Received, April 6th*, 1960.]

1012. *Fluorine-substituted* N-*Alkylanilines and* N-*Alkyl*-N-*phenylhydrazines.*

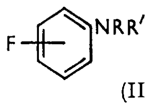
By F. L. ALLEN, R. E. JEWELL, and H. SUSCHITZKY.

THE preparation of fluorine-substituted *N*-alkyl-anilines and -phenylhydrazines was of interest in connection with the synthesis of certain *N*-heteroaromatic fluorine compounds (unpublished work). The required fluoroanilines were monoalkylated by Hickinbottom's method;[1] the resulting mixture of primary and secondary amines was separable because the fluoroanilines, unlike the secondary amines,[2] form insoluble addition compounds with zinc chloride.

An unsuccessful attempt was made to prepare *N*-alkyl-*N*-fluorophenylhydrazines (I; R = alkyl) by reduction of the stable nitroso-compounds (II; R = alkyl, R′ = NO). With zinc dust, acetic acid, and ethanol as the reducing medium denitrosation occurred invariably although Hartman and Roll[3] claim good yields (52—56%) in the preparation of *N*-methyl-*N*-phenylhydrazine by this method. Similarly, lithium aluminium hydride reduced the *N*-nitrosamines to the corresponding secondary amines. Although Poirier and Bonington[4] prepared *NN*-diphenylhydrazine by this reduction method, other workers[5] obtained only diphenylamine. Direct alkylation of fluorophenylhydrazines proved successful. In this route[6] the required monofluorophenylhydrazine, prepared as previously described,[7] was dissolved in liquid ammonia, and the sodium derivative (II; R = Na, R′ = H) treated with the appropriate alkyl halide.



(I)



(II)

The *N*-alkyl-*N*-fluorophenylhydrazines are pale-yellow oils, decomposing within a few hours but yielding stable derivatives.

Experimental.—N-*Alkylfluoroanilines*. The fluoroaniline (1 mol.) was heated with the appropriate alkyl halide (0·4 mol.) under reflux for about 5 hr. After addition of alkali the mixture of primary and secondary amines was extracted with light petroleum (b. p. 60—80°), and an aqueous solution of zinc chloride added to the extract. After 12 hr. the mixture was filtered off, the filtrate dried (potassium carbonate), the solvent removed, and the residue distilled under reduced pressure. The *anilines* thus obtained are listed in Table 1.

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[1] Hickinbottom, *J.*, 1930, 992.
[2] Reilly and Hickinbottom, *J.*, 1920, 127.
[3] Hartman and Roll, *Org. Synth.*, 1933, **13**, 66.
[4] Poirier and Bonington, *J. Amer. Chem. Soc.*, 1952, **74**, 3192.
[5] Scheuler and Hanna, *J. Amer. Chem. Soc.*, 1951, **73**, 4996.
[6] Audrieth, Weisiger, and Carter, *J. Org. Chem.*, 1941, **6**, 417.
[7] Suschitzky, *J.*, 1953, 3326.

TABLE 1. N-*Alkylfluoroanilines*, NHRR′.

			Found (%)		Reqd. (%)	Yield	Benzoate		
								Found (%)	Reqd. (%)
R	R′	B. p.	N	Formula	N	(%)	M. p.	N	N
o-F·C_6H_4	Me	90°/40 mm.	11·1	C_7H_8FN	11·2	65	107°	6·0	6·1
m-F·C_6H_4	Me	94/19	11·1	,,	,,	87	134	6·1	,,
p-F·C_6H_4	Me	79/11	11·1	,,	,,	72	75	6·5	,,
o-F·C_6H_4	Et	115/68	10·0	$C_8H_{10}FN$	10·1	70	98	5·9	5·8
m-F·C_6H_4	Et	90/11	10·0	,,	,,	70	76	5·7	,,
p-F·C_6H_4	Et	92/14	10·2	,,	,,	78	71	5·4	,,
o-F·C_6H_4	Pr^n	114/68	9·0	$C_9H_{12}FN$	9·1	70	—	—	
m-F·C_6H_4	Pr^n	101/10	9·3	,,	,,	65	—	—	
p-F·C_6H_4	Pr^n	109/14	9·0	,,	,,	62	—	—	

N-*Alkylfluoro*-N-*nitrosoanilines*. To a solution, kept below 10°, of the alkylfluoroaniline in excess of concentrated hydrochloric acid an equivalent amount of sodium nitrite was added as an aqueous solution (20%) during 5—10 min. After 1 hr. the oily product was taken up in benzene and dried ($MgSO_4$). Removal of the solvent and distillation of the residue gave the nitroso-compounds listed in Table 2 as orange-red oils.

TABLE 2. *N-Alkylfluoro*-N-*nitrosoanilines*, N(NO)RR′.

			Found (%)		Reqd. (%)	
R	R′	B. p.	N	Formula	N	Yield (%)
o-F·C_6H_4	Me	144°/63 mm.	18·4	$C_7H_7FN_2O$	18·2	47
m-F·C_6H_4	Me	133/24	18·6	,,	,,	49
p-F·C_6H_4	Me	111/7	17·8	,,	,,	50
o-F·C_6H_4	Et	151/53	17·0	$C_8H_9FN_2O$	16·7	45
m-F·C_6H_4	Et	118/11	16·3	,,	,,	47
p-F·C_6H_4	Et	114/6	16·4	,,	,,	50
o-F·C_6H_4	Pr^n	145/63	15·7	$C_9H_{11}FN_2O$	15·4	42
m-F·C_6H_4	Pr^n	130/12	15·5	,,	,,	53
p-F·C_6H_4	Pr^n	129/11	15·1	,,	,,	54

N-*Alkyl*-N-*fluorophenylhydrazines*. The monofluorophenylhydrazine (5·0 g.), prepared as reported previously,[7] was dissolved in anhydrous liquid ammonia (100 ml.). To the stirred, well-cooled solution (carbon dioxide–ether) finely powdered sodamide (1·6 g.) was added,

TABLE 3. N-*Alkyl*-N-*fluorophenylhydrazines*, NH_2·NRR′.

			Found (%)		Reqd. (%)	
R	R′	B. p.	N	Formula	N	Yield (%
o-F·C_6H_4	Me	106°/16 mm.	19·7	$C_7H_9FN_2$	20·0	50
m-F·C_6H_4	Me	108/9	19·9	,,	,,	55
p-F·C_6H_4	Me	109/13	19·7	,,	,,	73
o-F·C_6H_4	Et	108/15	18·5	$C_8H_{11}FN_2$	18·2	48
m-F·C_6H_4	Et	111/9	18·1	,,	,,	58
p-F·C_6H_4	Et	112/15	18·5	,,	,,	46
o-F·C_6H_4	Pr^n	115/13	16·5	$C_9H_{13}FN_2$	16·7	43
m-F·C_6H_4	Pr^n	116/8	16·9	,,	,,	42
p-F·C_6H_4	Pr^n	111/10	16·3	,,	,,	43

Derivatives

		Benzylidene				Benzoate			
			Found (%)		Reqd. (%)		Found (%)		Reqd. (%)
R	R′	M. p.	N	Formula	N	M. p.	N	Formula	N
o-F·C_6H_4	Me	96°	12·4	$C_{14}H_{13}FN_2$	12·3	196°	11·2	$C_{14}H_{13}FN_2O$	11·5
m-F·C_6H_4	Me	114	11·9	,,	,,	192	11·2	,,	,,
p-F·C_6H_4	Me	93	12·1	,,	,,	139	11·2	,,	,,
o-F·C_6H_4	Et	188	11·7	$C_{15}H_{15}FN_2$	11·6	197	10·7	$C_{15}H_{15}FN_2O$	10·9
m-F·C_6H_4	Et	75	11·3	,,	,,	135	10·6	,,	,,
p-F·C_6H_4	Et	62	11·6	,,	,,	165	10·7	,,	,,
o-F·C_6H_4	Pr^n	97	11·0	$C_{16}H_{17}FN_2$	10·9	141	10·2	$C_{16}H_{17}FN_2O$	10·3
m-F·C_6H_4	Pr^n	115	10·8	,,	,,	189	10·1	,,	,,
p-F·C_6H	Pr^n	54	10·5	,,	,,	139	10·1	,,	,,

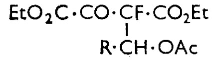
followed by methyl iodide (11·4 g.). Ammonia was allowed to evaporate overnight and the residue was extracted with ether. Removal of the solvent and distillation of the residue yielded the alkylated fluorophenylhydrazines as yellow oils. They were stable in a refrigerator for several days. A number of cognate derivatives were prepared in the usual way; all compounds thus made are listed in Table 3.

West Ham College of Technology, West Ham, E.15.
Royal Technical College, Salford, Lancs. [Received, April 27th, 1960.]

1013. Organic Fluorine Compounds. Part XIX.* The Reaction of Diethyl Oxalofluoroacetate and Aliphatic Aldehydes.

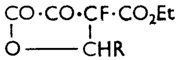
By Ernst D. Bergmann and Israel Shahak.

In view of a recent publication by Gault, Rouge, and Gordon[1] on the condensation of diethyl oxalofluoroacetate and formaldehyde, we report our experience with the reaction between this ester and aliphatic aldehydes in general. Two reactions have been observed under the influence of sodium acetate as catalyst: in the presence of acetic anhydride, the aldol-like compound initially formed underwent acetylation to give the ester (I); in the



$EtO_2C{\cdot}CO{\cdot}CF(CHR{\cdot}OAc){\cdot}CO_2Et$

(I)



(II)

$HO_2C{\cdot}CO{\cdot}CHF{\cdot}CHR{\cdot}OAc$

(III)

absence of the anhydride a lactone (II) was formed. Acidic hydrolysis of the acetoxy-ester (I) is accompanied by loss of one carboxyl group and γ-acetoxy-β-fluoro-α-oxo-acids (III) are formed. As examples, the reactions of isobutyraldehyde and formaldehyde are described; an analogous behaviour has been observed for heptanal, butyl glyoxalate, glyoxal, and 2-methyl-3-oxopentanal.

The lactones (II) are converted into acetoxy-esters (I) by successive treatment with acetic anhydride and with anhydrous ethanol in the presence of hydrogen chloride. Conversely, the esters (I) yield the lactones (II) upon treatment with cold sodium hydrogen carbonate solution. With strong alkali, lactones (II) are split into oxalic acid and derivatives of α-fluoroacrylic acid, as already observed by Gault and his co-workers[1] for the unsubstituted acid. It is possible to prepare these unsubstituted acids without isolation of the intermediate compounds. This is described for the preparation of 2-fluoronon-2-enoic acid.

Experimental.—*Ethyl* 4-*acetoxy*-3-*ethoxycarbonyl*-3-*fluoro*-5-*methyl*-2-*oxohexanoate* (I; R = Pr^i). (*a*) To diethyl oxalofluoroacetate[2] (20·6 g.) in ether (50 ml.), were added successively sodium acetate (10 g.), isobutyraldehyde (10 g.), and acetic anhydride (12 g.). The mixture was refluxed and stirred for 5 hr., and the solution filtered and distilled, first under 30 mm., then under 1 mm. pressure. The *hexanoate* (10 g., 31%) finally had b. p. 134°/1 mm.; it gave no reaction with ferric chloride (Found: C, 52·4; H, 6·9; F, 6·0. $C_{14}H_{21}FO_7$ requires C, 52·5; H, 6·6; F, 5·9%).

(*b*) As described previously,[3] the enolate of diethyl oxalofluoroacetate was prepared from 0·1 mole each of ethyl fluoroacetate, diethyl oxalate, and sodium hydride; it was then treated with glacial acetic acid (7 g.), and isobutyraldehyde and acetic anhydride were added as above.

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* Part XVIII, Shahak and Bergmann, *Bull. Res. Council Israel*, 1960, in the press.

[1] Gault, Rouge, and Gordon, *Compt. rend.*, 1960, **250**, 1073.

[2] Blank, Mager, and Bergmann, *J.*, 1955, 2190.

[3] Bergmann and Shahak, *J.*, 1960, 3225.

Working-up gave a 30% yield of (I; R = Pr^i). The infrared spectrum shows a very strong peak at 1754 cm.$^{-1}$ and the C–F bond at 1110 cm.$^{-1}$ (broad).

Ethyl 4-*acetoxy*-3-*ethoxycarbonyl*-3-*fluoro*-2-*oxobutyrate* (I; R = H) was obtained analogously by using paraformaldehyde; it boiled at 120—122°/1 mm.; yield 21—22% (Found: C, 47·1; H, 5·3; F, 6·7. $C_{11}H_{15}FO_7$ requires C, 47·5; H, 5·4; F, 6·8%).

Interconversion of the acetoxy-ester (I) *and the lactone* (II). (*a*) Solutions of (I; R = Pr^i) (10 g.) in ether (100 ml.) and sodium hydrogen carbonate (15 g.) in water (250 ml.) were mixed and refluxed with agitation for 3 hr. The ethereal layer was evaporated, washed with water, dried, and distilled. The product boiled at 129—130°/1 mm. and was further identified as the lactone (II; R = Pr^i) by analysis (Found: OEt, 19·7. Calc. for $C_{10}H_{13}FO_5$: OEt, 19·4%).

(*b*) A solution of the lactone (II; R = Pr^i) (5 g.) in acetic anhydride (5 ml.) was saturated with gaseous hydrogen chloride, kept at room temperature for 1 hr., and refluxed for a further 2 hr. The volatile constituents of the mixture were evaporated on the water-bath under 30 mm., the residue was dissolved in ethanol (50 ml.), and the solution saturated with hydrogen chloride and refluxed for 5 hr. After addition of benzene (70 ml.), the product was distilled, first at atmospheric pressure on the water-bath, then *in vacuo*. The product (I; R = Pr^i) boiled at 134°/1 mm. and was further identified by analysis (Found: OEt, 27·5. Calc. for $C_{14}H_{21}FO_7$: OEt, 28·1%).

4-*Acetoxy*-3-*fluoro*-5-*methyl*-2-*oxohexanoic acid* (III; R = Pr^i). The ester (I; R = Pr^i) (10 g.) was refluxed for 3 hr. with a mixture of glacial acetic acid (25 ml.) and concentrated hydrochloric acid (7 ml.). Volatile products were distilled off under 30 mm. pressure, and the residue was fractionated at 0·1 mm. pressure. The *product*, b. p. 137—138°/0·1 mm., slowly solidified and was recrystallized from benzene; it then melted at 87—88° (Found: C, 48·9; H, 5·8; F, 8·8. $C_9H_{13}FO_5$ requires C, 49·1; H, 5·9; F, 8·6%).

Ethyl 3-*fluoro*-2-*isopropyl*-4,5-*dioxotetrahydrofuran*-3-*carboxylate* (II; R = Pr^i). A mixture of diethyl oxalofluoroacetate (10 g.), isobutyraldehyde (15 g.), and sodium acetate (8 g.) was heated at 100° with stirring for 4 hr. The product was poured into ice and dilute hydrochloric acid and isolated by extraction with benzene. The *furan* (3·5 g.; 30%) boiled at 129—130°/1 mm. (Found: C, 52·0; H, 5·5; F, 8·0. $C_{10}H_{13}FO_5$ requires C, 51·7; H, 5·6; F, 8·2%). The infrared spectrum shows a very strong carbonyl band at 1754 cm.$^{-1}$, and the C–F frequency is at 1180 and 1110 cm.$^{-1}$.

2-*Fluoronon*-2-*enoic acid and its ethyl ester.* To a suspension of sodium hydride (6 g.) in xylene (100 ml.), diethyl oxalate (38 g.), anhydrous ethanol (0·5 g.), and ethyl fluoroacetate (3·5 g.) were added and the mixture was heated at 40° until reaction set in. Then, the remainder of the ethyl fluoroacetate (23 g.) was added, and the mixture slowly (during 1 hr.) heated to 60—75°. The ethanol formed was distilled off under 30 mm. (until xylene began to distil), and the residue heated for 30 min. at 70°. Freshly distilled heptanal (28·5 g.) was added, and the mixture heated at 100° for 30 min., cooled, and poured into water (500 ml.). The organic layer was separated, washed with water, 5% sodium carbonate solution, and again with water, and distilled, first at 30 mm., then at 2 mm. *Ethyl* 2-*fluoronon*-2-*enoate* (26 g., 52%) boiled at 99—101°/2 mm. (Found: F, 9·6. $C_{11}H_{19}FO_2$ requires F, 9·4%). The residue of this fraction was distilled until the vapour temperature reached 165°, and the second distillate treated with cold alcoholic potassium hydroxide solution. Water was added, the alcohol distilled off *in vacuo*, and the aqueous solution acidified and extracted with benzene. Thus, 2-*fluoronon*-2-*enoic acid* (6 g., 14%), b. p. 115—117°/1 mm., was obtained. The same acid was prepared by analogous hydrolysis of the ethyl ester (Found: C, 62·4; H, 8·3; F, 10·6. $C_9H_{15}FO_2$ requires C, 62·1; H, 8·6; F, 10·9%).

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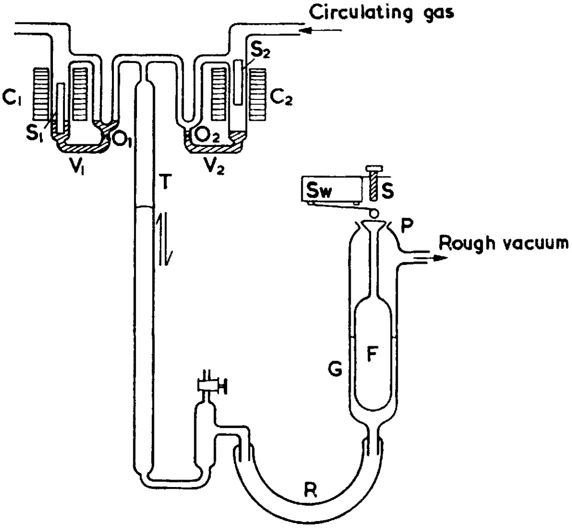
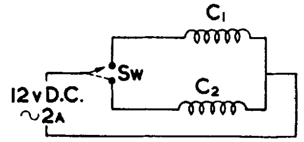
1014. *A Gas-circulating Pump which operates over a Wide Range of Pressure.*

By E. R. S. WINTER and L. D. EATON.

IN gas-kinetic problems it is often necessary to circulate gas at fixed and known rates around a closed system; it is usually desirable also to be able to do this over a wide range of pressure. The most satisfactory device, especially when working with very clean materials in a glass high-vacuum system, is in our experience an oscillating mercury pump which gives a positive displacement of gas,[1] but this method suffers from the disadvantage that the ground-glass one-way valves in the gas-flow line will not work reliably below pressures of a mm. or so. Diffusion pumps have been used [2] at lower pressures but it is not then possible to determine, except indirectly, the rate of circulation. The pump shown in the Figure, basically that described by Reilly and Rae,[1] is easy to construct, robust and reliable in operation, and gives positive and measurable rates of gas circulation, from pressures of at least 76 cm. to well below 0·1 mm. (*i.e.*, down to pressures at which diffusion becomes important) without any alteration or adjustment except of the level of the reservoir G.





The operation of the system is as follows: The rough vacuum applied to G causes the mercury to rise until buoyancy pushes up the float F, letting air in through the ground-glass valve P and so pushing the mercury in G down and repeating the cycle. The rise and fall of mercury in G causes a corresponding fall and rise of mercury in T. As F rises and falls, it activates a microswitch Sw which is firmly clamped in a suitable position above R; fine adjustment of the operation of Sw is achieved by restricting the vertical movement of the arm of Sw (and of F itself) by an adjustable screw S, provided with

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[1] Reilly and Rae, " Physico-Chemical Methods," Vol. I, p. 267, Methuen, London, 1940.

[2] Dodd and Robinson, " Experimental Inorganic Chemistry," p. 117, Elsevier, London, 1954.

locking nuts. S is fixed to a small brass plate upon which Sw is mounted, and the whole assembly is best made integral with the movable support for G. Sw is a single pole change-over switch (Honeywell Controls, No. BA-2RV2-A2) and operates to pass current through coils C_1 and C_2 alternately, as shown in the circuit diagram. C_1 and C_2 are two identical coils on brass formers, comprising about 2,500 turns of 24 s.w.g. enamel-covered copper wire; they surround the widebore (~1 cm. internal diameter) portion of the two mercury valves V_1 and V_2 and raise and lower iron slugs S_1 and S_2 (~10 g. of soft iron, sealed in glass), so lowering and raising to the cut-off point the level of mercury in the narrower U-tubes (~3 mm. internal diameter). The synchronisation of this operation with the rise and fall of mercury in T forces a one-way circulation upon the gas in the closed system, of which V_1 and V_2 form a part. To reduce oscillation of the mercury in V_1 and V_2, the connection to the bottom of the U-tubes is slightly constricted at O_1 and O_2. It is convenient to construct the tube T from a burette to facilitate calculation of the rate of circulation of gas. The speed and capacity of the pump may be altered by constricting the rubber tubing R connecting G and T and by changing the dimensions of F and G: with F = 1·9 cm. (external diameter) and G = 2·3 cm. (internal diameter) our pump had a stroke of 10—12 ml. and a maximum displacement rate of about 400 ml./min., independent of the total pressure in the apparatus.

The pump described here will not operate against a positive pressure of more than about 5 mm., since blow-back will otherwise occur round the mercury cut-offs.

When it is necessary to force the gas against an appreciable resistance, *e.g.*, through a closely-packed reactor or through a series of bubblers for purposes of purification or analysis, the same principle can be used, V_1 and V_2 being replaced by magnetically-operated cut-offs of a different design. For example, ground-glass valves can be used, with slugs of iron sealed in the plungers, or where permissible stainless-steel ball-bearings in ground-glass cups.

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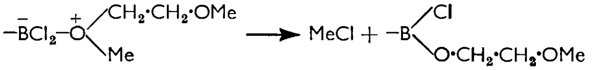
1015. *The Reaction of Propionic Acid with Alkylboron Chlorides.*

By A. G. MASSEY.

BROWN and MURRAY [1] have described the reductive fission of the boron trialkyls by refluxing them with various carboxylic acids in a high-boiling ether:

$$BR_3 + nR'{\cdot}CO_2H \longrightarrow nRH + BR_{3-n}(O{\cdot}COR')_n \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In this work propionic acid and 1,2-bis(dichloroboryl)ethane $(BCl_2{\cdot}CH_2{\cdot})_2$ in ethylene glycol dimethyl ether were heated in sealed tubes at 100—150°. Some ethane was produced, together with methane, hydrogen, and ethylene, but the predominating product was methyl chloride, which no doubt arose from two reactions: (i) An ether-splitting reaction:



$$-\overset{-}{B}Cl_2-\overset{+}{O}\genfrac{}{}{0pt}{}{\diagup CH_2{\cdot}CH_2{\cdot}OMe}{\diagdown Me} \longrightarrow MeCl + -B\genfrac{}{}{0pt}{}{\diagup Cl}{\diagdown O{\cdot}CH_2{\cdot}CH_2{\cdot}OMe} \quad . \; . \; . \; . \; . \quad (2)$$

and (ii) attack of hydrogen chloride (formed by interaction of the boron–chlorine groups with the propionic acid) on the ethylene glycol dimethyl ether:

$$OMe{\cdot}CH_2{\cdot}CH_2{\cdot}OMe + HCl \longrightarrow MeCl + OMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH \quad . \; . \; . \; . \; . \quad (3)$$

However, the quantity of methyl chloride produced by reaction (3), when carried out in the presence of propionic acid, was small compared with the total yield obtained in the reductive fissions.

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[1] Brown and Murray, *J. Amer. Chem. Soc.*, 1959, **81**, 4108.

Further experiments involving the alkylboron chlorides were carried out in the absence of solvent to avoid the formation of methyl chloride. When mixtures of 1,2-bis(dichloroboryl)ethane and propionic acid were heated in sealed tubes at 100°, low yields of ethane were obtained and it was not until the temperature was increased to 140° that almost quantitative evolution of ethane was attained after extended reaction times; the yield of ethane was reduced to some extent by traces of ethylene, methane, and hydrogen formed as by-products. These products could not have arisen from the thermal decomposition of the 1,2-bis(dichloroboryl)ethane because previous work [2] has shown that evolution of hydrocarbons on pyrolysis is insignificant even at 200°. The reaction probably proceeds step-wise:

$$>B{\cdot}CH_2{\cdot}CH_2{\cdot}B< + Et{\cdot}CO_2H \longrightarrow >B{\cdot}CH_2{\cdot}CH_3 + >B{\cdot}O{\cdot}COEt$$

$$>B{\cdot}CH_2{\cdot}CH_3 + Et{\cdot}CO_2H \longrightarrow >B{\cdot}O{\cdot}COEt + CH_3{\cdot}CH_3$$

Dimethylboron chloride and methylboron dichloride produced only methane on being heated in sealed tubes with propionic acid at 150—160°, the yield of methane in both cases exceeding 98%, and the results being reproducible. Two experiments on methylboron dichloride containing a trace of boron trichloride produced 97·2% and 97·4% of the theoretical quantity of methane (the sample being assumed to have been pure CH_3BCl_2), *i.e.*, 2·7 ± 0·1% of boron trichloride was present as impurity.

It is therefore suggested that the reaction of propionic acid with methylboron chlorides can be used as a convenient method for the determination of alkyl groups in inseparable mixtures of boron trichloride and the two methylboron chlorides. Possible extension of the method to the analysis of methylboron fluoride mixtures [3] (where determination of the fluoride is difficult) and of methylated diboranes [3] is being investigated. Hydrolysis of the methylated diboranes by water produces the B–H content of the borane mixture as hydrogen, whereas reaction with propionic acid appears to yield both methane and hydrogen, so allowing a complete determination of the B–H and $B{-}CH_3$ groups in the mixture to be made.

Experimental.—The preparation of 1,2-bis(dichloroboryl)ethane has been described.[4]

Dimethylboron chloride was prepared by reaction of hydrogen chloride with trimethylboron in sealed tubes at 140—180°. In a typical experiment, trimethylboron (1·24 mmoles) and hydrogen chloride (2·45 mmoles) were heated at 140° for 7 hr.; the yield of methane was 0·47 mmole (38%). Further heating for 3 hr. at 180° produced another 0·635 mmole of methane. Fractionation of the material condensable at —112° yielded 1·02 mmoles of dimethylboron chloride (82%), of which 1·24 mmoles yielded 1·28 mequiv. of chloride ion on hydrolysis with water.

Methylboron dichloride was formed in 88% yield by heating boron trichloride (1·82 mmoles) and trimethylboron (0·91 mmole) at 450° for 12 hr.: $2BCl_3 + BMe_3 \longrightarrow 3BCl_2Me$, and 0·437 mmole of this on hydrolysis yielded 0·884 mequiv. of chloride ion (Calc.: 0·874 mequiv.).

Reaction of 1,2-*bis(dichloroboryl)ethane with propionic acid.* The results of four typical experiments are summarised in Table 1. Expts. 1 and 2 were conducted in the presence of ethylene glycol dimethyl ether, expts. 3 and 4 without solvent. Quantities are expressed in mmoles.

Reaction of hydrogen chloride with ethylene glycol dimethyl ether. Hydrogen chloride (1·89 mmoles) was sealed with ethylene glycol dimethyl ether (3 ml.) and heated at 140°; propionic acid (3 ml.) was added in order to simulate the conditions used in expts. 1 and 2 of Table 1. After 23 hr. the yield of methyl chloride was only 0·06 mmole: heating for a further 98 hr. at 150° increased the yield by 0·19 mmole; this contrasts with expt. 1 (Table 1) in which 0·42 mmole of methyl chloride was formed in only 30 hr. at 100°.

Reaction of propionic acid with methylboron dichloride and dimethylboron chloride. No ethylene

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[2] Holliday and Massey, *J.*, 1960, 2075.

[3] Duffy, Holliday, and Woodward, personal communication.

[4] Holliday and Massey, *J.*, 1960, 43.

glycol dimethyl ether was used in any of these experiments; three typical runs are summarised in Table 2. Quantities are again expressed in mmoles.

TABLE 1.

Experiment no.	1	2	3	4
Reaction time (hr.)	30	96	12	264
Reaction temp.	100°	150°	100°	140°
$C_2H_4B_2Cl_4$ used	1·19	1·56	1·86	1·01
Products: C_2H_6	0·05	0·37	0·08	0·99
C_2H_4	0·01	0·06	0·01	0·01
CH_4	trace	0·01	0·04	0·02
H_2	0·02	0·03	0·02	0·01
MeCl	0·42	1·82	0·00	0·00

TABLE 2.

Experiment no.	5			6		7	
x in $(CH_3)_xBCl_{(3-x)}$	2			1		1	
$(CH_3)_xBCl_{(3-x)}$ used	0·515			0·806		0·856	
Reaction temp.	160°			155—160°		155—160°	
Reaction time (hr.)	17·5	41·5	63·5	9·5	23·5	14	35
Methane removed	0·913	1·012	1·014	0·770	0·785	0·821	0·832
Ratio $CH_4 : (CH_3)_xBCl_{(3-x)}$	1·97 : 1			0·974 : 1		0·972 : 1	

The author thanks Dr. A. K. Holliday for his continued interest in this work and the Department of Scientific and Industrial Research for a maintenance grant.

THE UNIVERSITY, LIVERPOOL. [Received, May 26th, 1960.]

1016. *The Resolution of (±)-Propylenediamine by a Stereospecific Reaction.*

By H. IRVING and R. D. GILLARD.

IN a study of conformational effects on the stability constants of complex ions in solution we have prepared (±)- and (+)-propylenediaminetetra-acetic acid, $A_2N{\cdot}CHMe{\cdot}CH_2{\cdot}NA_2$ (pdta; A = $CH_2{\cdot}CO_2H$), and some of its metal derivatives. A recent paper by Dwyer and Garvan[1] has anticipated many of our results on the preparative side but the following example of a stereospecific reaction is new.

We find that racemic propylenediamine (pn) reacts with lævorotatory $[Co^{III}(+\text{-pdta})]^-$ to give dextrorotatory $[Co^{III}(+\text{-pn})_3]^{3+}$ from which (+)-propylenediamine can be isolated. A similar reaction has previously been noted with dextrorotatory $[Co(edta)]^-$ (where edta = ethylenediaminetetra-acetic acid).[2] Although there are differences between the infrared spectra of (±)-pdta and (+)[or (−)]-pdta which can be attributed to differences in hydrogen bonding in the solid state,[1] we find no such differences between the infrared spectra of their respective cobalt(III) complexes (measured as sodium salts in Nujol mulls), at least under the resolution employed, which suggests that the conformations of the anions are identical. This result agrees with Corey and Bailar's theory of chelate rings[3] which predicts no differences between molecules that are identical apart from having chelate rings formed by different optical antipodes.

Experimental.—Preparation of lævorotatory potassium (+)*-propylenediaminetetra-acetato-cobalt*(III) *trihydrate, lævorotatory* $K[Co(+\text{-pdta})],3H_2O$. Cobaltous chloride hexahydrate (0·6 g.), potassium acetate (4 g.), and (+)-propylenediaminetetra-acetic acid monohydrate [0·82 g.; from (+)-propylenediamine and chloroacetic acid) in water (12 ml.] were warmed to

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[1] Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1959, **81**, 2955.

[2] Kirschner, Yung Kang Wei, and Bailar, *J. Amer. Chem. Soc.*, 1957, **79**, 5877.

[3] Corey and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

30° and shaken while 3% hydrogen peroxide (8 ml.) was added gradually. Ethanol (8 ml.) was slowly added to the deep violet solution and the sides of the vessel were scratched until crystallisation began. The *salt*, lævorotatory $K[Co^{III}(+\text{-pdta})],3H_2O$ (1·01 g., 92% yield) separated and was recrystallised from water (10 ml.) by adding methanol and cooling (Found: Co, 12·8; C, 29·0; H, 4·15. $C_{11}H_{14}O_8N_2KCo,3H_2O$ requires Co, 13·0; C, 29·1; H, 4·4%).

Reaction between lævorotatory potassium (+)*-propylenediaminetetra-acetatocobalt*(III) *and* (±)*-propylenediamine.* The cobalt complex (0·65 g., 0·0015 mole), dissolved in water (5 ml.), was treated with a 100% excess of redistilled propylenediamine (0·83 ml., 0·009 mole) in water (2 ml.). The mixture was shaken at 25° for 5 min. during which the colour changed from violet to orange. After the mixture had been cooled in ice, 25% sodium iodide solution was added; scratching caused separation of dextrorotatory *tris-*(+)*-propylenediaminecobalt*(III) *iodide monohydrate* as orange-yellow crystals. These were collected, washed with acetone, and dried in the air (yield 0·9 g., 90%) (Found: C, 15·8; H, 4·85. $C_9H_{30}N_6CoI_3,H_2O$ requires C, 15·9; H, 4·7%). They had $[\alpha]_D^{20}$ +24·5° in 1% aqueous solution.

Recovery of (+)*-propylenediamine.* The cobaltammine (0·65 g.) was intimately mixed with sodium hydroxide (1 g.) and potassium metabisulphite (0·2 g.) and distilled over a free flame. The distillate was exactly neutralised to Methyl Red with 0·097N-hydrochloric acid (yield of diamine 50%); the rotation of the (+)-propylenediamine dihydrochloride was found to be $[\alpha]_D^{20}$ +4·2° (*c* 0·77 in H_2O) (lit.,[4] 3·9—4·1°).

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[4] Bailar, Jonassen, and Gott, *J. Amer. Chem. Soc.*, 1952, **74**, 3131.

1017. *Tetrakis*(*triphenylphosphine*)*-silver*(I) *and -copper*(I) *Complexes.*

By F. A. COTTON and D. M. L. GOODGAME.

ALTHOUGH considerable study has been made [1] of phosphine and arsine complexes of copper(I) and silver(I), no complexes containing four phosphine or arsine molecules bound to one of these metal ions seem to have been prepared.* We have now isolated several salts of the tetrakis(triphenylphosphine)-silver(I) and -copper(I) cations by using metal salts with anions having poor ligand properties, *viz.*, ClO_4^{1-}, BrO_3^{1-}, NO_3^{1-}. The only complexes of the type $[L_4Cu]^{1+}$ and $[L_4Ag]^{1+}$, where L is a ligand generally believed to engage significantly in π-bonding to the metal atom, are the tetrakis-(*p*-tolylisocyanide)-copper(I) and -silver(I) perchlorate [2] and some other copper(I) and silver(I) compounds of less certain structure [3] which may, however, contain tetrakis(isocyanide)-copper(I) and -silver(I) cations.

All the complexes reported are white, stable solids. The conductances (Table 1) of the compounds $[Ag(PPh_3)_4]X$ (X = ClO_4, BrO_3, NO_3) and $[Cu(PPh_3)_4]ClO_4$ in nitrobenzene and nitromethane show them to be, without doubt, uni-univalent electrolytes in view of the established ranges of molar conductances for such compounds.[4] The infrared spectra of anions (Table 2) in these tetrakis-complexes confirm this by demonstrating the presence of the free, unco-ordinated anions.

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* We were not aware of the work of Cochran, Hart, and Mann (*J.*, 1957, 2816) when writing this manuscript. These authors reported compounds of the type $\{[o\text{-}C_6H_4(PR_2)(AsR'_2)]_2Cu\}X$ and the corresponding silver compounds, which, while not exactly the sort reported here, are closely related to them. Our results do show, however, that chelation is not essential to the stability of such complex cations. We thank the Referee for calling the above reference to our attention.

[1] Mann, Purdie, and Wells, *J.*, 1936, 1503; Cass, Coates, and Hayter, *J.*, 1955, 4007; Ahrland and Chatt, *Chem. and Ind.*, 1955, 96; Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 276.

[2] Sacco, *Gazzetta*, 1955, **85**, 989.

[3] Klages, Mönkemeyer, and Heinle, *Chem. Ber.*, 1952, **85**, 109.

[4] Nyholm and his co-workers, *J.*, 1951, 38; 1956, 4375; 1959, 3447; *Nature*, 1959, **183**, 1039; Foss and Gibson, *J.*, 1949, 3063; Malatesta and Sacco, *Z. anorg. Chem.*, 1953, **373**, 248.

On treating copper nitrate with triphenylphosphine, we obtained, not the tetrakis-complex, but instead $(PPh_3)_2CuNO_3$. Its molar conductivity being nearly zero, the most reasonable structures to be considered for it are either a trico-ordinate monomer or a nitrate-bridged dimer. Unfortunately, it is too insoluble in suitable solvents to permit cryoscopic or ebullioscopic molecular-weight determinations. The presence of co-ordinated nitrate ion is amply demonstrated by the infrared spectrum. This may probably be taken to mean that the structure is tri-co-ordinate, monomeric, especially since nitrate bridging has not, to our knowledge, been demonstrated to occur. It may be noted, however, that a bridging nitrate, like a singly co-ordinated nitrate, will have C_{2v} symmetry and might thus have an infrared spectrum not fundamentally different from that of a singly co-ordinated nitrate.

Experimental.—*Tetrakis(triphenylphosphine)silver perchlorate.* A solution of silver perchlorate (1·55 g., 0·0067 mole) in hot absolute ethanol (4 ml.) was added to a solution of triphenylphosphine (7·87 g., 0·03 mole) also in hot ethanol (30 ml.). A colourless solid was immediately formed, and this was filtered off after the mixture had been cooled. The crude product recrystallized from acetonitrile (3 g. in 125 ml.), and the colourless crystals were washed with methanol and dried *in vacuo*; they had m. p. 290° (yield 77%) (Found: C, 69·1; H, 5·0; Ag, 8·7. $C_{72}H_{60}AgClO_4P_4$ requires C, 68·8; H, 4·8; Ag, 8·6%). The *compound* is insoluble in water, ethyl acetate, n-hexane, cyclohexane, carbon tetrachloride, di-isopropyl ether, and ligroin. It is slightly soluble on heating in the lower alcohols, butanol, acetone, ethyl methyl ketone, chloroform, benzene, toluene, chlorobenzene, nitrobenzene, nitromethane, 2-nitropropane, dioxan, acetonitrile, and dimethylformamide.

Tetrakis(triphenylphosphine)silver bromate. A solution of silver bromate (0·72 g., 0·00306 mole) in ammonia solution (*d* 0·880; 5 ml.) was added to one of triphenylphosphine (3·37 g., 0·0129 mole) in hot ethanol (25 ml.). The faint opalescence first formed disappeared on thorough mixing of the reactants. After a few minutes the clear solution yielded a white solid. The mixture was digested on a steam-bath for 45 min. and then stored overnight. The white solid was filtered off, washed twice with ethanol, and dried *in vacuo*; it had m. p. 160° (decomp.) (yield 3·53 g., 90%) (Found: C, 68·0; H, 4·8; P, 9·8. $C_{72}H_{60}AgBrO_3P_4$ requires C, 67·3; H, 4·7; P, 9·6%). The *compound* is soluble in nitrobenzene and slightly soluble in hot nitromethane and hot acetonitrile.

Tetrakis(triphenylphosphine)silver nitrate. A solution of silver nitrate (0·85 g., 0·005 mole) in hot acetonitrile (1 ml.) was added to one of triphenylphosphine (5·5 g., 0·021 mole) in hot absolute ethanol (14 ml.). After a few minutes colourless crystals began to separate. After several hours the solid product was filtered off, washed with ethanol, and dried *in vacuo*, then having m. p. 215° (yield theoretical) (Found: C, 71·7; H, 5·1; N, 1·36; P, 10·1. $C_{72}H_{60}AgNO_3P_4$ requires C, 70·9; H, 5·0; N, 1·15; P, 10·2%). The *compound* is readily soluble in nitrobenzene, nitromethane, and acetonitrile.

Tetrakis(triphenylphosphine)copper(I) *perchlorate.* A solution of cupric perchlorate (1·86 g., 0·005 mole) in absolute ethanol (5 ml.) was added to triphenylphosphine (6·55 g., 0·025 mole) in ethanol (25 ml.). A colourless solution was formed from which colourless crystals rapidly separated. These were filtered off, washed with ethanol, and dried *in vacuo* [m. p. 275° (decomp.); yield 5·96 g., 98%] (Found: C, 71·1; H, 5·1; Cl, 2·9; Cu, 5·3; P, 9·7. $C_{72}H_{60}CuClO_4P_4$ requires C, 71·3; H, 5·0; Cl, 2·9; Cu, 5·2; P, 10·2%). The *compound* recrystallized from absolute ethanol (2 g. in 65 ml.), the recovery being 65%. It is also soluble in nitromethane and in hot methanol, but insoluble in water.

Bis(triphenylphosphine)nitratocopper(I). A solution of cupric nitrate (1·82 g., 0·0075 mole) in hot methanol (10 ml.) was added to triphenylphosphine (8·25 g., 0·0315 mole) in hot ethanol (25 ml.). A colourless solution was obtained, and colourless needles separated on cooling. These were recrystallized from absolute ethanol (2 g. in 275 ml.), and colourless needles obtained in 50% recovery. The *compound* was washed with two portions of absolute ethanol and dried *in vacuo* (m. p. 237°); overall yield of pure product 28% (Found: C, 66·6; H, 4·6; Cu, 9·8; N, 2·2. $C_{36}H_{30}CuNO_3P_2$ requires C, 66·5; H, 4·65; Cu, 9·8; N, 2·15%). The compound is insoluble in water, very slightly soluble in benzene and ethylene dibromide, and soluble in hot alcohols, nitrobenzene, and nitromethane.

Electrolytic conductance. This was measured with a Serfass bridge. A conventional cell was used, previously calibrated with aqueous solutions of potassium chloride. The results are shown in Table 1.

TABLE 1. *Molar conductances of the complexes.*

Compound	Solvent	Temp.	Molar conductance (mho) for 10^{-3}M-solution
$[Ag(PPh_3)_4]ClO_4$	$Ph\cdot NO_2$	22·3°	27·9
$[Ag(PPh_3)_4]BrO_3$	$Ph\cdot NO_2$	25·7	16·6
$[Ag(PPh_3)_4]NO_3$	$Ph\cdot NO_2$	23·8	19·3
$[Cu(PPh_3)_4]ClO_4$	$Me\cdot NO_2$	24·8	89·3
$[Cu(PPh_3)_2]NO_3$	$Ph\cdot NO_2$	25·0	~0

Infrared absorption spectra. These spectra were obtained with a Perkin-Elmer 21 spectrophotometer, fitted with a rock-salt prism. Nujol mulls were used. The relevant data are shown in Table 2, together with reference data from the literature.

TABLE 2. *Infrared absorption spectra of the complexes and reference compounds.*

Compound	Absorption maxima (cm.$^{-1}$)	Ref.
$[Ag(PPh_3)_4]BrO_3$	805vs	
Ionic bromates	807—790vs	5
$[Ag(PPh_3)_4]NO_3$	1343vs	
Ionic nitrates	1450—1350s—vs, ~1050vw (or absent), 840—880vw—m	5, 6
$[Cu(PPh_3)_2]NO_3$	~1475m, 1275s, 1022s, 810m	
Co-ord. nitrate ($M\cdot O\cdot NO_2$)	1530—1480s—ms, 1290—1253s, 1035—970s, 820—780w—m	6, 7
$[Ag(PPh_3)_4]ClO_4$	1087vs	
$[Cu(PPh_3)_4]ClO_4$	1087vs	
Ionic perchlorates	1050—1150vs	5

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[5] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[6] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.
[7] Bannister and Cotton, *J.*, 1960, 2267.

1018. *π-Bonding in Tetrahedral Complexes.*

By F. A. COTTON.

IN view of the existence of many complexes of the tetrahedral $[ML_4]^{0,n+}$ type and interest in the nature of the metal–ligand bonding in them, it seems inportant that whatever information may be obtained from symmetry arguments concerning the bonding possibilities in such species be fully but correctly used. Since the question of how many M–L π-bonds may be formed is often of considerable importance, we here examine in somewhat more detail than can be found elsewhere the reasoning behind group-theoretical study of this question and, particularly, we note that statements to be found rather commonly in the literature concerning the number of π-bonds which may exist in tetrahedral complexes are often imprecise and sometimes incorrect.[1]

We assume that the central atom M in a tetrahedral complex, ML_4, has five *nd*, one $(n + 1)s$, and three $(n + 1)p$ orbitals in its valency shell and that each ligand atom, L, has an electron pair in a σ-orbital and two equivalent, empty *d*-orbitals. By the methods

[1] Although I had not, for personal reasons, intended to cite specific examples of the statements to which I refer, the Referees have suggested that a few such citations should be given. I have chosen the following impersonally and at random from the recent literature: Ahrland and Chatt, *Chem. and Ind.*, 1955, 96; Meriwether and Fiene, *J. Amer. Chem. Soc.*, 1959, **81**, 4207; Chatt and Hart, *J.*, 1960, 1382.

of elementary group theory,[2] the following results are obtained straightforwardly. The set of four ligand σ-orbitals spans the representations (of group T_d) A_1 and T_2, and the set of eight d-orbitals of the ligands spans the representations E, T_1, and T_2. The 9 valency-shell orbitals of the metal atom correspond to the irreducible representations in the following manner:

A_1: s
A_2: none
E: $(d_{z^2}, d_{x^2-y^2})$
T_1: none
T_2: (p_x, p_y, p_z) and (d_{xy}, d_{xz}, d_{yz})

This means that the possible combinations of metal orbitals which may hybridize to form orbitals useful for σ-bonding are

(*a*) s, p_x, p_y, p_z
(*b*) $s, d_{xy}, d_{xz}, d_{yz}$

while the sets of metal orbitals which are usable in π-bonding are

(*c*) $(d_{x^2-y^2}, d_{z^2}), (p_x, p_y, p_x)$
(*d*) $(d_{x^2-y^2}, d_{z^2})\ (d_{xy}, d_{xz}, d_{yz})$

From the above results it can be seen why the question of which metal orbitals, and how many, may be used in π-bonding does not have an unequivocal answer in the tetrahedral case. Both the σ- and the π-orbital sets require the use of T_2 orbitals, and the metal atom has two sets of T_2 orbitals, *viz.*, (p_x, p_y, p_z) and (d_{xy}, d_{xz}, d_{yz}). However, three cases may be considered.

(1) If the metal uses set (*a*) to form σ-bonds, then it can use set (*d*) to form π-bonds. In this event, *five π-interactions of equal strength* must occur. It can easily be shown, and has been,[3] that an E orbital (d_{z^2} or $d_{x^2-y^2}$) has the same overlap with the ligand π-orbitals as does a T_2 orbital (d_{xy}, d_{xz}, or d_{yz}). Hence, *if* the σ-orbitals are pure sp^3, all *five* d-orbitals contribute *equally* to the π-bonding providing we assume that, in the complex, their radial wave functions remain identical.

(2) At the other extreme, set (*b*) may be used for σ-bonding, whence only set (*c*) is available for π-bonding. We again have two π-interactions *via* the E type d-orbitals and now also three more *via* the p-orbitals. Naturally, these two sorts of metal π-orbitals will not in general interact to the same extent (per orbital) with the ligand π-orbitals, but there is no theoretical argument or computation known to us to justify the belief that the two d-orbitals will give strong π-bonds while the p-orbitals will give negligible ones.

(3) We may expect that in real complexes the σ- and π-hybridizations will be somewhere between the extremes considered under (1) and (2). In this case, there will still be the two E type d-orbitals to form π-bonds and then three more d–p-hybrids to form π-bonds. As noted under (2), there is not to our knowledge, any basis for assuming that the interaction of these d–p-hybrids with ligand π-orbitals must necessarily be negligible compared to that of the d_{z^2} and $d_{x^2-y^2}$ metal orbitals.

It is, of course, *possible* that in cases (2) and (3) the p-orbitals or the d–p-hybrids will overlap very poorly, relatively to the d_{z^2} and $d_{x^2-y^2}$ with ligand π-orbitals, and Kimball[4] seems to have made such an assumption although we cannot see that he gives any reason for so doing. $4d$- and $5d$-Orbitals and all s- and p-orbitals in the valency shells of transition-metal ions have radial nodes, and it is certainly not impossible that these might be so placed as to affect selectively some overlaps relative to others,[5] but our point is that there is no positive reason of which we are aware for assuming *a priori* that only two strong π-interactions may exist.

In cases where the π-bonding exists only to the extent of an average of $\frac{1}{2}$ π-bond or less

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[2] Eyring, Walter, and Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1949, especially Chapter 10 and section *d* of Chapter 12.

[3] Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

[4] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.

[5] We thank Professor W. R. Thorson for suggesting this factor.

per M–L link it is perhaps idle to entertain the question of whether there are two (or less) full π-bonds resonating among four positions, or whether there are more than 2, say n, π-interactions each having a strength equal to or less than $2/n$. It seems, however, that in the case of $[Fe(CO)_4]^{2-}$ the extremely low carbonyl stretching frequency (1788 cm.$^{-1}$ in the Raman spectrum [6]) suggests rather strongly that the metal–carbon π-bonding is far stronger than $\frac{1}{2}$ π-bond per M–C link. This, in turn, would show that more than 2 metal π-orbitals may interact strongly with the ligands and hence imply that smaller amounts of π-bonding in other compounds may be attributable to factors other than sheer inability of the metal atom to provide more than two suitable orbitals.

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[*Received, June 8th,* 1960.]

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[6] H. Stammreich, *et al.*, *J. Chem. Phys.*, 1960, **32**, 1482.

1019. *Synthesis of Potential Anti-cancer Agents. Part I. Benzaldehyde "Nitrogen Mustard" in the Knoevenagel Reaction.*

By FRANK D. POPP.

A RECENT note [1] reported the preparation of a series of compounds of type (I), including that derived from ethyl cyanoacetate and *p*-[*NN*-di-(2-chloroethyl)amino]benzaldehyde [2] (II). This ester was inactive against the Dunning leukæmia and non-toxic in the doses

$R{\cdot}CH{=}C(CN){\cdot}CO_2Et$ (I)

$p\text{-}(Cl{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}C_6H_4{\cdot}CHO$ (II)

$p\text{-}(Cl{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}C_6H_4{\cdot}CH{=}CRR'$ (III)

administrated.[3] Despite this, the aldehyde (II) has been used in the Knoevenagel reaction to afford a variety of compounds (III) listed in the Table, piperidine being used as catalyst. Preliminary screening tests show that the compounds obtained from malononitrile and cyanoacetamide are active at 2 mg./kg. (toxicity 25 mg./kg.) against the Dunning leukemia in rats.[3]

Compounds (III).

R	R′	M. p.	Yield (%)	Required (%)		Formula	Found * (%)	
				C	H		C	H
CN	CO_2Et	173—174·5° †	96					
CN	CO_2Me	167·5—168·5	88	55·1	4·9	$C_{15}H_{16}N_2O_2Cl_2$	55·1	4·9
CN	$CO{\cdot}NH_2$	191·5—192·5	68	53·9	4·8	$C_{14}H_{15}N_3OCl_2$	53·8	4·7
CN	CN	165—166	58	57·2	4·45	$C_{14}H_{13}N_2Cl_2$	57·3	4·5
CN	CO_2H	206—207	97	53·7	4·5	$C_{14}H_{14}N_2O_2Cl_2$	53·5	4·4
CO_2Et	CO_2Et	69—70	64	55·7	6·0	$C_{18}H_{23}NO_4Cl_2$	55·7	5·9

* By Spang Microanalytical Laboratory, Ann Arbor, Michigan. † Lit.,[1] 174—175°.

In attempts to condense benzyl cyanide with our aldehyde, only the aldehyde was recovered.

Experimental.—The author thanks Kay-Fries Chemicals, Inc., for gifts of methyl cyanoacetate, cyanoacetamide, and cyanoacetic acid, and Eastman Chemical Products, Inc., for a sample of *NN*-di-(2-hydroxyethyl)aniline.

Typical condensation. To a mixture of 2·46 g. (0·01 mole) of *p*-[*NN*-di-(2-chloroethyl)-amino]benzaldehyde [4] (2·46 g., 0·01 mole) and the reagent (0·01) containing active hydrogen in dry dioxan (15—25 ml.) at 0°, piperidine (~0·2 ml.) was added dropwise. After the mixture

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[1] Popp, *J. Org. Chem.*, 1960, **25**, 646.
[2] Anker and Cook, *J.*, 1944, 489.
[3] Dr. Ralph Jones, jun., personal communication.
[4] Elderfield, Covey, Geiduschek, Meyer, A. B. Ross, and J. H. Ross, *J. Org. Chem.*, 1958, **23**, 1749.

had been kept overnight at room temperature, crystals had been formed except in reactions of diethyl malonate and benzyl cyanide. For the malonate the mixture was concentrated *in vacuo* and benzene was added and distilled off to remove any water, the residue crystallizing. The *products* (see Table) were recrystallized from chloroform.

We acknowledge the assistance of S. Kotzen in the preparation of some of the aldehyde used. This work was supported in part by funds from an Institutional Grant of the American Cancer Society to the University of Miami and in part by a Research Grant (T 177) from the American Cancer Society.

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1020. *The Synthesis of α-Amino-β-1-pyrazolylpropionic Acid.*

By I. L. FINAR and K. UTTING.

THE amino-acid (VI) was isolated by Fowden, Noe, *et al.*[1] from *Citrullus vulgaris* (water melon) and synthesised by them in low yield by reaction between the silver salt of pyrazole and the methyl ester of β-chloroalanine hydrochloride. One possible synthetic approach to the acid seemed to be through oxidation of 1-2′-hydroxyethylpyrazole (I) to the corresponding aldehyde (II) followed by the Strecker reaction.

(I) R = $CH_2{\cdot}CH_2{\cdot}OH$
(II) R = $CH_2{\cdot}CHO$
(III) R = $CH_2{\cdot}CH{:}CH_2$
(IV) R = $CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$
(V) R = CH_2Cl,HCl
(VI) R = $CH_2{\cdot}CH(NH_2){\cdot}CO_2H$

Hydroxyethylhydrazine[2] was prepared by a modified method and treated with 1,1,3,3-tetraethoxypropane to yield 1-2′-hydroxyethylpyrazole, but attempts to oxidise this to the aldehyde failed. The preparation of this aldehyde was also attempted unsuccessfully by oxidation of 1-(1,2-dihydroxypropyl)pyrazole (IV) with periodic acid.[3] The dihydroxy-compound was prepared by hydroxylation[4] of 1-allylpyrazole (III) and also from 1,1,3,3-tetraethoxypropane and 3-hydrazinopropane-1,2-diol.[5]

A successful synthesis of the acid was carried out by using 1-chloromethylpyrazole hydrochloride (V) and diethyl sodioacetamidomalonate.

Experimental.—*2-Hydroxyethylhydrazine.*[2] To a cooled mixture of ethylene chlorohydrin (20·1 g., 0·25 mole), 100% hydrazine hydrate (25·0 g., 0·5 mole), and methanol (25 c.c.) was added dropwise, with cooling, sodium hydroxide (10·0 g., 0·25 mole) in water (15 c.c.), and the whole was kept overnight at room temperature. The precipitated sodium chloride was removed and the filtrate distilled to give 2-hydroxyethylhydrazine (11·6 g., 61%), b. p. 148—152°/30 mm.

1-2′-*Hydroxyethylpyrazole* (I). 2-Hydroxyethylhydrazine (13·2 g., 0·174 mole) and concentrated hydrochloric acid (32·5 c.c.) were mixed and cooled. 1,1,3,3-Tetraethoxypropane (38·3 g., 0·174 mole) and ethanol (35 c.c.) were then added. After refluxing for 1 hr. the mixture was cooled, basified with sodium carbonate (approx. 20 g.), and filtered. Distillation yielded 1-2′-*hydroxyethylpyrazole* (14·8 g., 76%), b. p. 129—131°/23 mm., n_D 1·5060 (Found: C, 53·5; H, 6·9; N, 25·3. $C_5H_8N_2O$ requires C, 53·6; H, 7·1; N, 25·0%). The alcohol yields the 3,5-*dinitrobenzoate* as needles (from benzene–ligroin), m. p. 99—100° (Found: N, 18·1. $C_{12}H_{10}N_2O_6$ requires N, 18·3%).

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[1] Fowden, Noe, Ridd, and White, *Proc. Chem. Soc.*, 1959, 131; Fowden and Noe, *Nature*, 1959, **184**, 69.
[2] Gabriel, *Ber.*, 1914, **47**, 3032; Gansser and Rumpf, *Helv. Chim. Acta*, 1953, **36**, 1430.
[3] Malaprade, *Bull. Soc. chim. France*, 1928, **43**, 683; Pyman and Stevenson, *J.*, 1934, 448.
[4] Witzemann, Evans, Hess, and Schroeder, *Org. Synth.*, Coll. Vol. II, 1943, p. 307.
[5] Freudenberg and Hess, *Annalen*, 1926, **448**, 126.

1-*Allylpyrazole* (III). A mixture of potassium hydroxide (5·6 g., 0·10 mole) in ethanol (50 c.c.), and pyrazole (6·8 g., 0·10 mole) in ethanol (20 c.c.), was set aside for 15 min. Allyl bromide (18·1 g., 0·15 mole) in ethanol (30 c.c.) was then added dropwise with cooling. After 1 hr. the mixture was refluxed for 1 hr. and filtered. Distillation yielded 1-*allylpyrazole* (7·0 g., 65%), b. p. 159°, n_D 1·4847 (Found: C, 66·5; H, 7·2; N, 26·3. $C_6H_8N_2$ requires C, 66·7; H, 7·4; N, 25·9%).

1-(1,2-*Dihydroxypropyl*)*pyrazole* (IV). (*a*) To 1-allylpyrazole (6·9 g., 0·064 mole) in water (100 c.c.), at 5°, was added dropwise with stirring a precooled solution of potassium permanganate (10·1 g., 0·064 mole) in water (190 c.c.), the temperature being kept below 6°. After 3 hr. the mixture was heated on the steam-bath for 1·25 hr. and then filtered. Evaporation to small bulk and distillation gave 1-(1,2-*dihydroxypropyl*)*pyrazole* (4·1 g., 45%), b. p. 124—126°/0·5 mm., n_D 1·5230 (Found: C, 50·6; H, 6·8; N, 19·9. $C_6H_{10}N_2O_2$ requires C, 50·7; H, 7·0; N, 19·7%).

(*b*) To 3-hydrazinopropane-1,2-diol hydrochloride[5] (7·0 g., 0·049 mole) in concentrated hydrochloric acid (10 c.c.) was added 1,1,3,3-tetraethoxypropane (10·8 g., 0·049 mole) in ethanol (10 c.c.). After 30 min., the solution was refluxed for 30 min., basified with sodium carbonate, and filtered. Distillation yielded the dihydroxypropylpyrazole (4·5 g., 64%) having the physical constants described above.

1-*Chloromethylpyrazole hydrochloride* (V). 1-Hydroxymethylpyrazole[6] (5·0 g., 0·05 mole) in dry chloroform (50 c.c.) was added dropwise to thionyl chloride (12·4 g., 0·104 mole) in chloroform (20 c.c.) at 0°. After 2 hr. at room temperature the excess of reagent and the solvent were removed under reduced pressure. The residue was washed with chloroform and dried *in vacuo*, to give 1-*chloromethylpyrazole hydrochloride* (6·3 g., 80%) (Found: Cl, 46·3. $C_4H_6Cl_2N_2$ requires Cl, 46·4%).

α-*Amino*-β-1-*pyrazolylpropionic acid* (VI). To sodium (1·5 g., 0·066 mole) dissolved in absolute ethanol (50 c.c.) was added diethyl acetamidomalonate[7] (14·3 g., 0·066 mole), and the mixture was set aside for 45 min., then cooled in ice and treated, dropwise with stirring, with 1-chloromethylpyrazole hydrochloride (4·3 g., 0·028 mole) in absolute ethanol (40 c.c.). After being kept at room temperature overnight, the solvent was removed under reduced pressure, and the residue dissolved in 4·6N-hydrochloric acid (150 c.c.) and extracted with ethyl acetate (2 × 60 c.c.). The solution was basified with sodium carbonate and extracted with ether (5 × 100 c.c.) which, after drying (Na_2SO_4), was evaporated to leave an oil which rapidly solidified. This solid was heated with concentrated hydrochloric acid (40 c.c.) for 5 hr. on the steam-bath, and the solution was then evaporated to dryness under reduced pressure. The residual oil was dissolved in water (10 c.c.), treated with charcoal, and brought to pH 5 with ammonia solution (*d* 0·880). Addition of two volumes of ethanol and cooling in ice gave α-amino-β-1-pyrazolylpropionic acid (2·6 g., 60%), m. p. 245—247° (decomp.) not depressed on admixture with an authentic specimen of the racemised L-acid (m. p. 247°). A paper chromatogram run on Whatman No. 4 filter paper with phenol–water (3 : 1 v/v) gave the same R_F value of 0·8 as an authentic sample and comparison of infrared spectra further confirmed the identity.

We thank Dr. Fowden for specimens of the naturally occurring L- and DL-amino-acid.

THE NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON, N.7. [*Received, June 14th*, 1960.]

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[6] Hüttel and Jochum, *Chem. Ber.*, 1952, **85**, 820.

[7] Tishler and Howe, U.S.P. 2,521,809/1950; Albertson and Archer, *J. Amer. Chem. Soc.*, 1945, **67**, 308; Jones, *ibid.*, 1949, **71**, 3994.

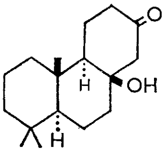
1021. *Oxidation Products of Manool.*

By P. K. Grant and R. Hodges.

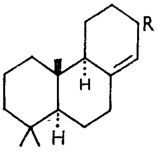
Oxidation of manool with potassium permanganate in acetone yielded, in addition to the compounds reported by Schenk *et al.*,[1] minute amounts of 8β-hydroxypodocarpan-13-one (I), first reported by Hosking.[2] Greatly increased yields of this compound were obtained by carrying the reaction out at 40°. On dehydration it gave podocarp-8(14)-en-13-one (II), identical with a sample prepared from isophyllocladene.[3] Reduction of the ketone with sodium borohydride gave podocarp-8(14)-ene-13α-ol (III) and its axial 13β-epimer, but hydrogenation over Adams catalyst in acetic acid gave the epimeric podocarpan-13α- and -13β-ol (IV), the proportion of axial epimer being increased by the acid conditions as expected. Chromic acid oxidation of podocarpan-13β-ol gave podocarpan-13-one (V).

The stereochemistry of compounds (I), (II), and (V) has been proved by rotatory dispersion measurements, the curves of (I) and (V) being identical with those of cholestan-3-one while that of (II) is similar to that of cholest-4-en-3-one.

Partial ozonolysis of manool in acetic acid gave, besides the ketone (VI), a substance whose infrared spectrum and mass spectrum were consistent with its formulation as (VII).

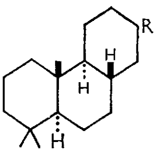


(I)



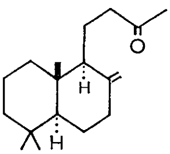
(II) R = :O

(III) R = OH

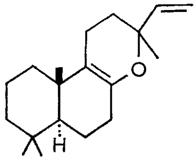


(IV) R = OH

(V) R = :O



(VI)



(VII)

Experimental.—M. p.s are corrected. Light petroleum had b. p. 60—80° unless otherwise stated. Alumina was B.D.H. grade " for chromatographic adsorption analysis."

8β-Hydroxypodocarpan-13-one (I). To manool (20·8 g.) in acetone (50 c.c.) at 40° potassium permanganate (66 g.) was added slowly until a faint pink colour persisted in the supernatant liquid. The acetone-soluble fraction was adsorbed on alumina from light petroleum; elution with 19 : 1 ether–acetone gave needles (0·9 g.) of the hydroxy-ketone. Recrystallisation from light petroleum and vacuum-sublimation gave material of m. p. 204—205° (lit., 198—199°,[2] 202—203° [4]), $\nu_{max.}$ (in Nujol) 3420 (OH), 1727 and 1686 (C=O) (reverting to 1722 in CCl_4), 1414 (" perturbed " CH_2) cm.$^{-1}$. A further quantity (0·05 g.) of this ketol was obtained from the manganese dioxide by working up as directed by Schenk *et al.*[1] and chromatographing the neutral fraction.

Podocarp-8(14)-en-13-one (II). Sulphuric acid (4 c.c.) was added dropwise to a solution of the ketol (0·5 g.) in methanol (75 c.c.), and the solution was heated to the b. p., then cooled, diluted, and extracted with ether. The αβ-unsaturated ketone (II) recrystallised from light petroleum (b. p. 40—60°) as needles (0·3 g.), m. p. 64—66° (lit.,[2] 71°) (Found: C, 82·7; H, 10·4. $C_{17}H_{26}O$ requires C, 82·9; H, 10·6%). Chromatography of the mother-liquor on alumina and elution with 19 : 1 light petroleum–ether gave a further quantity (0·1 g.). This ketone had $\nu_{max.}$ (in Nujol) 1657 (C=O), 1610 (C=C), 1419 (" perturbed " CH_2) cm.$^{-1}$, and gave a semicarbazone, m. p. 222—223° (from methanol) (lit.,[2] m. p. 212—213°), $\lambda_{max.}$ 269 mμ (log ε 4·46 in 95% EtOH).

Podocarp-8(14)-en-13-ol (III). The αβ-unsaturated ketone (0·2 g.) in methanol (10 c.c.) was treated with an excess of sodium borohydride, and the mixture was worked up as usual. Chromatography on alumina from a light petroleum solution and elution with 1 : 1 light

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[1] Schenk, Gutmann, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1952, **35**, 817; 1954, **37**, 543.

[2] Hosking, *Ber.*, 1936, **69**, 780.

[3] Grant and Hodges, *Tetrahedron*, 1960, **8**, 261.

[4] Jeger, Durst, and Buchi, *Helv. Chim. Acta*, 1947, **30**, 1853.

petroleum–ether gave the axial alcohol, podocarp-8(14)-en-13β-ol, m. p. 94—95° (after sublimation), followed by the 13α-*epimer*, m. p. 105—106° (after sublimation) (Found: C, 82·0; H, 11·1. $C_{17}H_{28}O$ requires C, 82·2; H, 11·4%), $\nu_{max.}$ (in Nujol) 3240 (OH), 1655 (C=C), 1002 (C–O *ax*) cm.$^{-1}$.

Podocarpan-13-*ol* (IV). The αβ-unsaturated ketone (II) (0·2 g.) in acetic acid (10 c.c.) was hydrogenated over Adams catalyst, 2 mols. being absorbed. Chromatography on alumina from a light petroleum solution and elution with 2 : 1 light petroleum–ether gave podocarpan-13β-ol (30 mg.), m. p. 155·5—156·5° (after sublimation), followed by the 13α-*alcohol* (120 mg.), m. p. 90—91° (after sublimation) (Found: C, 81·8; H, 12·4. $C_{17}H_{30}O$ requires C, 81·5; H, 12·1%), $\nu_{max.}$ (in Nujol) 3220 (OH), 1037 (C–O *eq*) or 999 (C–O *ax*) cm.$^{-1}$.

Podocarpan-13-*one* (V). Podocarpan-13β-ol (187 mg.) and chromium trioxide (100 mg.) in acetic acid (5 c.c.) were kept at room temperature for 18 hr. and worked up as usual. Chromatography on alumina from light petroleum and elution with 3 : 1 light petroleum–ether gave *podocarpan*-13-*one* as needles (120 mg.), m. p. 96—97° [after recrystallisation from light petroleum (b. p. 40—60°) and sublimation] (Found: C, 82·4; H, 11·2. $C_{17}H_{28}O$ requires C, 82·2; H, 11·4%), $\nu_{max.}$ (in Nujol) 1716 (C=O), 1423, 1413 (" perturbed CH_2 ") cm.$^{-1}$. The *semicarbazone* had m. p. 197—199° (from methanol) (Found: C, 70·4; H, 9·9; N, 13·7. $C_{18}H_{31}N_3O$ requires C, 70·78; H, 10·2; N, 13·8%).

Ozonolysis of manool. A stream of ozonised oxygen (2%) was passed through a solution of manool (1 g.) in acetic acid (25 c.c.) for 10 min. After decomposition of the ozonides by water on a steam-bath (15 min.), the products were adsorbed from light petroleum on alumina (50 g.). Elution with light petroleum gave the ketone (VII) (85 mg.) as prisms (from methanol–chloroform), m. p. 47·5—48° [Found: C, 82·9; H, 11·5%; *M* (mass spectrometric) 274 ± 2. $C_{19}H_{30}O$ requires C, 83·15; H, 11·0%; *M*, 274], $\nu_{max.}$ 1650 (C=O), 990, 923 ($CH{=}CH_2$) cm.$^{-1}$. Further elution with benzene–light petroleum (1 : 3) gave the ketone (VI) as an oil (120 mg.), $\nu_{max.}$ 1722 (C=O), 1650 (C=C), 890 ($C{=}CH_2$) cm.$^{-1}$, whose semicarbazone had m. p. 190—192° (lit.,[1] m. p. 191·5—193°) (Found: C, 71·2; H, 10·15; N, 13·2. Calc. for $C_{19}H_{33}N_3O$: C, 71·45; H, 10·4; N, 13·15%).

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1022. *Dialkyldithiocarbamate Complexes of Rhenium*(III).

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DIALKYLDITHIOCARBAMATE complexes are known for many transition metals,[1] but so far no such compounds have been reported for rhenium. Rhenium trichloride in acetone solution has been found to react on being shaken with the alkali-metal salts of several dialkyldithiocarbamates. The compounds are obtained as stable brown crystals, which decompose above 150° without melting, readily soluble in acetone and alcohol, rather less soluble in chloroform and nitrobenzene, but insoluble in water, ether, and benzene. We have been unable to obtain completely satisfactory molecular weights in solution but the products appear to be monomeric. Complexes are formed with the sodium and the potassium salts of dimethyl-, diethyl-, dibutyl-, and pentamethylene-dithiocarbamates and have the general formula $ReCl_2(NR_2{\cdot}CS_2)$. This stoicheiometry is unusual, as most tervalent transitional metals give complexes with the general formula $M(NR_2{\cdot}CS_2)_3$. The rhenium complexes are diamagnetic, non-electrolytes in nitrobenzene, and are best formulated as monomeric tetrahedral complexes of rhenium(III) with the d^3s-hybridisation previously suggested for the $(ReCl_4)^-$ ion [2] and $ReCl_3P(C_6H_5)_3$.[3]

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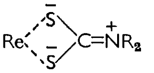
[1] Chatt, Duncanson, and Venanzi, *Suomen Kem.*, 1956, **29**, *B*, 75, where references to earlier literature are given.

[2] Nyholm, 10^e Conseil de l'Institut International de Chimie, Solvay, 1956.

[3] Colton, Levitus, and Wilkinson, *J.*, 1960, 4121.

The infrared spectra of the complexes in chloroform solution show a strong peak at about 1500 cm.$^{-1}$ which is probably due to contributions from ionic canonical forms such as that inset. Chatt and his co-workers[1] have discussed the position of this band for a number of transition-metal dialkyldithiocarbamates and obtained some correlation between the position of the band and the stereochemistry of the molecules. Thus for tetrahedral complexes the band is at about 1500 cm.$^{-1}$, and the present rhenium complexes show a band at the same position.



Experimental.—Rhenium trichloride[4] (0·3 g.) was dissolved in acetone (30 ml.), an acetone solution of excess of the alkali-metal salt of the dialkyldithiocarbamate (0·003 mole) slowly added, and the mixture shaken at room temperature for about an hour. The resultant brown solution was filtered from the precipitated alkali halide, and the solvent removed at 0·1 mm./20°. The rhenium complex was extracted with chloroform from the residue, which contained the excess of the alkali dialkyldithiocarbamate, and the operation repeated twice.

Typical preparations were *diethyl-* (Found: C, 14·9; H, 2·5; N, 3·7; Cl, 17·2. $C_5H_{10}NS_2ReCl_2$ requires C, 14·8; H, 2·5; N, 3·5; Cl, 17·5%) and *dimethyl-dithiocarbamatorhenium dichloride* (Found: C, 9·8; H, 1·8; N, 3·9; Cl, 18·3. $C_3H_6NS_2ReCl_2$ requires C, 9·5; H, 1·6; N, 3·7; Cl, 18·5%).

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[4] Geilman, Wrigge, and Biltz, *Z. anorg. Chem.*, 1933, **214**, 244.