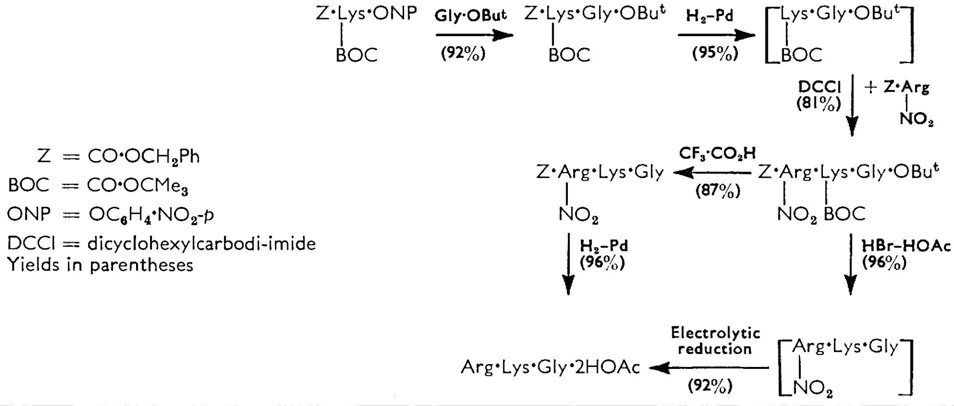
NOTES.

127. *Amino-acids and Peptides. Part XXII.*[1] *Synthesis of* N^{α}-L-*Arginyl*-L-*lysylglycine.*

By K. B. WALSHAW and G. T. YOUNG.

A NUMBER of peptides closely related to glutathione have been isolated from calf lens,[2] and a further investigation[3] gave electrophoretic evidence of the presence of a basic tripeptide thought to be arginyl-lysylglycine. We have synthesised this compound at the suggestion of Dr. S. G. Waley, who reports that in electrophoretic behaviour it differs from the unknown peptide present in calf lens extracts. The synthetic scheme is shown below.* The new method[1] using electrolytic reduction for the removal of the nitro-group from nitroarginine and nitroarginyl peptides proved to be satisfactory in this case also.



Z = $CO{\cdot}OCH_2Ph$
BOC = $CO{\cdot}OCMe_3$
ONP = $OC_6H_4{\cdot}NO_2$-*p*
DCCI = dicyclohexylcarbodi-imide
Yields in parentheses

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* The abbreviations for the amino-acid residues are those in the " Tentative Rules for Abbreviations and Symbols for Chemical Names of Special Interest in Biological Chemistry " (Appendix B to Information Bulletin No. 12, I.U.P.A.C.), and their mode of use in formulating intermediates are those recommended in " Peptides. Proc. Fifth European Peptide Symp., Oxford, 1962," ed. G. T. Young, Pergamon Press, Oxford, 1963, p. 261.

[1] Part XXI, P. M. Scopes, K. B. Walshaw, M. Welford, and G.T. Young, preceding Paper.

[2] S. G. Waley, *Biochem. J.*, 1956, **64**, 715; 1957, **67**, 172; 1958, **68**, 189; 1959, **71**, 132.

[3] D. H. Calam, *Exp. Eye Res.*, 1962, **1**, 436; D. H. Calam and S. G. Waley, *Biochem. J.*, 1964, **93**, 526.

Experimental.—Melting points were determined on a Kofler hot-stage apparatus, and optical rotations on an Ericsson automatic polarimeter. Paper chromatography was by descending flow on Whatman No. 4 paper, using as solvents " BWA " : butan-1-ol–water–acetic acid (62 : 26 : 12 by volume, freshly mixed), and " PW " : phenol saturated with water. Paper electrophoresis was on a hanging-strip, at 17v/cm. Evaporation was by rotary evaporator and solutions in organic solvents were dried over $MgSO_4$.

N^{α}-*Benzyloxycarbonyl*-N^{ϵ}-*t-butoxycarbonyl*-L-*lysylglycine t-butyl ester.* To N^{α}-benzyloxycarbonyl-N^{ϵ}-*t*-butoxycarbonyl-L-lysine *p*-nitrophenyl ester [4] (11·7 g.) in ethyl acetate (70 ml.) was added glycine t-butyl ester (3·0 g.). After 3 days at room temperature the mixture gave a negative ninhydrin test, and the solution was washed with N-ammonium hydroxide, water, ice-cold citric acid solution, and water, and dried. The residue obtained by evaporation was recrystallised from ether–light petroleum (b. p. 40—60°), giving the *protected dipeptide ester* (10·5 g., 92%), m. p. 67—68° (softening at 64°), $[\alpha]_D^{23}$ $-13·5$ (*c* 2·1 in MeOH) (Found, after drying at 20°/0·05 mm.: C, 60·7; H, 7·9; N, 8·8. $C_{25}H_{39}N_3O_7$ requires C, 60·8; H, 7·95; N, 8·5%).

N^{α}-(N^{α}-*Benzyloxycarbonyl*-N^{ω}-*nitro*-L-*arginyl*)-N^{ϵ}-*t-butoxycarbonyl*-L-*lysylglycine t-butyl ester.* A solution of the above protected dipeptide ester (1·0 g.) in absolute methanol (25 ml.) was hydrogenated for 48 hr. in the presence of palladium–charcoal (10%; 1·0 g.). The catalyst was filtered off, and evaporation of the filtrate left a colourless oil (700 mg., 95%), R_F 0·95 (BWA), 0·96 (PW) (one ninhydrin-positive spot only). The oil was taken up in dichloromethane (10 ml.) and added to a suspension of N^{α}-benzyloxycarbonyl-N^{ω}-nitro-L-arginine (880 mg.) in dichloromethane (10 ml.); a solution of dicyclohexylcarbodi-imide (500 mg.) in dichloromethane (10 ml.) was added, and stirring was continued for 12 hr. at 20°. The dicyclohexylurea was filtered off, the filtrate was evaporated, and the residue was taken up in ethyl acetate and washed (ice-cold citric acid, water, sodium hydrogen carbonate, saturated brine) and dried. The solution was concentrated and cooled to 0°, when a gel separated (1·1 g., 81%). The product was crystallised several times from acetonitrile, giving the *protected tripeptide ester*, m. p. 87—88° (softening at 84°), $[\alpha]_D^{22}$ $-16°$ (*c* 1·9 in MeOH) (Found, after drying at 50°/0·05 mm.: C, 53·4; H, 7·5; N, 15·7. $C_{31}H_{50}N_8O_{10}$ requires C, 53·6; H, 7·3; N, 16·1%).

N^{α}-(N^{α}-*Benzyloxycarbonyl*-N^{ω}-*nitro*-L-*arginyl*)-L-*lysylglycine.* The above protected tripeptide ester (350 mg.) was dissolved in trifluoroacetic acid (7 ml.; distilled from sulphuric acid). After 1 hr. at 20°, the solution was evaporated to dryness, and the residue was taken up in 20% acetic acid. The solution was passed through a column of Dowex-3 acetate resin (8 g.), and the eluate was evaporated to dryness at 20°/0·05 mm., leaving a glass which dissolved readily in methanol to give a yellow solution from which the *compound* separated as a white powder almost immediately (260 mg., 87%), m. p. 206—208°, R_F 0·54 (BWA), 0·94 (PW) (one ninhydrin-positive spot only); $[\alpha]_D^{16}$ $-11·5°$ (*c* 1·0 in 95% acetic acid) (Found, after drying at 20°/0·05 mm.: C, 49·35; H, 6·2; N, 20·4. $C_{22}H_{34}N_8O_8$ requires C, 49·0; H, 6·4; N, 20·8%).

N^{α}-L-*Arginyl*-L-*lysylglycine.* (*a*) *By hydrogenation.* N^{α}-(N^{α}-Benzyloxycarbonyl-N^{ω}-nitro-L-arginyl)-L-lysylglycine (375 mg.) in 50% acetic acid was hydrogenated for 36 hr. in the presence of palladium–charcoal (10%; 370 mg.). The catalyst was filtered off, and the filtrate was evaporated to dryness, leaving a glass (320 mg., 96%) which gave a single ninhydrin-positive spot on paper chromatography and on paper electrophoresis at pH 6; R_F 0·28 (BWA), 0·85 (PW). The *tripeptide diacetate* was dissolved in warm methanol and precipitated as a solid by ether, but could not be crystallised; $[\alpha]_D^{23}$ $-5°$ (*c* 1·0 in MeOH) (Found, after drying at 20°/0·05 mm.: C, 43·7; H, 8·15; N, 19·6. $C_{18}H_{37}N_7O_8,H_2O$ requires, C, 43·45; H, 7·9; N, 19·7%).

The *tripeptide di-*(O-p-*toluoyl*)-D-*tartrate* was prepared directly from the diacetate in methanol solution; ether was added until cloudiness appeared, and then cooling to 0° gave an oil which was separated by decantation and redissolved in warm methanol; on pouring this solution into a large volume of ether a gelatinous suspension was formed, which on standing changed to a white powder, m. p. 166—168° (Found, after drying at 110°/0·05 mm.: C, 51·7; H, 6·6; N, 12·65. $C_{34}H_{47}N_7O_{12},2H_2O$ requires C, 52·2; H, 6·6; N, 12·5%). Dr. S. G. Waley informs us that the tripeptide diacetate moved ahead of the suspected arginyl-lysylglycine from calf lens [3] during electrophoresis at pH 4.

(*b*) *By electrolytic reduction.* N^{α}-(N^{α}-Benzyloxycarbonyl-N^{ω}-nitro-L-arginyl)-N^{ϵ}-t-butoxycarbonyl-L-lysylglycine t-butyl ester (500 mg.) was treated with 2·3N-hydrogen bromide in

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[4] R. Schwyzer and W. Rittel, *Helv. Chim. Acta*, 1961, **44**, 159.

acetic acid at room temperature for 30 min. in the usual manner;[1] the solid nitro-L-arginyl-L-lysylglycine (320 mg., 96%) obtained by evaporation of the eluate from a Dowex-3 acetate column could not be crystallised and was very hygroscopic, but paper chromatography showed it to be homogeneous; R_F 0·09 (BWA), 0·79 (PW). It was reduced electrolytically as described in Part XXI,[1] 200 mg. requiring 2 hr. at 0·2 amp. The L-arginyl-L-lysylglycine diacetate (190 mg., 92%) was obtained by evaporation of the eluate from a Dowex-3 acetate column, and was reprecipitated from methanol by ether as a homogeneous, hygroscopic white powder, identical in chromatographic and electrophoretic behaviour with that obtained by hydrogenation.

We are grateful to the D.S.I.R. for a Grant for a Special Research and for a Research Studentship (held by K. B. W.), and to Miss L. Williams for technical assistance.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. *[Received, July 2nd, 1964.]*

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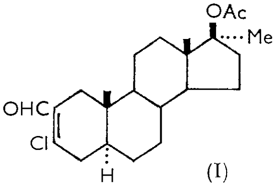
128. *The Formylation of Steroidal Ketones with Phosphorus Oxychloride and Dimethylformamide.*

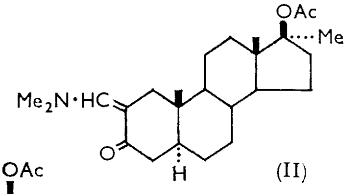
By G. W. MOERSCH and (MISS) W. A. NEUKLIS.

WE have previously reported[1] that steroidal Δ^4-3-ketones react with phosphorus oxychloride and dimethylformamide[2] to produce 3-chloro-3,5-dienes. Use of this reagent with saturated steroidal ketones yields products[3] having the β-chloroacraldehyde structure assigned to simpler examples by Ziegenbein[4] and by Arnold and their co-workers.[5]

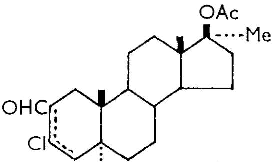
We report here several features of our own experience with this reagent which do not clearly appear in the French workers' abstract.[3] We have been able, in a 5α-androstane, to demonstrate that the product possesses the 3-chloro-2-formyl-Δ^2-system. The reaction with 17β-acetoxy-17α-methyl-5α-androstan-3-one can be carried out to yield an intermediate dimethylaminomethylene-3-ketone (II), which is also obtained from the reaction of dimethylamine with 17β-acetoxy-2-hydroxymethylene-17α-methyl-5α-androstan-3-one.



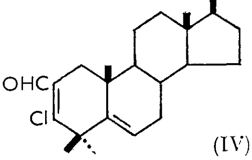
(I)



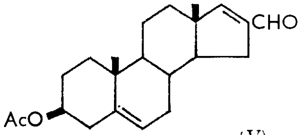
(II)



(III)



(IV)



(V)

Since the intermediate dimethylamino-compound can be converted into the formyl derivative with phosphorus oxychloride, the latter is assigned the structure 17β-acetoxy-3-chloro-2-formyl-17α-methyl-5α-androst-2-ene (I). The position of the double bond is assigned from the spectral requirement for an αβ-unsaturated carbonyl system and from the absence of a vinylic proton peak in the nuclear magnetic resonance (n.m.r.) spectrum.

We have also obtained analogous monoformylated products by reaction of the phosphorus oxychloride–dimethylformamide reagent with 4,4-dimethyl-androst-5-ene-3-one, and with

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[1] Moersch and Neuklis, *Canad. J. Chem.*, 1963, **41**, 1627.

[2] Vilsmeier and Haack, *Ber.*, 1927, **60**, 119.

[3] Schmitt, Panouse, Hallot, Cornu, Pluchet, and Comoy, Internat. Congress of Pure and Appl. Chem., 1963, Abstract A, A9–54, p. 339.

[4] Ziegenbein and Lang, *Chem. Ber.*, 1960, **93**, 2743.

[5] Arnold and Zemlička, *Proc. Chem. Soc.*, 1958, 227.

3β-acetoxyandrost-5-en-17-one. However, the use of a large excess of the reagent on 17β-acetoxy-17α-methyl-5α-androstan-3-one gave a 2,4-diformyl-3-chloro-system (III), in which the unsaturation is in either position 2 or 3.

Experimental.—Ultraviolet spectra were measured for methanol solutions, unless otherwise indicated, on a Cary double-beam recording spectrophotometer. Infrared spectra were determined in KBr discs or in solution (as indicated), with a Beckman IR-7 instrument. Only the principal absorptions are cited. N.m.r. data were obtained, with a Varian A-60 spectrometer, for deuterochloroform solutions. Resonances are reported as p.p.m. downfield from tetramethylsilane used as internal reference. M. p.s were determined in capillary tubes. $[\alpha]_D$'s are for $CHCl_3$ solutions.

17β-*Acetoxy*-3-*chloro*-2-*formyl*-17α-*methyl*-5α-*androst*-2-*ene* (I). Phosphorus oxychloride (7·8 ml.) was treated with dimethylformamide (DMF) (9 ml.) with stirring at 0°. To this reagent, at room temperature, was added 17β-acetoxy-17α-methyl-5α-androstan-3-one (17 g.) in DMF (170 ml.) during 15 min. Stirring was continued for another 15 min. until all the solid had dissolved. The mixture was warmed at 50—55° for 3·5 hr., cooled, and poured into ice–water. The precipitated yellow solid was separated, washed with water, and dissolved in benzene. The solution was washed with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and evaporated under reduced pressure to a yellow oil. Three crystallizations from aqueous ethanol gave the *formyl compound* (I), tan crystals (5·2 g., 27%), m. p. 143—144° (corr.), $\lambda_{max.}$ (Et_2O) 249 mμ (ε 13,700), $\nu_{max.}$ (KBr) 2765, 1725, 1667, 1621 cm.$^{-1}$, n.m.r. peaks at 0·72, 0·82, 1·38, 1·90, 10·2 δ, $[\alpha]_D^{24}$ +101° (*c* 0·545) (Found: C, 70·4; H, 8·5; Cl, 9·1. $C_{23}H_{33}ClO_3$ requires C, 70·3; H, 8·45; Cl, 9·0%).

17β-*Acetoxy*-2-*dimethylaminomethylene*-17α-*methyl*-5α-*androstan*-3-*one* (II). (*a*) A solution of 17β-acetoxy-17α-methyl-5α-androstan-3-one (5·0 g.) in DMF (50 ml.) was added to a reagent prepared from phosphorus oxychloride (9·0 ml.) and DMF (10 ml.), stirred at room temperature for 10 min., and poured on to a mixture of ice and aqueous sodium hydrogen carbonate. A yellow gum precipitated and was separated by decantation and dissolved in benzene. The solution was washed with water, dried ($MgSO_4$), filtered, and evaporated at 50° to a yellow gum which gave crystals (1·94 g., 34%) from ether–hexane. Further crystallization gave the *dimethylaminomethylene derivative*, needles, m. p. 199—201° (from ether–hexane), $\lambda_{max.}$ 333 mμ (ε 21,400), $\nu_{max.}$ (KBr) 1734, 1651, 1542 cm.$^{-1}$, $[\alpha]_D^{24}$ −225° (*c* 0·53), n.m.r. peaks at 0·84, 0·87, 1·40, 1·95, 3·08, 7·52 δ (Found: C, 74·6; H, 9·6; N, 3·5. $C_{25}H_{39}NO_3$ requires C, 74·75; H, 9·8; N, 3·5%).

(*b*) 17β-Acetoxy-2-hydroxymethylene-17α-methyl-5α-androstan-3-one [6] (2·5 g.) in benzene (140 ml.) was treated [7] with dimethylamine (1·5 ml.) and set aside at room temperature for 1 hr. Another 1·5 ml. of dimethylamine was added and the solution was set aside for a further hour. Evaporation under reduced pressure gave a yellow oil which was extracted with hot hexane (30 ml.). Concentration and cooling of the extract gave yellow crystals (1·5 g., 54%) which yielded the dimethylaminomethylene derivative (0·6 g.), m. p. 199—202° (corr.) (from ether–hexane) identical (mixed m. p., and infrared, ultraviolet, and n.m.r. spectra) with the product obtained in (*a*) (Found: C, 74·9; H, 9·9; N, 3·5%).

Conversion of the ketone (II) *into the formyl compound* (I). The ketone (1 g.) in benzene (40 ml.) was treated with phosphorus oxychloride (3 ml.) and the mixture refluxed for 35 min., cooled, and shaken with a saturated solution of sodium acetate. The benzene layer was separated and evaporated at 50° to a gummy residue which was dissolved in benzene. The solution was washed with 3N-hydrochloric acid, water, saturated sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), and evaporated to a pale yellow solid (0·8 g.). Crystallization twice from hexane gave the ester (I) (0·25 g.), m. p. 143—144° (corr.), identical (mixed m. p., and infrared, ultraviolet, and n.m.r. spectra) with the product prepared above (Found: C, 70·25; H, 8·3; Cl, 9·15%).

17β-*Acetoxy*-3-*chloro*-2,4-*diformyl*-17α-*methyl*-5α-*androst*-2(*or* 3)-*ene* (III). A solution of 17β-acetoxy-17α-methyl-5α-androstan-3-one (10 g.) in DMF (100 ml.) was added with stirring to a reagent prepared from phosphorus oxychloride (20·4 ml.) and DMF (24 ml.). The mixture was warmed at 50—55° for 18 hr., poured on to ice, treated with an excess of aqueous sodium

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[6] Palmer, *J.*, 1963, 3901.

[7] Arnold and Zemlička, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2378.

acetate solution on a steam-bath for 20 min., and filtered. The solid product was washed with water, sucked dry, and dissolved in benzene. The solution was washed with 3N-hydrochloric acid until the washings were colourless, sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), and evaporated to a gummy yellow solid. Trituration with hexane and filtration gave 5·1 g. of yellow solid which yielded the *diformyl compound* (1·0 g.), m. p. 192—193° (from ether–hexane), $\lambda_{max.}$ (MeOH–KOH) 408, 254 mμ (ε 40,000, 5000), $\lambda_{max.}$ (Et_2O) 312, 250 mμ (ε 3400, 9500), $\nu_{max.}$ (KBr) 2735, 1735, 1725sh, 1670, 1622 cm.$^{-1}$, $\nu_{max.}$ ($CHCl_3$) 2735, 1736, 1682, 1626 cm.$^{-1}$ (Found: C, 68·4; H, 7·85; Cl, 8·45. $C_{24}H_{33}ClO_4$ requires C, 68·45; H, 7·9; Cl, 8·4%).

The *dioxime*, prepared using hydroxylamine hydrochloride and sodium hydrogen carbonate by refluxing in ethanol and a little water, had m. p. 204° (decomp.) (from aqueous methanol), $\lambda_{max.}$ 250 mμ (ε 19,600), $\nu_{max.}$ (KBr) 3330, 1705, 1632 cm.$^{-1}$, $\nu_{max.}$ ($CHCl_3$) 3596, 3250, 1724, 1630 cm.$^{-1}$ (Found: C, 62·25; H, 8·05; Cl, 7·45; N(Kjeldahl), 5·75. $C_{24}H_{35}ClNO_4,CH_3OH$ requires C, 62·15; H, 8·15; Cl, 7·35; N, 5·8%).

17β-*Acetoxy*-3-*chloro*-2-*formyl*-4,4-*dimethylandrosta*-2,5-*diene* (IV). An ice-cold solution of 17β-acetoxy-4,4-dimethylandrost-5-en-3-one (1·79 g.)[8] in DMF (20 ml.) was added over 10 min. to a reagent prepared from DMF (5·9 ml.) and phosphorus oxychloride (5·65 ml.), stirred for 4 hr. at 50—60°, and poured, with stirring, on to ice and dilute sodium hydrogen carbonate. The precipitated solid was filtered off, washed with water, and dried *in vacuo* to yield the *dimethyl derivative* (1·25 g.), m. p. 176—177° (from ethanol), $\lambda_{max.}$ (MeOH–KOH) 256 mμ (ε 9700), $\lambda_{max.}$ (Et_2O) 254 mμ (ε 11,000), $\nu_{max.}$ (KBr) 2720, 1745, 1679, 1622 cm.$^{-1}$ (Found: C, 71·15; H, 8·3; Cl, 8·75. $C_{24}H_{33}ClO_3$ requires C, 71·2; H, 8·2; Cl, 8·75%). The compound gave a negative ferric chloride test.

3β-*Acetoxy*-17-*chloro*-16-*formylandrosta*-5,16-*diene* (V). Phosphorus oxychloride (57 ml.) was stirred under nitrogen at 0° and treated dropwise with DMF (60 ml.). The ice-bath was removed and stirring continued for 10 min. A solution of 3β-acetoxyandrost-5-en-17-one in DMF (160 ml.) was added in a steady stream. The mixture was heated at 60° for 3 hr., cooled, poured slowly on to ice, and diluted with water. The crude product was collected on a filter, washed well with dilute aqueous sodium hydrogen carbonate and water to give the *aldehyde* (13·21 g., 69%), m. p. 180—181° (corr.) (from aqueous acetone), $\lambda_{max.}$ (Et_2O) 254 mμ (ε 13,500), $\lambda_{max.}$ 259 mμ (ε 11,400), $\nu_{max.}$ (KBr) 2730, 1734, 1679, 1592 cm.$^{-1}$, $[\alpha]_D^{24}$ −137° (*c* 0·52) (Found: C, 70·15; H, 7·9; Cl, 9·65. $C_{22}H_{29}ClO_3$ requires C, 70·1; H, 7·75; Cl, 9·5%).

A solution of the aldehyde (V) (0·25 g.) in anhydrous tetrahydrofuran (7 ml.) was refluxed with hydrazine (0·1 ml.) for 5 hr. and evaporated under reduced pressure to a white solid which gave the *hydrazone* white needles, m. p. 182—183° (from methanol) (Found: C, 67·55; H, 8·05; Cl, 9·10; N, 7·25. $C_{22}H_{31}ClN_2O_2$ requires C, 67·6; H, 8·0; Cl, 9·05; N, 7·15%).

The elemental analyses were performed by Mr. C. E. Childs and the staff of our Microanalytical Laboratory; the spectra and rotations were determined by Dr. J. M. Vandenbelt and the staff of our Physical Chemistry Laboratory; n.m.r. data were obtained by Mr. R. B. Scott in our Physical Chemistry Laboratory. We are indebted also to Dr. L. M. Long for his support of this work.

PARKE, DAVIS AND COMPANY, RESEARCH LABORATORIES,
ANN ARBOR, MICHIGAN, U.S.A.

[*Received, January 20th*, 1964.]

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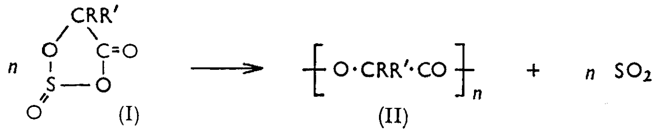
[8] Ringold and Rosenkranz, *J. Org. Chem.*, 1957, **22**, 606.

129. *Polyesters from the Anhydrosulphites of α-Hydroxy-acids.*

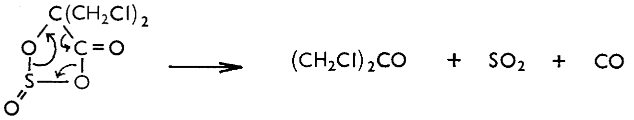
By J. B. Rose and C. K. Warren.

Blaise [1] prepared the anhydrosulphite (Ia) by treating α-hydroxyisobutyric acid with thionyl chloride and showed that thermal decomposition of this compound gave sulphur dioxide and the polyester (IIa). This reaction was examined in greater detail by Alderson [2] who developed improved experimental techniques to obtain polymers of high molecular weight. We have investigated the scope of this reaction by preparing compounds (Ib—e), and comparing their thermal decompositions with that of (Ia). We could not obtain pure samples of (If) or (Ig) and isolated only α-chloro-αα-diphenylacetic acid from the reaction between benzilic acid and thionyl chloride.

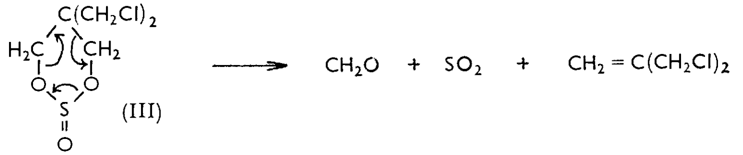


I and II	a	b	c	d	e		g
R	Me	Me	Et	Me	CH_2Cl	H	$[CH_2]_5$
R′	Me	Et	Et	CH_2Cl	CH_2Cl	H	

Polymers of high molecular weight were readily obtained from (Ia) by following Alderson's procedure, and using chlorobenzene as the solvent. The other purified anhydrosulphites (Ib—d) gave polymers of lower molecular weight, as indicated by solution viscosity measurements, while the impure compounds (If and Ig) gave polymers of very low molecular weight. The bischloromethyl derivative (Ie), which is crystalline, gave low yields of polymer when heated (30% at most), the greater proportion of (Ie) being decomposed to give sulphur dioxide, carbon monoxide, and *sym*-dichloroacetone by a fragmentation process which may be formulated thus:



A similar pattern of reactivity has been observed in the pyrolysis of propane-1,3-diol cyclic sulphites where the 2,2-dimethyl derivative is stable to 500° [3] whereas the bischloromethyl compound (III) decomposes rapidly at this temperature by a fragmentation process.[4]



It was found that addition of catalytic quantities of pyridine increased the rate of polymer formation from (Ia) and enabled high yields of polymer to be obtained from (Ie), but the latter polymers were of very low molecular weight.

Experimental.—Anhydrosulphites. These were prepared by minor adaptations of Alderson's [2] procedure from thionyl chloride and the α-hydroxy-acids (obtained by conventional methods *via* ketone cyanohydrins). Fractional distillation of the crude products gave: α-hydroxyisobutyric acid anhydrosulphite (Ia), b. p. 58—59°/13 mm., n_D^{20} 1·4301 (Alderson

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[1] Blaise and Montagne, *Compt. rend.*, 1922, **174**, 1553.
[2] Alderson, U.S.P. 2,811,511; Sorenson and Campbell, " Preparative Methods of Polymer Chemistry," Interscience Publishers, Inc., New York, 1961, p. 243.
[3] Wawzonek and Loft, *J. Org. Chem.*, 1959, **24**, 641.
[4] Matlack and Breslow, *J. Org. Chem.*, 1957, **22**, 1723.

records n_D^{25} 1·4290); *α-hydroxy-α-methylbutyric acid anhydrosulphite*, b. p. 60—61°/9 mm., n_D^{20} 1·4452 (Found: C, 36·8; H, 5·0; S, 19·9. $C_5H_8O_4S$ requires C, 36·6; H, 4·9; S, 19·6%); *α-hydroxy-α-methylbutyric acid anhydrosulphite* (Ic), b. p. 52°/2 mm., n_D^{20} 1·4457 (Found: C, 40·8; H, 5·9. $C_6H_{10}O_4S$ requires C, 40·6; H, 5·7%). *Glycollic acid anhydrosulphite* (If), b. p. 71—72°/11 mm. (Found: C, 20·0; H, 1·5; S, 26·4. $C_2H_2O_4S$ requires C, 19·7; H, 1·7; S, 26·3%), and 1-*hydroxycyclohexanecarboxylic acid anhydrosulphite* (Ig), b. p. 56—68°/0·7 mm. (Found: C, 44·4; H, 5·5; S, 17·0. $C_7H_{10}O_4S$ requires C, 44·2; H, 5·3; S, 16·9%) were roughly purified by distillation under reduced pressure through a short Vigreux column, sulphur dioxide being evolved during this procedure.

β-*Chloro-α-hydroxy-α-methylpropionic acid anhydrosulphite* (Id), separated as large crystals from the product of reaction of β-chloro-α-hydroxy-α-methylpropionic acid and thionyl chloride. Removal of excess of thionyl chloride by evaporation at 15 mm., followed by crystallisation from dry ether gave the anhydrosulphite, m. p. 73—76°, in 76% yield (Found: C, 26·1; H, 2·8. $C_4H_5ClO_4S$ requires C, 26·0; H, 2·8%). Two further recrystallisations gave a product of m. p. 74—76°.

αα-*Bischloromethyl-α-hydroxyacetic acid anhydrosulphite* (Ie) was obtained as an oil by removing at 15 mm. excess of thionyl chloride from the product of reaction of αα-bischloromethyl-α-hydroxyacetic acid and thionyl chloride. This solidified overnight and after two crystallisations from dry ether had m. p. 43—46° (Found: C, 22·2; H, 2·0; Cl, 33·0; S, 14·0. $C_4H_4Cl_2O_4S$ requires C, 21·9; H, 1·9; Cl, 32·4; S, 14·7%); the yield was 53%.

Polymerisations. These were carried out according to Alderson's [2] procedure by use of dry refluxing chlorobenzene. The specific viscosities, η_s, (viscosity of the solution/viscosity of the solvent) − 1, of solutions containing 0·5 g. of polymer per 100 ml. of *o*-chlorophenol were measured at 25°; the best samples of polymers (IIa—d) had $\eta_s = 0{\cdot}56, 0{\cdot}20, 0{\cdot}17$, and 0·16 respectively, while the polymers (IIe—h) had $\eta_s = 0{\cdot}05$.

Attempted polymerisation of (Ie) in refluxing chlorobenzene gave only low yields of polymer, and *sym*-dichloroacetone was isolated in 71% yield as its 2,4-dinitrophenylhydrazone (m. p. 132—135°, not depressed by admixture with an authentic specimen), the yield of carbon monoxide being 75%. Addition of catalytic quantities of pyridine to the polymerisation mixture resulted in an almost quantitative yield of a buff powder (capillary m. p. 283—288°) which had an infrared spectrum consistent with the postulated structure (IIe).

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130. *The Hydrogen Isotope Effect in the Thermal Decomposition of Malonic Acid.*

By A. T. Blades and M. G. H. Wallbridge.

The thermal decomposition of solid or molten malonic acid is of the first order, yielding only carbon dioxide and acetic acid;[1] this has been verified [2] for the melt, and a new value given for the rate constant. The system has been much used for the study [3] of the carbon (C^{12}–C^{13}) isotope effect, this being interpreted in terms of various transition states. The catalysed decomposition in non-aqueous solvents containing a nucleophilic atom has been used to deduce characteristics of the transition complex, and to study the nature of polar liquids.[4]

However, the mechanism of the decomposition and the nature of the transition state

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[1] Hinshelwood, *J.*, 1920, 156.

[2] Clark, *J. Phys. Chem.*, 1963, **67**, 138.

[3] Bigeleisen and Wolfsberg, " Advances in Chemical Physics," Interscience Publishers Inc., New York, 1958, Vol. I, p. 15.

[4] (*a*) Clark, *J. Phys. Chem.*, 1960, **64**, 41; (*b*) Fraenkel, Bedford, and Yankwich, *J. Amer. Chem. Soc.*, 1954, **76**, 15.

remains obscure. Decomposition through a six-membered ring has been suggested for decarboxylation of substituted malonic acids[5] $R_2C{\cdot}(CO_2H)_2$, where R = alkyl, and since this is similar to the postulated transition state in the pyrolysis of the alkyl esters,[6] it appeared that, as in the latter system measurement of any hydrogen isotope effect in the decomposition might clarify the nature of the transition complex.

We now report results for the decomposition of molten $CH_2(CO_2H)_2$ and $CD_2(CO_2D)_2$ and of the former in glacial acetic acid. A preliminary result for the decomposition of $CH_2(CO_2H)_2$ in the gas phase is also given.

Experimental.—" White label grade " $CH_2(CO_2H)_2$ (Eastman-Kodak Co.), after sublimation at 95—100° was, by acidimetric titration, at least 99·9% pure. This (m. p. 134·0—134·4°, decomp.) was used. $CD_2(CO_2D)_2$ (Merck and Co., Ltd.) was purified similarly (m. p. 129·4—130·3 decomp.). Acetic acid was purified as described by Vogel.[7]

The decarboxylation apparatus consisted of a thin pear-shaped bulb fitted with a vacuum connection and a break-seal. Its volume was such that the liberated acetic acid did not condense. The malonic acid (0·1—0·2 g.) was introduced into the weighed dry vessel, and after evacuation for several hours the vessel was sealed off and re-weighed, with suitable corrections. The vessel was then immersed in an oil-bath regulated to within ±0·1°, the temperature being taken on a calibrated thermometer marked in 0·1°. The vessel was pre-heated in boiling water and, after pyrolysis, quenched in cold water, and attached to the vacuum line through the break-seal. The volume of carbon dioxide was measured by a Toëpler pump, and the acetic acid titrated with 0·2N-sodium hydroxide. A blank showed that all of the acetic acid could be distilled from the vessel. In all runs the quantities of carbon dioxide and acetic acid produced agreed. In each run about 50% of the acid was decomposed; this avoided any complication from the acetic acid vapour. Various runs showed that the rate constant did not vary over a range of percentage decompositions.

In the decompositions in the gas-phase the malonic acid was sublimed at 95—100° into a stream of toluene vapour and thence passed directly into the decomposition chamber, the apparatus being similar to that described earlier[8] except for the introduction of the small furnace for sublimation.

Results and Discussion.—The apparent first-order rate constants (Table) for the decomposition of the molten acids were calculated from the volume of carbon dioxide evolved. The average deviation from the mean value of *k* is shown.

Apparent first-order rate constants for the decarboxylation of molten malonic acids.

	$CH_2(CO_2H)_2$					$CD_2(CO_2D)_2$	
Temp.	136·0°	139·8°	145·3°	150·3°	153·2°	139·8°	145·3°
No. of runs	3	3	5	3	3	3	2
10^4k (sec.$^{-1}$)	2·37 ± 0·02	3·40 ± 0·05	5·99 ± 0·04	9·69 ± 0·19	12·94 ± 0·10	3·12 ± 0·02	5·38 ± 0·01

The rate expression for $CH_2(CO_2H)_2$ is given in eqn. (1):

$$k_{\text{H}} = (6{\cdot}4 \pm 1{\cdot}8) \times 10^{14} \exp([-34500 \pm 500]/\boldsymbol{R}T) \text{ sec.}^{-1} \qquad (1)$$

and the observed isotope effects, $k_{\text{H}}/k_{\text{D}}$ at 139·8 and 145·3° are 1·09 ± 0·02 and 1·11 ± 0·01, respectively. These values may be compared with the maximum values of the deuterium isotope effect, calculated assuming tunneling to be unimportant, for a single O–H stretching vibration as a function of temperature,[9] namely $k_{\text{H}}/k_{\text{D}} = 6{\cdot}6$ at 100° and 4·4 at 200°.

The rate constant for decomposition of $CH_2(CO_2H)_2$ in acetic acid at 110·9° was 3·47 ×

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[5] King, *J. Amer. Chem. Soc.*, 1947, **69**, 2738.
[6] Blades and Gilderson, *Canad. J. Chem.*, 1960, **38**, 1401.
[7] Vogel, *J.*, 1948, 1814.
[8] Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 6219.
[9] Wiberg, *Chem. Rev.*, 1955, **55**, 713.

10^{-5} sec.$^{-1}$ [cf. $1{\cdot}48 \times 10^{-5}$ sec.$^{-1}$ calculated with eqn. (1)]. It is significant that the rate of decomposition is essentially the same in the melt, acetic acid, and propionic acid (in propionic acid $3{\cdot}4 \times 10^{-4}$ sec.$^{-1}$ at 140° [4a]), and it has been suggested that the mechanism of decomposition is the same in each case.[4a]

The absence of any appreciable isotope effect in the melt confirms that the O–H bond changes very little in character in the rate-determining step of the decomposition. Therefore, any intramolecular mechanism as postulated for the alkyl esters appears unlikely, since a low isotope effect would only be consistent with this type of mechanism if the normal molecules were hydrogen-bonded unimolecularly, and the transition state was very similar with relatively little change in the O–H bond. For such a transition state the major activation would arise in the C–C bonds, and this would require modification of the mechanism proposed by Yankwich and his co-workers.[4b]

The very low isotope effect observed may be compared with the relatively large effect, $k_H/k_D = 4{\cdot}5$ at 190°, observed in the decarboxylation of the dimethylmalonic acid $HO_2C{\cdot}CMe_2{\cdot}CO_2D$.[10] However, here the isotope effect probably arises from an intramolecular transfer process in the intermediate $(CH_3)_2C{=}C(OH)OD$. Since this is formed after the loss of the carbon dioxide such an isotope effect affords no information about the nature of the decomposition itself.

Yankwich and his co-workers [4b] have shown that in basic solvents malonic acid decarboxylates by a bimolecular process where the rate-determining step is the formation of the co-ordinated complex between the acid and the solvent molecules. The small isotope effect for the molten acid supports the idea of such a catalysed decomposition, the hydroxyl oxygen of one carboxyl group donating electrons to the carbonyl carbon atom of another. Such co-ordination may be intramolecular, or more likely intermolecular, since both the donor and acceptor atoms may exist in molecules which are hydrogen-bonded into aggregates. Such aggregates are known to exist in the solid acid [11] and probably exist in smaller units in the melt. The decomposition then proceeds by the loss of carbon dioxide from the co-ordinated molecule, with the proton transfer not being involved in the rate-determining step. Unfortunately the carbon isotope effect for the melt is of little help in this direction beyond suggesting a weakening of both carboxyl groups in the transition state.

The decomposition in the gas phase was attempted in order to extend the temperature range and obtain a temperature coefficient of the isotope effect. Preliminary experiments showed however that the decomposition was heterogeneous, and attempts to isolate the homogeneous component of the decomposition proved unsuccessful.

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[10] Dunn and Warkentin, *Canad. J. Chem.*, 1956, **34**, 75.
[11] Gaedkoop and McGillavry, *Acta Cryst.*, 1957, **10**, 125.

131. *Orientation in the Nitration of Trisubstituted Benzenes.*

By C. A. Howe, (Mrs.) A. Howe, C. R. Hamel, H. W. Gibson,
and R. R. Flynn.

Trisubstituted benzenes with a *meta*-directing substituent at position 1 and *ortho,para*-directing substituents at positions 2 and 5 undergo nitration extensively (in most cases predominantly) in the 6 position.[1] It has been suggested that such substitution, which is not predicted by the classical rules, results from stabilization of the intermediate cation (and the transition state involved in its formation) either by conjugation between the ring substituents[2] at positions 1 and 2, or by dipole–dipole interaction[3] between the entering electrophilic reagent and the substituent at position 1. The results of the present study are consistent with the first of these hypotheses but not with the second.

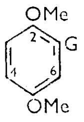
We have determined the isomer distributions resulting from the mononitration of a series of trisubstituted benzenes of general formula (I). Isomer distributions have been established for the nitration of 1,4-dimethoxy-2-nitrobenzene, α-chloro-2,5-dimethoxyacetophenone, α-bromo-2,5-dimethoxyacetophenone, 2,5-dimethoxybenzaldehyde, and 2,5-dimethoxyphenylacetic acid; those for 2,5-dimethoxyacetophenone and 2,5-dimethoxyethylbenzene have been reported previously.[4] While nitration of 2,5-dimethoxyphenylacetic acid and 1-ethyl-2,5-dimethoxybenzene occurs exclusively at ring position 4, nitration of the other compounds, in which G in each case represents an unsaturated, *meta*-directing group, occurs predominantly at ring position 6 (formula I). The results are summarized in the Table.

Isomer distributions for nitrations of (I).

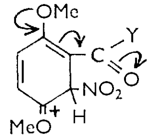
G	NO_2	$CO{\cdot}CH_2Cl$	$CO{\cdot}CH_2Br$	COMe	CHO	$CH_2{\cdot}CO_2H$	Et
6-Nitration (%) ...	93	92	89	78	76	—	—
4-Nitration (%) ...	7	*	11	22	24	100	100

* Not established.

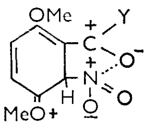
Structure (II) illustrates the suggested stabilization of the intermediate cation involved in 6-nitration by conjugation between the ring substituents at positions 1 and 2; structure (III) illustrates the suggested stabilization by dipole–dipole interaction between the entering nitro-group and the substituent at position 1.



(I)



(II)



(III)

Our results are consistent with only the first of these modes of stabilization. The probable order of electron-attracting power for the G groups, based on the dipole moments of monosubstituted benzenes[5] and on σ values,[6] is $NO_2 > CO{\cdot}CH_2Cl > CO{\cdot}CH_2Br > CHO \sim COMe > CH_2{\cdot}CO_2H > Et$. This order parallels that of the percentages of 6-nitration and is consistent with an increase in stabilization by conjugation with an increase in the electron-attracting power of G. No such stabilization is possible, of course, when G is $CH_2{\cdot}CO_2H$ or Et. On the other hand, the fact that nitration of the α-halogeno-2,5-dimethoxyacetophenones leads to a higher percentage of 6-substitution than does that of 2,5-dimethoxyacetophenone appears inconsistent with the second hypothesis. The

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[1] Howe and Howe, *J.*, 1963, 6064.

[2] Dewar, *J.*, 1949, 463.

[3] Hammond, Modic, and Hedges, *J. Amer. Chem. Soc.*, 1953, **75**, 1388.

[4] Howe, Hamel, Stedman, and Hyman, *J. Org. Chem.*, 1960, **25**, 1245.

[5] McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company, San Francisco, 1963.

[6] Jaffe, *Chem. Rev.*, 1953, **53**, 191.

negative charge on the carbonyl oxygen should be reduced by an α-halogen atom, thus decreasing the dipole–dipole interaction between the carbonyl oxygen and the entering nitro-group. Moreover, 2,5-dimethoxyphenylacetic acid, which might be expected to undergo 6-nitration through stabilization of the intermediate cation by dipole–dipole interaction (resulting in a six-membered cyclic structure), reacts exclusively at the 4-position.

Nitrations were carried out in concentrated nitric acid at low temperature in order to prevent side-reactions, minimize steric effects, and ensure high selectivity. The nitration products were analysed quantitatively either by gas chromatography or by infrared spectrophotometry.

Experimental.—Nitration of 1,4-*dimethoxy*-2-*nitrobenzene.* 1,4-Dimethoxy-2-nitrobenzene (3·0 g.), m. p. 72—74°, was added slowly with stirring to concentrated nitric acid (*d* 1·42; 20 ml.) at −10°. The mixture was stirred for 2 hr. at −10°, then poured into ice–water. The crude product was isolated by filtration, washed, and dried. The yellow powder (3·3 g.), m. p. 160—175°, thus obtained was analysed by gas chromatography in a 2-ft. column (internal diam. 4 mm.) packed with 15% QF-1-0065 fluorosilicone on Chromosorb P, at 210°; 7-methoxy-6-nitrohomochroman-5-one [7] was used as the internal standard; response factors were determined with artificial mixtures of the internal standard, starting material, and authentic samples of 1,4-dimethoxy-2,3-dinitrobenzene, m. p. 186—187°,[8] and 1,4-dimethoxy-2,5-dinitrobenzene, m. p. 203—204°.[9] The mixture was shown to consist of 1,4-dimethoxy-2,3-dinitrobenzene (93%) and 1,4-dimethoxy-2,5-dinitrobenzene (7%), exclusive of a small amount of starting material. No evidence for the presence of 1,4-dimethoxy-2,6-dinitrobenzene was obtained. A second nitration, carried out in identical conditions, gave the same results.

Nitration of α-*Chloro*-2,5-*dimethoxyacetophenone.* α-Chloro-2,5-dimethoxyacetophenone (8·0 g.), m. p. 86—87°,[10] was nitrated at −15° by the procedure described above. The crude product was obtained as a yellow powder (9·2 g.), m. p. 94—106°. Crystallization from methanol yielded α-*chloro*-3,6-*dimethoxy*-2-*nitroacetophenone*, yellow needles, m. p. 109—110° (Found: C, 45·8; H, 3·9; N, 5·5. $C_{10}H_{10}ClNO_5$ requires C, 46·2; H, 3·8; N, 5·4%), which gave an indigotin on treatment with yellow ammonium sulphide solution.[11] No other component was isolated from the nitration mixture in a pure condition. The mixture was analysed by gas chromatography as above at a temperature of 175—275°, programmed for a temperature rise of 4° per min.; *p*-nitroacetophenone was used as the internal standard; response factors were determined with artificial mixtures. α-Chloro-3,6-dimethoxy-2-nitroacetophenone was shown to represent approximately 92% of the nitration mixture, exclusive of a small amount of starting material. A second nitration, carried out in identical conditions, gave the same results.

Nitration of α-*bromo*-2,5-*dimethoxyacetophenone.* α-Bromo-2,5-dimethoxyacetophenone (8·0 g.), m. p. 86°,[11] was nitrated at −20° by the procedure described above. The crude product was obtained as a yellow powder (9·4 g.) which was shown to consist of α-bromo-3,6-dimethoxy-2-nitroacetophenone (90%) and α-bromo-2,5-dimethoxy-4-nitroacetophenone (10%) by infrared spectral analysis [8] (solvent: carbon disulphide; analytical bands: 7·90 and 8·17 μ, respectively). Reference samples of the two nitro-compounds, m. p.s 102—103° and 117—118°, respectively,[11] were obtained by fractional crystallization of the crude nitration product. No evidence for the presence of α-bromo-2,5-dimethoxy-3-nitroacetophenone was obtained. Comparison of the infrared spectrum of the mixture with those of the reference samples showed no extraneous absorption bands. A second nitration, carried out at 0°, yielded 88% and 12% of the two isomers.

Nitration of 2,5-*dimethoxybenzaldehyde.* 2,5-Dimethoxybenzaldehyde (3·0 g.), m. p. 49—50°, was nitrated at −20° by the procedure described above. The crude product was obtained as a yellow powder (3·6 g.). Fractional crystallization from ethanol yielded 3,6-dimethoxy-2-nitrobenzaldehyde as pale yellow needles, m. p. 164—165° [12] (Found: C, 51·0; H, 4·6; N, 6·6.

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[7] Musselman, Thesis, Clarkson College of Technology, New York, U.S.A., 1963.

[8] Howe, Pecore, and Clinton, *J. Org. Chem.*, 1962, **27**, 1923.

[9] Nietzki and Rechberg, *Ber.*, 1890, **23**, 1211.

[10] Auwers and Pohl, *Ann.*, 1914, **405**, 281.

[11] Bost and Howe, *J. Amer. Chem. Soc.*, 1951, **73**, 5864.

[12] Rubenstein, *J.*, 1925, **127**, 1998.

Calc. for $C_9H_9NO_5$: C, 51·2; H, 4·3; N, 6·6%), and 2,5-*dimethoxy*-4-*nitrobenzaldehyde* as orange-yellow needles, m. p. 163—165° (Found: C, 51·2; H, 4·3; N, 6·4%); mixed m. p. 135—147°. Oxidation of these compounds with alkaline permanganate yielded 3,6-dimethoxy-2-nitrobenzoic acid, m. p. 193—194°, and 2,5-dimethoxy-4-nitrobenzoic acid, m. p. 192—194°, respectively, identical (mixed m. p.s and spectra) with authentic samples.[4] The crude nitration product was analysed by gas chromatography in a 10-ft. column (internal diam. 4 mm.) packed with 20% silicone gum rubber on Chromosorb P, at 235°; *p*-nitroacetophenone was used as the internal standard; response factors were determined with artificial mixtures. The nitration product was shown to consist of 3,6-dimethoxy-2-nitrobenzaldehyde (76%) and 2,5-dimethoxy-4-nitrobenzaldehyde (24%), exclusive of a small amount of starting material. A second nitration, carried out in identical conditions, gave the same results. Nitrations carried out at higher temperatures as reported by Rubenstein [12] resulted in low yields of a crude product of high nitrogen content.

Nitration of 2,5-*dimethoxyphenylacetic acid.* 2,5-Dimethoxyphenylacetic acid (3·0 g.), m. p. 120—122°, was nitrated at −10° by the procedure described above except that the ageing period was shortened to 30 min. The crude product was obtained as a yellow powder (3·2 g.), m. p. 199—202°, which gave one discrete band on gas chromatography on a silicone gum rubber column and which had an infrared spectrum identical with that of 2,5-*dimethoxy*-4-*nitrophenylacetic acid*, yellow needles, m. p. 203—204° (Found: C, 50·1; H, 4·7; N, 5·6. $C_{10}H_{11}NO_6$ requires C, 49·8; H, 4·6; N, 5·8%). This compound, obtained by crystallization of the crude product from ethanol, on treatment with alkaline permanganate yielded 2,5-dimethoxy-4-nitrobenzoic acid, m. p. 193—194°, identical (mixed m. p. and infrared spectra) with an authentic sample.[4]

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132. *Acceptor Properties of Metal Halides. Part III.*[1] *Solvation Effects of Arsenic Trichloride in the Racemisation of α-Methylbenzyl Chloride in Acetone, Catalysed by Mercuric Chloride.*

By (MRS.) R. S. SATCHELL.

THE rate of racemisation of α-methylbenzyl chloride induced by mercuric halides in nitrobenzene,[2] and by mercuric and zinc halides in acetone,[1] shows both a first-order and a second-order dependence on catalyst concentration. We have interpreted the second-order component in terms of solvation of the transition state ($^{\delta+}R \cdots Cl \cdots MX_2^{\delta-}$) by a second metal halide molecule.[1] Such solvation could arise from strong specific interaction of a second metal halide molecule, leading to the formation of metal halide dimers at the site of reaction,[3] or from weak, generalised electrostatic interaction of other metal halide molecules. If dimers form, the solvation effect is expected to be related to the chloride-acceptor properties of the metal halides. (Strong acceptors tend to form dimers easily.[3]) On the other hand, a weak ion-dipole interaction with the transition state is expected to be related to the polarity of the metal halide. In order to clarify these solvation effects we studied the mercuric chloride catalysis in acetone in the presence of arsenic trichloride, which is

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[1] Part II, Satchell, *J.*, 1964, 5464.

[2] Satchell, *J.*, 1963, 5963.

[3] Jensen, Marino, and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3303; Olah in " Friedel–Crafts and Related Reactions," Vol. I, Interscience, 1963, p. 228.

a much weaker chloride-ion acceptor than mercuric chloride,[4] but a molecule of similar polarity.[5]

No racemisation of α-methylbenzyl chloride was observed in the presence of arsenic trichloride (0·6M) alone in acetone at 25° during 20 hours. Added arsenic trichloride does, however, accelerate the racemisation induced by mercuric chloride. This is seen in the values of the observed rate-constants given in the Table for mixtures of the two halides. The increase in the rate produced by a given concentration of arsenic trichloride depends on the mercuric chloride concentration: the greater the concentration of the latter, the greater is the rate-enhancement produced by a given concentration of the former.

In the absence of arsenic trichloride, the observed rate constant can be expressed [1] by equation (1).

$$k_0 = k_1[\mathrm{HgCl_2}] + k_2[\mathrm{HgCl_2}]^2. \qquad (1)$$

The second-order term $k_2[\mathrm{HgCl_2}]^2$ represents the rate-enhancement caused by solvation of the transition state by mercuric chloride molecules. The similar increase due to arsenic trichloride is given by $k_{\mathrm{obs}} - k_0$ (see Table). In order to compare the two effects, it is preferable to rewrite equation (1) in the form

$$k_0 = [\mathrm{HgCl_2}](k_1 + k_2[\mathrm{HgCl_2}]). \qquad (2)$$

Racemisation of α-methylbenzyl chloride in the presence of mixtures of arsenic trichloride and mercuric chloride in acetone at 25°.

[Ph·CHMeCl] = *ca.* 0·05M in all experiments.

$[\mathrm{HgCl_2}]$ (M)	$[\mathrm{AsCl_3}]$ (M)	10^4k_{obs} (sec.$^{-1}$)	10^4k_0 † (sec.$^{-1}$)	$10^4k_2[\mathrm{HgCl_2}]^2$ ‡ (sec.$^{-1}$)	$10^4\Delta k$ § (sec.$^{-1}$)	$10^4k_2[\mathrm{AsCl_3}]$ ‡ (sec.$^{-1}$ l. mole^{-1})	$10^4\Delta k$ §/$[\mathrm{HgCl_2}]$ (sec.$^{-1}$ l. mole^{-1})
0·496	0·478	2·43	1·92	1·48	0·51	2·87	1·0
0·496	0·956	4·27	1·92	1·48	2·35	5·74	4·74
0·496	1·195	4·27	1·92	1·48	2·35	7·17	4·74
0·497	1·195	4·45	1·93	1·48	2·52	7·17	5·07
0·493	1·79	5·60	1·90	1·46	3·70	10·74	7·51
0·497	1·79	6·20	1·93	1·48	4·27	10·74	8·59
0·496	2·27	9·65	1·92	1·48	7·73	13·62	15·6
0·496	2·39	11·2	1·92	1·48	9·3	14·3	18·8
0·496	2·39	12·2	1·92	1·48	10·3	14·3	20·8
0·104	1·20	0·529	0·158	0·065	0·371	7·20	3·57
0·210	1·20	1·24	0·45	0·26	0·79	7·20	3·76
0·303	1·20	2·11	0·82	0·55	1·29	7·20	4·26
0·564	1·20	5·25	2·42	1·91	2·83	7·20	5·02
0·696	1·20	7·16	3·35	2·91	3·81	7·20	5·47
0·796	1·20	9·48	4·51	3·80	4·97	7·20	6·24
0·374	1·79	4·32	1·27	0·84	3·05	10·7	8·16
0·618	1·79	9·42	2·84	2·29	6·58	10·7	10·6

† k_0 The rate constant in the absence of arsenic trichloride [1] calculated by using equation (1) with $k_1 = 0{\cdot}9 \times 10^{-4}$ sec.$^{-1}$ l. mole^{-1} and $k_2 = 6 \times 10^{-4}$ sec.$^{-1}$ l.^{2} mole^{-2}. ‡ $k_2 = 6 \times 10^{-4}$ sec.$^{-1}$ l.^{2} mole^{-2}. § $\Delta k = k_{\mathrm{obs}} - k_0$; *i.e.*, the increase in the rate caused by the presence of arsenic trichloride.

In the presence of arsenic trichloride this equation becomes

$$k_{\mathrm{obs}} = [\mathrm{HgCl_2}](k_1 + k_2[\mathrm{HgCl_2}] + f[\mathrm{AsCl_3}]), \qquad (3)$$

where f is some function of the arsenic trichloride concentration. The increase in the rate due to the addition of arsenic trichloride can be represented by $(k_{\mathrm{obs}} - k_0)/[\mathrm{HgCl_2}]$. The comparable expression for mercuric chloride under the same conditions will then be given by $k_2[\mathrm{HgCl_2}]$, where $[\mathrm{HgCl_2}]$ is now equal to the concentration of arsenic trichloride. By the use of these two expressions it is possible to compare the effect of arsenic trichloride with that which would be produced by the addition of the same concentration of mercuric chloride in place of the arsenic trichloride; the values given in the last two columns of the

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[4] Baaz and Gutmann in " Friedel–Crafts and Related Reactions," ed. Olah, Vol. 1, Interscience 1963, p. 388.

[5] Grassi and Puccianti, *Nuovo cim.*, 1937, **14**, 461; Smith, *Proc. Roy. Soc.*, 1932, *A*, **136**, 256; McCusker and Curran, *J. Amer. Chem. Soc.*, 1942, **64**, 614; Curran, *ibid.*, 1941, **63**, 1470; Tourky and Rizk, *Canad. J. Chem.*, 1957, **35**, 630; Tourky, Rizk, and Girgis, *J. Phys. Chem.*, 1960, **64**, 565; Curran, *J. Amer. Chem. Soc.*, 1942, **64**, 830.

Table permit this comparison. It is seen that the increase due to arsenic trichloride varies from approximately one third to one and one half times that which would be found for the same concentration of mercuric chloride.

The fact that arsenic trichloride alone does not induce racemisation is expected from its known weakness as a chloride-ion acceptor. Its marked accelerating effect on the mercuric chloride-induced racemisation cannot therefore arise from strong complex formation, *via* chlorine, with the mercuric chloride (the analogue of dimer formation for mercuric chloride alone) at the reaction site. The effect of arsenic trichloride must arise from a weak interaction with the transition state of an ion-dipole nature. Since the solvation effects of arsenic trichloride and mercuric chloride are of the same order of magnitude, it can be concluded that most of the solvation effects of mercuric chloride alone probably also arise from similar phenomena, and not from incipient dimer formation. We were reluctant to reach this conclusion in previous Papers, because the solvent itself has a dipole moment of comparable magnitude to that of the metal halides. The solvent's own solvation effects would, we argued, swamp that of the catalyst if straightforward electrostatic effects were dominant in solvation. The present results force us to reconsider this view. Solvation of the negatively charged part of the transition state by another molecule will depend partly on the latter's dipole moment, but partly also on the accessibility of the positive end of its dipole. This end of the dipole is much more readily available for the metal halide species than for the solvents acetone and nitrobenzene, and this may be the reason for their surprisingly small contributions to solvation in these systems.

Experimental.—The optically active α-methylbenzyl chloride,[2] dry acetone,[1] and mercuric chloride[2] have been previously described. Arsenic trichloride (B.D.H.) was distilled in an atmosphere of nitrogen; it had b. p. 130°/762 mm. Reaction mixtures containing mercuric chloride were prepared as before.[1] Arsenic trichloride was added to these mixtures by pipette in a dry-box. The loss of optical activity was measured as previously described.[2]

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[*Received, April* 14*th*, 1964.]

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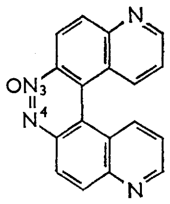
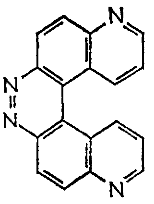
133. *Polycyclic Reduction Products of* 6-*Nitroquinoline.*

By W. V. FARRAR.

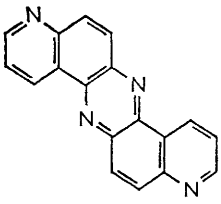
By reduction of 6-nitroquinoline with methanolic sodium methoxide, Knueppel[1] obtained a high-melting crystalline compound $C_{18}H_{10}N_4O$ which he called " azoxydichinyl." He did not speculate about its structure, though he showed that distillation over iron filings gave " azodichinyl " $C_{18}H_{10}N_4$. Much later,[2] without any further evidence, the structures (I) and (II) were ascribed to these compounds.



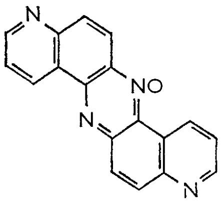
(I)



(II)



(III)



(IV)

It has now been found that " azodichinyl " is identical (mixed m. p. and infrared spectrum) with a compound obtained[3] by oxidation of 6-aminoquinoline with hypobromite, and regarded as the dipyridophenazine (III). Since 6-amino-5-bromoquinoline gave the same

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[1] Knueppel, *Annalen*, 1899, **310**, 75.

[2] Huisgen, *Annalen*, 1948, **559**, 128.

[3] Meigen and Nottebohm, *Ber.*, 1906, **39**, 746.

product[3] this formula is almost certainly correct. " Azoxydichinyl " must therefore be the *N*-oxide (IV).

Knueppel[1] also described the preparation of 6-azoquinoline by reduction of the nitro-compound with iron and calcium chloride. Doubts have been expressed[4] about the nature of this compound, but its structure has been confirmed.[5] In the present work, 6-azoxyquinoline was once obtained instead of the azo-compound; its formula was confirmed by reduction to 6-azoquinoline with zinc and alkali. This compound, however, differed from the supposed 6-azoxyquinoline obtained[6] by alkaline glucose reduction of 6-nitroquinoline, and characterised only by a nitrogen analysis. Since (I), (IV), and 6-azoxyquinoline are the only products of empirical formula $C_{18}H_{10-12}N_4O$ likely to be produced by reduction of 6-nitroquinoline (cf. related work with 2-nitronaphthalene[7]), the compound obtained with glucose and alkali[6] must be (I). Reduction with zinc and alkali gave the oxygen-free compound (II).

Experimental.—" Azoxydichinyl " and " azodichinyl " were obtained by the methods of Knueppel[1] and Huisgen.[2] The former had m. p. 335° (decomp.) (lit.,[2] 330°); the latter had m. p. 379° (with partial sublimation) alone, or mixed with (III), prepared by the method of Meigen and Nottebohm.[3]

Pyridazino[4,3-f:5,6-f′]*diquinoline* 3-*oxide* (I), was prepared (3 g.) from 6-nitroquinoline (17 g.) by alkaline glucose reduction.[6] It formed bright yellow *prisms*, (from pyridine or dioxan), m. p. 274° (decomp.) (lit.,[6] 260—262°) (Found: C, 72·0; H, 3·4; N, 18·8. $C_{18}H_{10}N_4O$ requires C, 72·5; H, 3·4; N, 18·8%). Solutions in acids were light green. Reduction of this compound (1 g.) by refluxing it for 1 hr. with sodium hydroxide (5 g.) in 90% ethanol (50 c.c.) and excess of zinc dust, gave (II) as dull yellow needles (0·75 g.) (from dioxan) with no definite m. p., but decomposing above 280° (Found: C, 76·0; H, 3·3; N, 19·7. $C_{18}H_{10}N_4$ requires C, 76·6; H, 3·6; N, 19·8%).

6-*Azoxyquinoline.* In the preparation of 6-azoquinoline by reduction of the nitro-compound with iron and calcium chloride[1] (three experiments), 6-*azoxyquinoline* was once obtained instead; it formed pale yellow needles (from ethanol), m. p. 212° (Found: C, 72·1; H, 4·0; N, 19·1. $C_{18}H_{12}N_4O$ requires C, 72·0; H, 4·0; N, 18·7%). Reduction with zinc and sodium hydroxide as described above gave 6-azoquinoline (m. p. and mixed m. p. 249°; lit.,[1] 248°) (Found: C, 75·9; H, 4·3; N, 19·7. Calc. for $C_{18}H_{12}N_4$: C, 76·0; H, 4·3; N, 19·7%).

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[*Received, April* 22*nd*, 1964.]

[4] Morley and Simpson, *J.*, 1952, 2602.

[5] Badger and Buttery, *J.*, 1955, 2816.

[6] Galbraith, Degering, and Hitch, *J. Amer. Chem. Soc.*, 1951, **73**, 1323.

[7] Meisenheimer and Witte, *Ber.*, 1903, **36**, 4153, 4164.

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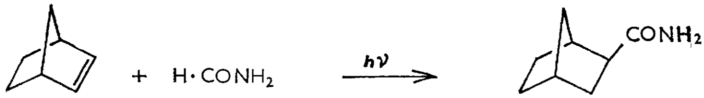
134. *The Stereospecific Photoaddition of Formamide to Norbornene.*

By DOV ELAD and JOSHUA ROKACH.

THE light-induced addition of formamide to terminal olefins has been described.[1] We now report the stereospecific photoaddition of formamide to norbornene at room temperature, which leads to norbornane-2-*exo*-carboxyamide. The reaction can be induced directly by light, or initiated photochemically by acetone with higher yields.



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[1] Elad and Rokach, *J. Org. Chem.*, 1964, **29**, 1855.

The free-radical chain mechanism [1] for the light-induced reaction of formamide with terminal olefins may be extended to the present case. Here the addition of the carbamoyl radical, $\cdot CONH_2$, to the double bond seems to take place from the less hindered (*exo*) side of the norbornene molecule,[2] since the *exo*-amide is formed exclusively (87%). No *endo*-isomer could be detected.[3a] 2 : 1 Telomers, resulting from the reaction of two molecules of norbornene with one molecule of formamide, were also obtained in small yields and characterized by elemental analyses and molecular weight.

Addition of acetone (when used as initiator) to norbornene took place to some extent (5—6% based on norbornene). Stereospecificity was observed here too, the product being 2-*exo*-acetonylnorbornane.[4]

Experimental.—Merck " Acid washed " alumina was used for chromatography. Light petroleum had b. p. 60—80°. Organic solutions were dried (Na_2SO_4) before removal of solvent. Infrared spectra were recorded on a Perkin-Elmer 137 Infracord. Experiments with ultraviolet light were conducted in an immersion apparatus [1] which was cooled externally with running water, and oxygen-free nitrogen was passed through the mixture throughout the irradiation. Hanau Q81 high-pressure mercury-vapour lamps, fitted into quartz or Pyrex immersion tubes, were used for the direct light-induced and the acetone-initiated reactions, respectively. Reactions in sunlight were performed in Pyrex tubes. The system was flushed with nitrogen after each addition of the olefin. Formamide was freshly distilled at 0·2 mm. Acetone was anhydrous. t-Butyl alcohol was distilled from sodium. Norbornene was freshly distilled.

Norbornene and formamide with ultraviolet light. A mixture of norbornene (0·7 g.), formamide (40 g.), t-butyl alcohol (35 ml.), and acetone (5 ml.) was irradiated for 1 hr. A solution of norbornene (4 g.), t-butyl alcohol (15 ml.), and acetone (3 ml.) was then added in seven equal portions at 1 hr. intervals, and the mixture was irradiated for a further 4 hr. Formamide was distilled from the mixture at 0·2 mm., and the residue treated with water. The resulting precipitate crystallized from acetone–light petroleum to yield norbornane-2-*exo*-carboxyamide (2 g.). The aqueous solution was extracted with chloroform, the solvent removed, and the residue combined with that from the mother-liquor and treated with a small volume of acetone–light petroleum to yield an additional crop (1·25 g.), m. p. 181—183° (from acetone–light petroleum) (lit.,[3a,b] 184—184·5° and 182°). It did not depress the m. p. of the authentic amide, and had the same infrared spectrum. (The stereoisomers have nearly identical infrared spectra (KBr) except for the 1140 $cm.^{-1}$ region, where the *exo*-isomer has a weak band and the *endo* has a fairly strong one which can be detected in mixtures of the two isomers.) Further recrystallization did not increase the m. p.[3a]

The residue (2·6 g.) from the mother liquors was chromatographed on alumina (130 g.). (a) Elution with acetone–light petroleum (1 : 9) gave an oil (300 mg.) thought to contain the higher telomers. (b) The same solvent mixture further eluted a 2 : 1 telomer (350 mg.), m. p. 172—174° (from acetone–light petroleum) [Found: C, 76·8; H, 9·6; N, 5·9% *M* (Rast), 203. $C_{15}H_{23}NO$ requires C, 77·2; H, 9·9; N, 6·0%, *M*, 233]. The R_F-value of this compound on thin-layer chromatography was different from those of either the 2-*exo* or the 2-*endo*-amide of norbornane. (c) Acetone–light petroleum (1 : 9) finally eluted norbornane-2-*exo*-carboxyamide (1·65 g.). (d) Ethanol–acetone (1 : 7) eluted a glassy oil (300 mg.).

The recovered formamide distillate was diluted with saturated aqueous sodium chloride solution and extracted with chloroform. Evaporation of the solvent left an oil (910 mg.) which was chromatographed on alumina (50 g.). Light petroleum eluted 2-*exo*-acetonylnorbornane (630 mg.). Its 2,4-dinitrophenylhydrazone and semicarbazone had m. p.s and mixed m. p.s 139—141° (from ethanol) and 197—198° (from methanol), respectively (lit.,[4] 138—140° and 194—195°). Elution with acetone–light petroleum led to norbornane-2-*exo*-carboxyamide (270 mg.).

Norbornene and formamide in sunlight. A mixture of norbornene (1 g.), formamide (40 g.), t-butyl alcohol (25 ml.), and acetone (5 ml.) was left in direct sunlight for 1 day. A solution

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[2] Bohm and Abell, *Chem. Rev.*, 1962, **62**, 599; Trecker and Henry, *J. Amer. Chem. Soc.*, 1963, **85**, 3204, and references therein.

[3] Cf. (*a*) Berson and Suzuki, *J. Amer. Chem. Soc.*, 1959, **81**, 4088; (*b*) Alder, Heimbach, and Reubke, *Chem. Ber.*, 1958, **91**, 1516.

[4] Reusch, *J. Org. Chem.*, 1962, **27**, 1882.

of norbornene (3·7 g.) in t-butyl alcohol (35 ml.) and acetone (4 ml.) was then added in four equal portions at 1 day intervals, and the mixture was left in sunlight for a further 3 days. Working up as before yielded norbornane-2-*exo*-carboxyamide (3 g.), m. p. 181—183° (from acetone–light petroleum). The residue from the extraction and mother-liquor, on treatment with a little acetone, yielded an additional crop (1·5 g.), m. p. 173—177°.

The residue from the mother-liquor (1·41 g.) was chromatographed on alumina (90 g.), as described above, leading to (a) a mixture of telomers (220 mg.), (b) a 2 : 1 telomer (120 mg.), (c) norbornane-2-*exo*-carboxyamide (1 g.), and (d) a glassy oil (50 mg.). The recovered formamide distillate was worked up in the usual way, to yield 2-*exo*-acetonylnorbornane (490 mg.) and 2-norbornane-2-*exo*-carboxyamide (500 mg.).

A total of 6 g. (87% based on norbornene) of norbornane-2-*exo*-carboxyamide was obtained.

Norbornene and formamide with ultraviolet light (*without acetone*). A quartz immersion tube was used for this experiment. The general procedure described above was followed, leading to norbornane-2-*exo*-carboxyamide (1·85 g.), m. p. 179—183°, as the first crop. The residue from the mother-liquors (2·6 g.) was chromatographed on alumina (130 g.), yielding (a) a mixture of telomers (250 mg.), (b) a solid (300 mg.), m. p. 104—112° (from acetone–light petroleum) (Found: C, 77·7; H, 10·0; N, 6·4. Calc. for $C_{15}H_{23}NO$: C, 77·2; H, 9·9; N, 6·0%), which was probably a 2 : 1 telomer, (c) a 2 : 1 telomer (50 mg.), m. p. 172—174° (from acetone–light petroleum), which was identical with the 2 : 1 telomer isolated from the acetone-initiated reaction (mixed m. p., infrared spectra, and thin-layer chromatography), (d) norbornane-2-*exo*-carboxyamide (1·7 g.), and (e) a glassy oil (330 mg.). A total of 3·55 g. of norbornane-2-*exo*-carboxyamide (51%) was obtained. Longer irradiation periods led to increased yields of the amide (61% after 21 hr.).

We are indebted to Professor F. Sondheimer for his interest, and to Professor J. A. Berson and Dr. W. Reusch for samples of the norbornane *endo*- and *exo*-amides and the 2,4-dinitrophenylhydrazone and semicarbazone of 2-*exo*-acetonylnorbornane.

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REHOVOTH, ISRAEL. [*Received, April 27th,* 1964.]

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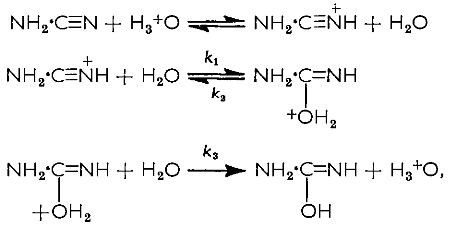
135. *The Acid Hydrolysis of Cyanamide.*

By BARBARA R. MOLE, JULIE P. MURRAY, and J. G. TILLETT.

GRUBE and SCHMID [1] followed the rate of hydrolysis of cyanamide in nitric acid over the range 0·5—5·0 molar and, from their results, Hammett and Paul subsequently showed [2] that log k_1 was linear with $-H_0$, implying that the rate-determining step involves only the conjugate acid of cyanamide. This correlation with H_0 has been more recently confirmed by Kilpatrick *et al.*,[3] who, however, suggested that rapid addition of a water molecule to the conjugate acid of cyanamide may be followed by a rate-determining proton transfer, *i.e.*,



$$NH_2\cdot C\equiv N + H_3{}^+O \rightleftharpoons NH_2\cdot C\equiv \overset{+}{N}H + H_2O$$

$$NH_2\cdot C\equiv \overset{+}{N}H + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_2\cdot \underset{+OH_2}{\underset{|}{C}}=NH$$

$$NH_2\cdot \underset{+OH_2}{\underset{|}{C}}=NH + H_2O \xrightarrow{k_3} NH_2\cdot \underset{OH}{\underset{|}{C}}=NH + H_3{}^+O,$$

where $k_2 \gg k_3$ and k_3 is rate-determining.

Bunnett has shown,[4] however, that the w values for catalysis by nitric acid fall in the

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[1] Grube and Schmid, *Z. phys. Chem.*, 1945, **118**, 145.

[2] Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **54**, 830.

[3] Kilpatrick and Sullivan, *J. Amer. Chem. Soc.*, 1945, **67**, 1815; Kilpatrick, *ibid.*, 1947, **69**, 40.

[4] Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.

range corresponding to water acting as a nucleophile in the rate-determining step, *i.e.*, in the above scheme $k_3 \gg k_2$ and k_1 is rate-determining. On the basis of this criterion, the correlation between rate and H_0 appears to be fortuitous and to provide one more example of the breakdown of the Zucker–Hammett hypothesis.

We have attempted to resolve these conflicting correlations, by studying this reaction further in both nitric acid and perchloric acid.

Experimental.—Cyanamide (" Aero cyanamide-100 "; Cyanamid Ltd.) was purified by recrystallisation from ether and melted at 44°. The rates of hydrolysis were determined by a modified version of Grube and Schmid's procedure; [1] this involved precipitation under alkaline conditions of the cyanamide as its silver salt, which was dissolved in acid and titrated against standard ammonium thiocyanate. Values of k_1 were calculated by using the usual first order rate equation.

Observed first-order rate coefficients for the hydrolysis of cyanamide.

(a) *At 25° with nitric acid.*

[HNO$_3$] (M)	1·00	2·00	3·00	4·00	1·00	2·00	3·00
[NaNO$_3$] (M)	—	—	—	—	3·00	2·00	1·00
$10^3 k_1$ (min.$^{-1}$)	2·23	6·14	12·0	24·0	4·12	9·15	14·7

(b) *At 25° with perchloric acid.*

[HClO$_4$]	1·00	1·00 *	2·00	2·50	3·00	4·00	1·00	2·00	2·00 †
[NaClO$_4$]	—	—	—	—	—	—	2·00	1·00	—
$10^3 k_1$ (min.$^{-1}$)	2·33	2·84	4·57	6·00	7·80	14·8	2·36	4·81	6·78

(c) *With* 1·00M-*perchloric acid at different temperatures.*

T°	25·0	27·3	30·0	32·5	35·0	39·8
$10^3 k_1$ (min.$^{-1}$)	2·23	2·47	3·10	4·30	5·41	8·65

* In 97% D$_2$O. † With 1·0M-sodium nitrate.

Influence of Temperature.—The entropy (ΔS^*) and the energy of activation (ΔE) are calculated by using the formula $k = (e\mathbf{k}T/\mathbf{h}) \exp(\Delta S^*/\mathbf{R}) \exp(-\Delta E/\mathbf{R}T)$. Values of H_0 were taken from Long and Paul's review.[5]

Discussion.—Our values for nitric acid agree with those of Grube and Schmid.[1] The slope of the Hammett plot (log k_1 *versus* $-H_0$) is 0·85. Such a pseudo Hammett correlation could be given by a bimolecular reaction on which was superimposed a large positive salt effect. That this is indeed the case for cyanamide, as was originally suggested by Grube and Schmid,[1] is shown by the fact that, in mixtures of nitric acid and sodium nitrate at approximately constant nitrate-ion concentration (4·00 M), the rate is more nearly proportional to the stoicheiometric acidity. In perchloric acid, the rate increases much less rapidly with increase in acid concentration than with nitric acid and varies linearly up to *ca.* 2·0 molar acid. If the perchlorate ion concentration is maintained constant, the rate varies approximately linearly with acid concentration, except at the highest acidities used.

Positive deviations from linearity at high acid concentration are observed in both sets of experiments at constant ionic strength. It is generally assumed that, in such mixtures, the ionic-strength effect will be approximately independent of the nature of the cation. However, for the hydrolysis of cyanamide, Grube and Schmid have already shown [1] that smaller cations are more effective in catalysis. Thus in 0·25 M-nitric acid the effectiveness of added nitrates is in the order Li > NH$_4$ > Na > K. The positive deviations observed probably arise, at least in part, from this effect as sodium cations are gradually replaced by protons. The pseudo Hammett correlation in nitric acid therefore arises from the large positive salt effect exerted by the nitrate ion. By comparison, the effect of the perchlorate ion is rather small. Thus, in 2·0 molar perchloric acid the addition of 1·0 molar sodium

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[5] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

perchlorate and sodium nitrate increases the value of 10^3k from 4·57 min.$^{-1}$ to 4·81 and 6·78 min.$^{-1}$, respectively.

We therefore conclude that, for this reaction, the rate-dependence in perchloric acid may be regarded as giving a more accurate picture of the mechanism. According to the Zucker–Hammett hypothesis, since this rate correlates with stoicheiometric acidity, the reaction would be classed as an A-2 process in which k_1 is the rate-determining step. This hypothesis, however, may be applied only to reactions that show specific hydrogen-ion catalysis. Kilpatrick and Sullivan's experiments indicate [3] that this reaction undergoes general acid catalysis, although unusual effects were observed. Thus, trichloracetic acid was a better catalyst than the oxonium ion, while hydrochloric and hydrobromic acids at higher concentration strongly retarded the rate of formation of urea. With the halogen acids, salts are considered to be formed [4] by nucleophilic attack of the anion of the acid competing with water as a nucleophile for the conjugate acid. These salts appear to be resistant to hydrolysis and, as a result, the rate passes through a maximum with increase in acid concentration.

According to the Bunnett criterion for the function of water in the rate-determining steps, $w < 0$ implies no involvement of water, $+1{\cdot}2 < w < +3{\cdot}3$, implies water acting as a nucleophile, and $w > 3{\cdot}3$ indicates the water acting as a proton transfer agent. For hydrolysis by nitric acid, values of w of $+0{\cdot}8$, $+1{\cdot}4$, and $+1{\cdot}5$ have been calculated.[4] These fit moderately well into the second group. The abnormally high salt effect of the nitrate ion might be expected, however, to give unusually low w values. Thus, with perchloric acid we find $w = +8{\cdot}0$; this implies that water is acting both as a nucleophile and as a proton transfer agent. Attempts to determine simultaneous contributions to w of nucleophilic and proton transfer functions of water have been discussed.[6] Similar slow proton transfers have been suggested for the hydrolysis of γ-butyrolactone [4,7] ($w = 8{\cdot}5$) and *NN*-diphenylformamidine [8] ($w = 7{\cdot}75$) and the iodination of acetophenone [4] ($w = 6{\cdot}7$).

The observed deuterium solvent effect ($k^{\text{D}}/k^{\text{H}}$) in perchloric acid is 1·2. For a reaction that undergoes general acid catalysis with an initial slow proton transfer, the expected value of $k^{\text{D}}/k^{\text{H}}$ would be less than unity,[9] and so this mechanism is precluded. General acid catalysis with a pre-equilibrium proton transfer followed by a subsequent slow proton transfer is shown for cyanamide in the reaction scheme above. A first step involving an equilibrium isotope effect ($k^{\text{D}}/k^{\text{H}} > 1$) followed by a step in which only minor solvent effects would show up, and a final slow proton transfer with $k^{\text{D}}/k^{\text{H}} < 1$ could combine to give an overall isotope effect $k^{\text{D}}/k^{\text{H}}$ less than or greater than unity.[10-12] Long and Pritchard have shown [13] that, for reactions involving specific hydrogen ion catalysis, the ratio of the rate constants in deuterium oxide and water ($k^{\text{D}}/k^{\text{H}}$) for known *A*-2 hydrolyses usually lies between 1·37 and 1·7. However, values less than this have been obtained, *e.g.*, for diethyl sulphite [14] (1·33). The value for cyanamide lies only slightly outside this range.

On balance therefore, the evidence seems to indicate that the hydrolysis of cyanamide is an *A*-2 process, the rate-determining step involving attack of a water molecule on the conjugate acid. The high value of w in perchloric acid may be due to anomalous hydration changes,[4] which are masked in nitric acid by the large salt effect. The unusual type of apparent general acid catalysis observed by Kilpatrick *et al.*[3] may be due to the effect of the anions present competing with water molecules as nucleophiles. That a water molecule is involved in some role in the rate-determining step is confirmed by the value of

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[6] Martin, *J. Amer. Chem. Soc.*, 1962, **84**, 4130.

[7] Martin, Hedrick, and Parcell, *J. Org. Chem.*, 1964, **29**, 158.

[8] De Wolfe, *J. Amer. Chem. Soc.*, 1960, **82**, 1585.

[9] Long and Bigeleisen, *Trans. Faraday Soc.*, 1959, **55**, 2077.

[10] Hogfeldt and Bigeleisen, *J. Amer. Chem. Soc.*, 1960, **82**, 15.

[11] Challis, Long, and Pocker, *J.*, 1957, 4679.

[12] Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 3207.

[13] Long and Pritchard, *J. Amer. Chem. Soc.*, 1956, **78**, 2663.

[14] Tillett, *J.*, 1960, 5138.

the entropy of activation ($\Delta S^* = -21{\cdot}5$ e.u.), which falls into the range expected for a bimolecular process.[15]

We thank Cyanamid of Great Britain Ltd., for a sample of cyanamide.

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[15] Long, Pritchard, and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 2362.

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136. *Photochemical and Non-photochemical Reaction of Bromide Ion with* p-*Nitrobenzenediazonium Ion in Dimethyl Sulphoxide.*

By M. D. JOHNSON.

IN aqueous solution the reaction of bromide ion with *p*-nitrobenzenediazonium ion is first-order in the latter, and at low concentrations is approximately zero-order in bromide ion.[1] As the concentration of bromide ion increases, the rate increases slightly, but the suggestion that this is due to the onset of bimolecular displacement of nitrogen by the bromide ion has been criticised on the basis of volume of activation measurements.[2] The bimolecular mechanism dominates in the reaction between bromide ion and the more reactive *p*-phenylenebis(diazonium ion) in water,[3] and it was thought that, because of the very high reactivity of bromide ion in dimethyl sulphoxide, the reaction with *p*-nitrobenzenediazonium ion in this solvent might also be bimolecular.

Pure *p*-nitrobenzenediazonium ion is stable in dimethyl sulphoxide for many hours at room temperature but on addition of sodium or lithium bromide a rapid reaction takes place, which is markedly accelerated by sunlight and by illumination with a mercury-vapour lamp,* but the yield of the product, *p*-bromonitrobenzene (70 ± 5%), is unchanged. The " dark " reaction is also accelerated by traces of water, but *p*-bromonitrobenzene is still the major product even when the concentrations are sodium bromide 0·2M, diazonium ion 0·01M, and water 0·2M.

The kinetics of the " dark " reaction were examined by following the rate of evolution of nitrogen in a Warburg apparatus at 29·8°. All runs were carried out using a large excess of sodium bromide, and reasonable pseudo-first-order behaviour was observed except at the lower concentrations of diazonium ion, when the initial liberation of nitrogen was sluggish, perhaps because of an induction period. However, even in these cases, quite good first-order Guggenheim [4] plots were obtained when the first 20—25% of the reaction was ignored.

Because dimethyl sulphoxide is hygroscopic it was extremely difficult to obtain absolutely consistent results with different batches of purified solvent, but the results in the Table show that the reaction is approximately first-order in *p*-nitrobenzenediazonium ion and in bromide ion. Assuming strict second-order behaviour, the calculated second-order rate coefficients (k_2) differ by less than a factor of 2 for a four-fold change in sodium bromide concentration, and for runs in a single batch of solvent this discrepancy is even less. Moreover, the sodium bromide concentration is sufficiently high for ion-pairing to be

10^2[NaBr] (M)	7·3 *	9·5 *	14·2 *	29·0 *	13·5 †	17·7 †	30·0 †
$10^2 k_{\text{obs.}} \pm 20\%$ (min.$^{-1}$)	1·8	1·9	2·6	4·6	2·1	2·3	4·0
$10 k_2 \pm 20\%$ (l. mole^{-1} min.$^{-1}$)	2·4	2·0	1·8	1·6	1·6	1·3	1·3

* With first batch of dimethyl sulphoxide. † With second batch of dimethyl sulphoxide.

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* Phillips Lamps Ltd., catalogue number MB/U, with glass envelope removed.

[1] Lewis and Hinds, *J. Amer. Chem. Soc.*, 1952, **74**, 304.

[2] Brower, *J. Amer. Chem. Soc.*, 1960, **82**, 4535.

[3] Lewis and Johnson, *J. Amer. Chem. Soc.*, 1960, **82**, 5408.

[4] Guggenheim, *Phil. Mag.*, 1926, Ser. 7, **2**, 538.

significant,[5] and hence the bromide ion concentration is less than the stoicheiometric sodium bromide concentration, particularly at the highest concentrations considered.

The kinetics are therefore consistent with the bimolecular mechanism, but the photochemical catalysis suggests that the expected simple nucleophilic displacement of nitrogen is not involved. Whilst evidence in favour of alternative mechanisms is limited, the formation and radical cage decomposition of the covalent diazobromide is a distinct possibility.

The reaction with other halide ions has also been studied. Iodide ion reacts instantaneously, as in water, to give 85 ± 5% of *p*-iodonitrobenzene, but chloride ion reacts more slowly and the product contains only 24 ± 5% of *p*-chloronitrobenzene. The remaining products contain *p*-nitrophenol together with coupled products which are also formed in the reaction with fluoride ion which gives no *p*-fluoronitrobenzene. If these reactions were straightforward nucleophilic displacements, the product yield of *p*-halogenonitrobenzene would be expected to increase in the order *p*-iodo < *p*-bromo < *p*-chloro because the accepted reactivity order[5,6] of the free halide ions in dipolar aprotic solvents like dimethyl sulphoxide is $Cl^- > Br^- > I^-$. Nucleophilic displacement of nitrogen can thus be ruled out in these cases also.

Brief studies of the reaction of chloride, bromide, and iodide ion with benzenediazonium ion in dimethyl sulphoxide showed that phenol and dimethyl sulphide are formed rather than the appropriate halogenobenzene.

Owing to the difficulties involved in obtaining meaningful kinetic data, the partial yield of halogenobenzenes, and the apparent differences in mechanism between the reactions in water and dimethyl sulphoxide, it is not intended to continue this work.

Experimental.—*Materials.* Dimethyl sulphoxide, purified by treatment with molecular sieves (B.D.H. grade 5A), followed by drying (barium oxide) and fractional distillation under reduced pressure, had b. p. 80°/12 mm. *p*-Nitrobenzenediazonium fluoroborate and benzenediazonium fluoroborate were prepared by the method of Lewis and Hinds,[1] and recrystallised from acetone and from methanol. Sodium bromide was recrystallised twice from distilled water. Sodium chloride was precipitated from its aqueous solution by gaseous hydrogen chloride. Sodium iodide was recrystallised from water. Sodium fluoride was precipitated from solutions of recrystallised potassium fluoride and sodium chloride. The halides were all dried *in vacuo* at 140—145°.

Product studies. The diazonium ion, either in solution or in a solid, was added to a solution of the halide in dimethyl sulphoxide. The mixture was left for from 10 min. (with sodium bromide in sunlight) to several hours and poured into a large excess of water. The halogenonitrobenzene was extracted with ether, and the ethereal solution washed with dilute alkali and water, dried, the ether evaporated, and the residue chromatographed on alumina with benzene and light petroleum (b. p. 60—80) mixtures as eluents. The reaction in sunlight was carried out under conditions where the rate of the photochemical reaction was at least ten times faster than the rate of the " dark " reaction.

Kinetic studies. A Warburg flask containing sodium bromide (*ca.* 100 mg.) and dimethyl sulphoxide (5·0 ml.) in one limb and the solid diazonium salt (*ca.* 5 mg.) in another was placed in a thermostat-bath and shaken for from 1 to 1·5 hr. under slight nitrogen pressure. At time zero the flask was shaken so that the diazonium salt dissolved immediately, and the increase in pressure due to nitrogen evolution was followed at constant volume, as a function of time. The first-order rate coefficients were calculated by the method of Guggenheim.[4]

The author is indebted to Mr. C. Cooksey and Mr. C. Hedley for experimental assistance.

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[*Received, May 4th*, 1964.]

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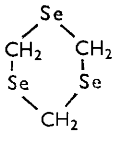
[5] Parker, *Quart. Rev.*, 1962, **16**, 163.

[6] Weaver and Hutchison, *J. Amer. Chem. Soc.*, 1964, **86**, 261.

137. *Preparation and Structure of* 1,3,5-*Triselenan.*

By L. Mortillaro, L. Credali, M. Mammi, and G. Valle.



During investigations on formaldehyde, thioformaldehyde, selenoformaldehyde, and their oligomers and polymers, we have examined the compound obtained by reaction of hydrogen selenide with formaldehyde in aqueous solution, in the presence of concentrated hydrochloric acid. It had been prepared previously[1] and its empirical formula obtained from elemental analysis, but its molecular weight was not measured owing to its low solubility in the usual organic solvents. By *X*-ray analysis we have shown that the compound is the cyclic trimer (I) of selenoformaldehyde, namely, 1,3,5-triselenan.

Experimental.—We followed the previous preparation.[1] The crude product was extracted with ethanol (Soxhlet) for 72 hr.; much of the product, at present under examination, remained unextracted. After 24 hr. the ethanol solution deposited silky crystals which were filtered off, washed with a small quantity of ethanol and ether, and dried at 50° for 1 hr. Sublimation at *ca.* 190° under a vacuum gave long colourless needles which became green-yellow after long exposure to light. (Found: C, 13·1; H, 2·3; Se, 84·3. Calc. for $C_3H_6Se_3$: C, 12·9; H, 2·15; Se, 85·0%). At 20°, the solubility (%) is 0·53 in dioxan, 0·39 in benzene, 0·47 in tetrahydrofuran, and 0·76 in dimethylformamide. The melting point cannot be determined in the air; at 160° the crystals, examined with a microscope, are seen to break into smaller crystals, a garlic-like smell being apparent, and at 189° they partially sublime and decompose with formation of small drops; " melting " is complete at 209°. However, by sealing the crystals in a very narrow capillary, they melted sharply at 226—228°. Different values (between 205 and 215°) reported in the literature[1,2] may be due to the above phenomena.

X-*Ray analysis.*—This was carried out on single crystals obtained, by sublimation at 190°, as long colourless rhombic prisms elongated along the *c*-axis; they blackened after long exposure to *X*-rays. The results are as follows, the corresponding data for 1,3,5-trithian being given in parentheses: both were orthorhombic with space group $Pmn2_1$ (C_{2v}^7); $a = 7{\cdot}985$ (7·668), $b = 7{\cdot}265$ (7·003), $c = 5{\cdot}442$ (5·285) Å, $U = 315{\cdot}7$ (283·8) Å^3, $Z = 6 \times CH_2Se$ ($2 \times [CH_2S]_3$), $D_m = 2{\cdot}905$ (1·590) (by flotation), $D_c = 2{\cdot}916$ (1·608). Cu K_α-radiation; rotation, Weissenberg, and precession photographs. (The data for 1,3,5-trithian were obtained during the present work; cf. refs. 3 and 4).

By comparing these figures and the diffraction intensities, the isomorphism of the two structures was established. The compound under examination is therefore the triselenoformaldehyde with the same cyclic structure as trithioformaldehyde, that is, with the chair configuration.[3,4] There are two such molecules in the unit cell. These results are independent of any consideration of the exactness of the trithian structure data, whose previous determination by trial and error is unsatisfactory.[3,5a]

Triselenoformaldehyde and trithioformaldehyde are isomorphous, whilst trioxan crystallizes with a different packing (space group $C_{3v}^6 = R3c$).[6] This agrees with the experimental results for several oxygenated and sulphurated compounds, and can be justified by theoretical considerations of atomic radii and packing efficiency.[5b] Further, these three cyclic molecules provide a rather unusual case in crystallography, as each of them retains in the crystal symmetry one element only of their molecular symmetry $3m$, but

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[1] L. Vanino and A. Schinner, *J. prakt. Chem.*, 1915, **91**, 116.
[2] T. G. Pearson, R. H. Purcell, and G. S. Saigh, *J.*, 1938, 409.
[3] N. F. Moermann and E. H. Wiebenga, *Z. Krist.*, 1957, *B*, **97**, 323.
[4] J. Toussaint, *Bull. Soc. roy. Sci. Liège*, 1957, **26**, 73.
[5] A. J. Kitaigorodskii, " Organic Chemical Crystallography," Consultant Bureau, New York, 1961, (*a*) pp. 134, 449; (*b*) p. 223.
[6] V. Busetti, M. Mammi, and G. Carazzolo, *Z. Krist.*, 1963, **119**, 310.

not the same one; trioxan loses its mirror plane and retains its three-fold axis, whilst the opposite is true for the thio- and seleno-compounds.

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138. *Fluorocyclopentanes. Part II.*[1] *Hexafluorocyclopentadiene.*

By J. Burdon, T. M. Hodgins, D. R. A. Perry, R. Stephens, and J. C. Tatlow.

In the first synthesis of hexafluorocyclopentadiene,[2] perchlorocyclopentadiene was fluorinated to give tetrachlorohexafluorocyclopentane which was dechlorinated by zinc dust in dioxan. We now report two other routes to this important diene, based on the partial fluorination of either cyclopentane or cyclopentadiene.[1]

In the earlier work, 3*H*- and 4*H*-heptafluorocyclopentene were prepared, but neither afforded hexafluorocyclopentadiene when refluxed with aqueous alkali.[1] Extensive decomposition was observed, and this was ascribed to nucleophilic attack by aqueous alkali on the fluoro-diene. An alternative approach was sought by addition of chlorine to 4*H*-heptafluorocyclopentene followed by dehydrofluorination with aqueous potassium hydroxide to give a 3,4-dichlorohexafluorocyclopentene. Dechlorination of this by pyrolysis over heated nickel, or with unactivated zinc dust in various solvents, *viz.*, ethanol, acetamide, dioxan, was unsuccessful, however, paralleling the observations[2] with tetrachlorohexafluorocyclopentane and zinc dust in ethanol and in n-butanol. However, addition of bromine to 4*H*-heptafluorocyclopentene, followed by dehydrofluorination of the dibromo-adduct with aqueous alkali, afforded a 3,4-dibromohexafluorocyclopentene which could be converted into the diene.

Three debromination procedures were examined. Potassium iodide in methanol at room temperature had no effect, but both zinc dust in glacial acetic acid and magnesium turnings in tetrahydrofuran gave hexafluorocyclopentadiene (yields 33 and 22%, respectively). The latter debromination may well proceed through the Grignard reagent but no attempts were made to establish this.

Subsequently, other dehydrofluorination processes were applied to 3*H*- and 4*H*-heptafluorocyclopentene. Pyrolysis over sodium fluoride, known to dehydrofluorinate polyfluorocycloalkanes,[3] resulted in isomerisation[3,4] but no dehydrofluorination. Thus, 4*H*-heptafluorocyclopentene starting material was recovered in admixture with the isomeric 1*H*- and 3*H*-olefins. However, molten potassium hydroxide gave hexafluorocyclopentadiene in 37% yield from both 3*H*- and 4*H*-heptafluorocyclopentene, separately and in admixture (these olefins are produced together [1]). A short contact time was employed to minimise decomposition. This reaction is of interest as a possible general route to related polyfluorocyclopentadienes.

Hexafluorocyclopentadiene displayed in general the properties reported previously.[2] Chlorination of hexafluorocyclopentadiene gave the 1,2,3,4-tetrachlorohexafluorocyclopentane[2] formed also on chlorination of 3,4-dichlorohexafluorocyclopentene. Hexafluorocyclopentadiene dimer was obtained as a waxy solid displaying the properties described already.[2] It was of interest to note that de-dimerisation did not occur even after 16 hours

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[1] Part I, Heitzman, Patrick, Stephens, and Tatlow, *J.*, 1963, 281.
[2] Banks, Haszeldine, and Walton, *J.*, 1963, 5581.
[3] Rimmington, Stephens, and Tatlow, unpublished work.
[4] Miller, Fried, and Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091.

at 200°. Fluorination of the dimer in the vapour phase with cobaltic fluoride gave a highly crystalline fluorocarbon, $C_{10}F_{16}$, by saturation of the double bonds. A Diels–Alder dimerisation process was indicated by the isolation, in small yield, of the same fluorocarbon, presumably perfluoro-*endo*-tricyclo[5,2,1,0]decane, from the cobaltic fluoride fluorination of tetrahydro-*endo*-dicyclopentadiene.

Experimental.—Pyrolysis of 4H-*heptafluorocyclopentene over sodium fluoride.* The olefin (8·1 g.) was vaporised during 2 hr. in a stream of nitrogen (3 l./hr.) passing through a glass tube (70 cm. × 50 mm. diam), at 330°, packed with sodium fluoride pellets. The product (7·4 g.), trapped at −180° was separated by gas chromatography [column A (4·8 m. × 75 mm., dinonyl phthalate–kieselguhr); 90°; N_2 55 l./hr.], to give (i) 1*H*- and 4*H*-heptafluorocyclopentene (3·4 g.) and (ii) 3*H*-heptafluorocyclopentene (2·8 g.) with correct i.r. spectra.

Dehydrofluorination of the mixed 3H- *and* 4H-*heptafluorocyclopentenes.* The liquid mixed olefins (2·0 g.) were introduced below the surface of molten potassium hydroxide (5·0 g.) at 260° in an all-glass apparatus, a very vigorous reaction occurred with the production of a dark colour, and the product (1·3 g.) was collected at −180°. Gas-chromatographic separation [column B (4·8 m. × 35 mm., dinonyl phthalate–kieselguhr); 62°; N_2 15 l./hr.] of the combined products (2·8 g.) of two experiments gave: (i) hexafluorocyclopentadiene (0·97 g.), b. p. 29° was the lowest value obtained by the capillary tube method and rose on repeating the measurement or after keeping at room temperature; mass spectrometry showed a large parent mass peak at 174 (C_5F_6) and a consistent fragmentation pattern;[5] $\nu_{max.}$ 1765 cm.$^{-1}$ (CF:CF); $\lambda_{max.}$ 2730 Å (ε 2885) in ethanol, and 2730 Å (ε 905) in cyclohexane; (ii) mixed 3*H*- and 4*H*-heptafluorocyclopentene (1·10 g.) with a correct i.r. spectrum.

3*H*-Heptafluorocyclopentene (1·5 g.) in the same way gave a liquid product (1·1 g.) which was shown by gas chromatography (peak areas) to contain starting material and hexafluorocyclopentadiene (44%). 4*H*-Heptafluorocyclopentene (1·8 g.) under the same conditions gave a similar product (1·2 g.) containing starting material and hexafluorocyclopentadiene (46%).

After being kept at room temperature for several days hexafluorocyclopentadiene gave a solid dimer[2] (70%), m. p. 42—43° (lit.,[2] 42·5—43°) (Found: C, 34·0; F, 64·8. Calc. for $C_{10}F_{12}$: C, 34·5; F, 65·5%); mass spectrometry gave a parent mass peak at 348 ($C_{10}F_{12}$); $\nu_{max.}$ 1760 cm.$^{-1}$ (CF:CF). The dimer (1·4 g.) was fluorinated in the vapour phase over cobaltic fluoride in the normal way at 180°, to give a saturated *fluorocarbon* (1·3 g.), m. p. 117° (Found: C, 27·9; F, 72·0. $C_{10}F_{16}$ requires C, 28·3; F, 71·7%); mass spectrometry gave a top mass peak of 424 ($C_{10}F_{16}$); ^{19}F n.m.r. spectrum of a saturated solution in hexafluorobenzene gave no signals ascribable to CF_3 groups.[6]

Chlorination of 4H-*heptafluorocyclopentene* (with R. J. Heitzman). The olefin (19·0 g.) and chlorine (30 g.) in a quartz flask surmounted by a condenser at −78° were irradiated with ultraviolet light for 3½ hr. The chlorine-freed product (24·0 g.) was dried (P_2O_5) and distilled. Gas chromatography of the distillate showed two peaks neither of which was starting material and the i.r. spectrum showed absorption at 2900 cm.$^{-1}$ ($\rightarrow$CH), but none for C:C groups.

Dehydrofluorination of 1H-3,4-*dichloroheptafluorocyclopentane* (with R. J. Heitzman). This compound (24·0 g.) potassium hydroxide (27 g.) and water (27 c.c.) were refluxed for 2 hr., to give a 3,4-*dichlorohexafluorocyclopentene* (20·7 g.), b. p. 87·5—88° (Found: C, 24·8; Cl, 28·4; F, 46·2. $C_5Cl_2F_6$ requires C, 24·5; Cl, 28·9; F, 46·5%), $\nu_{max.}$ 1770 cm.$^{-1}$ (CF:CF), g.l.c. (dinonyl phthalate) showed one peak.

Bromination of 4H-*heptafluorocyclopentene.* The olefin (21·8 g.) and bromine (46·6 g.) in a quartz flask were irradiated with ultraviolet light for 49 hr. The bromine-freed product (38·4 g.), b. p. 141—143°, contained no starting material as shown by i.r. spectroscopy.

Dehydrofluorination of 1H-3,4-*dibromoheptafluorocyclopentane.* This compound (45·4 g.), potassium hydroxide (60·0 g.), and water (60 c.c.) were shaken together at room temperature for 12 hr. The organic layer (28·6 g.) was separated by gas chromatography (column A; 98°; N_2 50 l./hr.), to give a 3,4-*dibromohexafluorocyclopentene* (21·7 g.), b. p. 121° (Found: C, 17·9; H, 0·0; Br, 48·0. $C_5Br_2F_6$ requires C, 17·9; Br, 47·9%), $\nu_{max.}$ 1760 cm.$^{-1}$ (CF:CF).

Debromination of 3,4-*dibromohexafluorocyclopentene.* (a) *With zinc.* The dibromide (0·6 g.), zinc dust (5·0 g.), and glacial acetic acid (12 c.c.) were heated together, and a low-boiling material

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[5] Majer, personal communication.

[6] Thomas, personal communication.

trapped at −180°. Analytical gas chromatography indicated, in addition to acetic acid, the presence of one major and three minor components; preparative g.l.c. (column B; 100°; N_2 15 l./hr.) gave hexafluorocyclopentadiene (0·1 g.) with a correct i.r. spectrum.

(b) *With magnesium.* The dibromide (4·5 g.) was added to dry magnesium turnings (7·3 g.) in redistilled tetrahydrofuran (100 c.c.), and a small crystal of iodine was added. After 2 hr. at room temperature the magnesium had become black. The mixture was stirred and heated to reflux while a stream of nitrogen (1 l./hr.) was passed through it. The gas stream leaving the condenser was passed through a trap at −180°. After 8 hr. the contents of the trap were separated by g.l.c. (column B; 100°; N_2 15 l./hr.), to give: (i) tetrahydrofuran; (ii) hexafluorocyclopentadiene (0·5 g.) with a correct i.r. spectrum.

Chlorination of 3,4-*dichlorohexafluorocyclopentene and of hexafluorocyclopentadiene.* The dichloro-olefin (1·2 g.) and chlorine (1·1 g.) in a sealed Pyrex tube were irradiated with ultraviolet light for 6 hr.; excess of chlorine was removed, to leave 1,2,3,4-tetrachlorohexafluorocyclopentane (1·1 g.), b. p. 153° (lit.,[2] 150—151°) (Found: C, 19·3. Calc. for $C_5Cl_4F_6$: C, 19·0%). The diene (0·1 g.) in the same way gave an identical material (0·06 g.) as shown by i.r. spectroscopy.

The authors thank Dr. J. R. Majer and Dr. L. F. Thomas for the mass-spectral and n.m.r. measurements, and the Hooker Chemical Corporation for grants (to T. M. H. and D. R. A. P.).

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139. *Nuclear Magnetic Resonance Spectra of Some Substituted Oxirans.*

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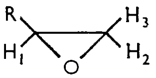
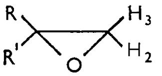
THE ring protons of monosubstituted oxirans (I) and some disubstituted oxirans (II) give n.m.r. spectra characterised by coupling constants with approximate average values 5·5, 3·8, and 2·6 c./sec. The largest constant can be assigned unambiguously to J_{23} (see below) but it is impossible to assign J_{12} and J_{13} from the spectral analysis of a given compound. However, in *trans*-disubstituted oxirans [1,2] the coupling constant J_{13} is approximately 2 c./sec., which suggests that a reasonable assignment for the monosubstituted oxirans is $J_{13} \approx 2·6$ and $J_{12} \approx 3·8$.



(I)



(II)

The n.m.r. spectral parameters of twelve substituted oxirans are summarised in the Table. Precise values for chemical shifts of the H_1 proton cannot be given for most of the monosubstituted compounds because of coupling to protons of the substituent group R, but the existence of this interaction makes the assignment unambiguous. In the case of phenyloxiran the R–H_1 interaction is very weak but here the perturbing effect of the phenyl group aids assignment, and a detailed analysis of this spectrum is available [1] elsewhere. Only in t-butyloxiran is the chemical shift of H_1 in serious doubt. Our selection of $\tau = 7·40$ is based simply on the fact that the average coupling constant $\langle J \rangle = 3·53$ c./sec. deduced from this AB_2 spectrum [3] is more consistent with the arithmetic mean of J_{12} and J_{13} (3·2) than with the two other possible combinations which give $\langle J \rangle = 4·0$ and 4·8.

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[1] Reilly and Swalen, *J. Chem. Phys.*, 1960, **32**, 1378.

[2] C. A. Reilly, personal communication (1962).

[3] Wiberg and Nist, " Interpretation of N.M.R. Spectra," Benjamin, New York, 1962, pp. 11 ff.

N.m.r. spectra of substituted oxirans.

	$H_1(R')$	Ph	H_1	H_2	H_3	CH_2	CH_3	J_{12}	J_{13}	J_{23}
R		τ						c./sec.		
H	H	—	7·45	7·45	7·45	—	—	—	—	—
CH_3	H	—	7·20	7·40	7·77	—	8·68	—	2·5	5·5
CD_3	H	—	7·19	7·43	7·75	—	—	3·4	2·6	5·3
C_2H_5	H	—	7·2	7·3	7·66	8·54	9·02	—	2·9	5·6
$C(CH_3)_3$	H	—	7·40	7·52	7·52	—	9·09	$\langle J \rangle = 3{\cdot}53$		
$CH_2{\cdot}C(CH_3)_3$	H	—	7·17	7·40	7·75	8·64	9·00	3·9	2·5	5·6
CH_3	CH_3	—	—	7·58	7·58	—	8·74	—	—	—
C_6H_5	H	2·75	6·25	7·07	7·45	—	—	$3{\cdot}9_5$	2·50	$5{\cdot}7_5$
C_6H_5	CH_3	2·75	—	7·22	7·45 *	—	8·34	—	—	$5{\cdot}7_5$
C_6H_5	C_2H_5	2·69	—	7·05	7·30	8·1	9·09	—	—	5·8
cis-Stilbene oxide	H	2·62	6·11	6·11	—	—	—	—	—	—
trans-Stilbene oxide	H	2·80	5·63	—	5·63	—	—	—	—	—

* The high-field " doublet " of this AB " quartet " is a pair of quartets, each with $J = 0{\cdot}55$ c./sec., due to long-range coupling with the CH_3 group.

Following the identification of H_1, values for J_{23} can be deduced from the fine-structure of a spectrum. They lie between 5·5 and 5·7 c./sec. and compare well with the results for 1,1-disubstituted oxirans. Finally, H_2 and H_3 have been assigned with the assumption that J_{12} is always greater than J_{13}. On this basis H_3 lies consistently to high field of H_2. This is consistent with the findings of Williamson *et al.*[4]

The high-resolution spectra of solutions of monosubstituted oxiran polymers show that the chemical shifts of H_1, H_2, and H_3 move downfield when the ring is opened. The ABC spectra of these protons in poly(methyloxiran) and poly-(t-butyloxiran) collapse to a strong central peak with wings indicating that differences in the chemical shifts have also been reduced, and in poly(phenyloxiran) the methylene protons are virtually equivalent. The chemical shifts (τ) are: $[\overline{CH_2{\cdot}CH_2{\cdot}O}]_n$ 6·45 (singlet); $[\overline{CH(CH_3){\cdot}CH_2{\cdot}O}]_n$ 6·7 (centre of ABC pattern); $[\overline{CH(CMe_3){\cdot}CH_2{\cdot}O}]_n$ 6·6 (centre of ABC pattern); $[\overline{CHPh{\cdot}CH_2O}]_n$ 6·58 ($-CH_2$), 5·67 ($-CH$). The displacement to low field observed on ring-opening is similar in magnitude ($\Delta\tau \gtrsim 1{\cdot}0$) to that observed in the corresponding case of cyclopropane derivatives.[5] Thus, it appears that loss of ring strain is primarily responsible for the change in chemical shift of the ring protons on polymerisation. The electronegative oxygen atom seems to have little influence, despite the fact that it is primarily responsible for the low τ-values of the protons in oxirans and polyoxirans.

Experimental.—The oxirans were commercial products except neopentyl-,[6] t-butyl-,[5] and 1-methyl-1-phenyl-oxiran.[7] They were purified by fractional distillation and their purity checked by vapour-phase chromatography.

N.m.r. spectra were obtained from 10% solutions in CCl_4 or $CDCl_3$ using a Varian A60 spectrometer. The AB_2 spectrum of t-butyloxiran was also obtained at 25 Mc./sec. on an A.E.I. RS 2 instrument, and by comparison with the 60 Mc. spectrum a value of $\langle J \rangle$ was obtained.

We thank Dr. J. M. Bruce and Mr. S. J. Hurst for gifts of neopentyl- and t-butyl-oxiran.

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[4] Williamson, Lanford, and Nicholson, *J. Amer. Chem. Soc.*, 1964, **86**, 762.
[5] Graham and Rogers, *J. Amer. Chem. Soc.*, 1962, **84**, 2249.
[6] Hurst and Bruce, *J.*, 1963, 1321.
[7] Tiffeneau, *Ann. Chim.* (*France*), 1907, [8], **10**, 176, 191.

140. *Tritertiary Phosphine Monocarbonyl Complexes of Nickel.*

By J. Chatt and F. A. Hart.

Some time ago we measured the electric dipole moments and infrared carbonyl stretching frequencies of the complexes $[Ni(CO)_3X]$, $[Ni(CO)_2X_2]$, and $[Ni(CO)_2t]$ where X = PPh_3 and $AsPh_3$ and t = various ditertiary phosphines and arsines.[1] From these we estimated that the Ni–P bond moment is about 3·4D in all these compounds and that the Ni–P bond order lay between 1·4 and 1·7.

Since then, there have been many attempts to estimate the bond orders of Ni–P and Ni–CO bonds in tertiary phosphine substituted nickel carbonyl,[2-4] but little use has been made of dipole moments for this purpose. We have, therefore, extended our previous study by preparing the stable trisubstituted complexes $[NiCO\{PhP(o\text{-}C_6H_4PEt_2)_2\}]$ (I) and $[NiCO\{MeC(CH_2PPh_2)_3\}]$ (II). These have dipole moments of 5·2 and 4·9D and carbonyl stretching frequencies of 1912 and 1901 cm.$^{-1}$, respectively. They are also new representatives of a rare class of compound in which only one carbonyl group is attached to a metal in its zero-oxidation state.

Models show that (II) is not stereochemically rigid enough for bond-moment calculations, but (I) is. Using the same assumptions as previously,[1] we arrive at a Ni–P bond moment of about 3·2D in (I). As substitution of CO by tertiary phosphines proceeds, the M–CO bond order increases, and this has been shown by increased M–C and decreased C–O stretching frequencies.[3] Similar decrease of ν(C–O) is observed along our series, *e.g.*, $[Ni(CO)_3PPh_3]$ (2063, 1987 cm.$^{-1}$), $[Ni(CO)_2\{o\text{-}C_6H_4(PEt_2)_2\}]$ (1986, 1925 cm.$^{-1}$) and $[NiCO\{PhP(o\text{-}C_6H_4PEt_2)_2\}]$ (1912 cm.$^{-1}$). It is surprising that the Ni–P bond moment should remain approximately constant throughout this series, since decreased ν(C–O) is indicative of greater negative charge density on the nickel atom, and this should be dissipated to some extent on to both the phosphine and carbonyl groups by increased π-bonding and decreased σ-bonding. It seems likely that this occurs, but that the dissipation on to the phosphine and carbonyl groups just balances. This possibility severely limits the accuracy with which we can estimate individual bond moments and bond orders from these results.

It is interesting that, in this series of substituted nickel carbonyls, no discontinuity is observed in the values of the apparent Ni–P bond moment in passing from the di- to trisubstituted complexes. A discontinuity would be expected if the tetrahedral nickel(0) atom could form only two strong π-bonds as predicted by Kimball.[5] Cotton,[6] on the other hand, has shown that nickel(0) may form 5 strong π-bonds. The absence of discontinuity suggests that it does.

Experimental.—Microanalyses were made in these laboratories. All experiments and measurements were done under nitrogen.

Carbonylphenylbis-(o-*phenylenediethylphosphine*)*phosphinenickel*, $[NiCO\{PhP(o\text{-}C_6H_4PEt_2)_2\}]$. The triphosphine (0·546 g.) in benzene (5 c.c.) was treated at 20° with nickel carbonyl (0·161 c.c., 1 mol.). After 30 min. the orange solution was taken to dryness at 12 mm. and the residue recrystallised from ethanol, giving orange crystals (0·46 g.), m. p. 189—191·5° *in vacuo* (Found: C, 61·5; H, 6·3%; *M*, ebullioscopically in 0·54% benzene soln., 508; in 1·01% benzene soln., 556. $C_{27}H_{33}OP_3Ni$ requires C, 61·7; H, 6·3%; *M*, 525). The complex is very sensitive to air. It is diamagnetic and a non-conductor in acetone solution.

*Carbonyl-*1:1:1-*tris*(*diphenylphosphinomethyl*)*ethanenickel*, $[NiCO\{CH_3C(CH_2PPh_2)_3\}]$. The triphosphine (2 g.) in benzene (10 c.c.) was treated with nickel carbonyl (0·415 c.c., 1 mol.) at

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[1] Chatt and Hart, *J.*, 1960, 1378.
[2] Meriwether and Leto, *J. Amer. Chem. Soc.*, 1961, **83**, 3192.
[3] Bigorgne, *Bull. Soc. chim. France*, 1960, 1986.
[4] Stammreich, Kawai, Sala, and Krumholz, *J. Chem. Phys.*, 1961, **35**, 2168.
[5] Kimball, *J. Chem. Phys.*, 1940, **8**, 194.
[6] Cotton, *J.*, 1960, 5269.

20°. The initial effervescence soon stopped, but the almost colourless solution effervesced further, and turned yellow, on warming to 70° for 10 min. The solution was boiled to small bulk, and on cooling deposited yellow prisms (1·39 g.). These were twice recrystallised from benzene, giving 0·45 g., m. p. 317° (decomp., with darkening from 290°) *in vacuo* (Found: C, 70·6; H, 5·9%; *M*, ebullioscopically in 0·80% benzene, 722; in 1·46% benzene soln., 709. $C_{42}H_{39}NiOP_3$ requires C, 70·9; H, 5·5%; *M*, 711). The complex is air-sensitive, diamagnetic and a non-conductor in acetone solution.

Dipole moments. These were determined as described previously[7] and, in addition, the apparatus was adapted so that all solutions were made up and measurements made in a nitrogen atmosphere. The densities of the solutions were estimated. The refractive index is for the Na_D line.

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2 n/\omega$	$-\Delta\varepsilon/\omega$	P_T	P_E	P_O	μ
[NiCO{PhP(o-$C_6H_4PEt_2)_2$}]							
2·047	6·364	—					
2·406	6·044	—					
2·747	6·193	—					
3·276	6·144	—					
3·753	6·422	—					
4·859	6·035	—					
29·37	—	14·00					
46·27	—	15·04	0·40	730	158	549	5·18 ± 0·2 D
[NiCO{$CH_3C(CH_2PPh_2)_3$}]							
2·345	4·417						
3·413	4·398		0·40	749	216 *	500	4·95 ± 0·2 D

* Calculated from group refractivities because of insolubility.

Preparation of the tri-tertiary phosphines. We are indebted to W. Hewertson and H. R. Watson[8] for our sample of the triphosphine, Me·C($CH_2PPh_2)_3$. The *o*-phenylene triphosphine was prepared by the method described by Hart.[9]

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[7] Chatt and Shaw, *J.*, 1959, 705.
[8] Hewertson and Watson, *J.*, 1962, 1490.
[9] Hart, *J.*, 1960, 3324.

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141. *Dicyclohexylcarbodi-imide: A New Agent for Carbohydrate Epimerization and Isomerization. Part I. Psicose Formation.*

By SUSANA PASSERON and EDUARDO RECONDO.

CARBODI-IMIDES have been successfully used for nucleotide synthesis.[1] They also react with carboxylic acids,[2] phosphoric esters,[3] and sulphonic acids.[4] On the other hand, alcohols[5] and phenols[6] react only at high temperatures to form crystalline ethers of pseudourea. There is no description in the literature of reaction of carbodi-imides with sugars or related substances.

During the course of experiments designed for the preparation of glycosides, it was found that carbodi-imides lead to epimerization of reducing sugars. On heating fructose with dicyclohexylcarbodi-imide in anhydrous methanol, no formation of glycoside was observed but paper chromatography showed that a mixture of glucose, mannose, and psicose had been formed.

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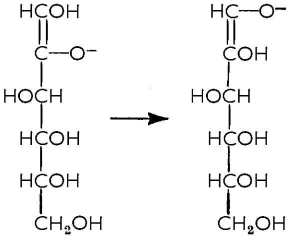
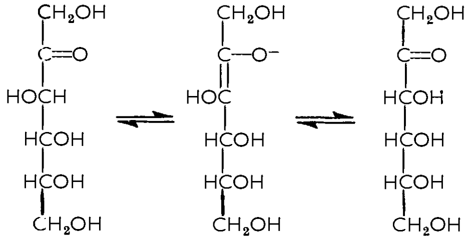
[1] Christie, Elmore, Kenner, Todd, and Weymouth, *J.*, 1953, 2947.
[2] Smith, Moffatt, and Khorana, *J. Amer. Chem. Soc.*, 1958, **80**, 6204.
[3] Khorana and Todd, *J.*, 1953, 2257.
[4] Khorana, *Canad. J. Chem.*, 1953, **31**, 585.
[5] Lengfeld and Steizlitz, *Ber.*, 1894, **27**, 926.
[6] Bush, Blume, and Preugs, *J. prakt. Chem.*, 1909, **79**, 513.

Epimerizations are known [7] to proceed under acid or basic conditions but as far as we know, not in neutral solutions, such as is the case with dicyclohexylcarbodi-imide. The evidence accumulated indicates that all such transformations arise by an enolization mechanism.

Carbodi-imides, in common with other classes of compounds containing twinned double bonds, readily undergo 1,2-addition reactions, and a mechanism can be visualized similar to that postulated [2] for anhydride formation. Dicyclohexylcarbodi-imide would work as a Brønsted base by removing a proton from fructose. Anion (I) would be isomerized to anion (II) which then equilibrates with glucose and mannose.


(I) (II)


D-Fructose (III) D-Psicose

Psicose formation would be explained by a similar mechanism by way of anion (III). The advantage of the use of a neutral reagent for the Lobry de Bruyn–van Ekenstein transformation is obvious. Side-reactions would be minimized and yields would increase. In fact, starting with D-fructose, D-psicose is obtained in a yield as high as 25%.

D-Galactose shows a similar reaction pattern, and in this case D-tagatose is the main product. Application of dicyclohexylcarbodi-imide and other carbodi-imides to the different sugar series and substituted sugars is now being studied.

Optimum conditions for the reaction have been determined. Several solvents, such as ethanol, ethylene glycol dimethylether, acetone, acetonitrile, and pyridine were tried without significant improvements. By increasing time or temperature, compounds which chromatographed very slowly in butanol–pyridine–water were obtained. On electrophoresis they behave like glucuronic acid and are presumably mixtures of saccharinic acids.[8]

Experimental.—Analyses by Mr. Charles Beazley, Microtech Laboratories, Skokie, Ill., U.S.A. Evaporations were carried out under reduced pressure. The following solvent mixtures were used to separate and identify the sugars by paper chromatography: (A) butanol–pyridine–water (6 : 4 : 3), (B) butanol–ethanol–water (40 : 11 : 19), and (C) butanol–pyridine–0·05M-morpholine borate (7 : 5 : 2). Paper electrophoresis was carried out in an apparatus similar to that described by Markham and Smith.[9] A 600v potential was applied for 2 hr. In all cases, sugars were located with an alkaline silver reagent.[10]

Qualitative Experiments.—(*a*) *Fructose.* Greatest yields were obtained by heating fructose (0·009 g., 50 μmoles) and dicyclohexylcarbodi-imide (0·051 g., 250 μmoles) in methanol (0·5 ml.) at 85° for 15 hr. In all cases the reaction was stopped by adding an equal volume of water and aliquots were chromatographed in solvent (A).

(*b*) *Galactose.* Galactose (0·018 g., 100 μmoles), dicyclohexylcarbodi-imide (0·103 g., 500 μmoles), and methanol (1 ml.) were heated at 100° for 1½ hr. Water (1 ml.) was added and the mixture extracted with ether (2 × 2·0 ml.). The clear solution was submitted to paper chromatography in solvents (A) and (C), with appropriate standards. The latter distinguishes clearly between tagatose, sorbose, and fructose. Tagatose was formed in a high yield and a small amount of sorbose was also detected.

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[7] Speck, *Adv. Carbohydrate Chem.*, 1958, **13**, 63.

[8] Kenner and Richards, *J.*, 1954, 278; Corbett and Kenner, *J.*, 1954, 3274.

[9] Markham and Smith, *Biochem. J.*, 1952, **52**, 552.

[10] Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444.

Quantitative experiments. A solution of D-fructose (0·018 g.) and dicyclohexylcarbodi-imide (0·10 g.) in methanol (1 ml.) was heated at 85° for 15 hr. The reaction was stopped by adding 1 ml. of water. Three ether extractions were carried out to remove excess of dicyclohexylcarbodi-imide and coloured products. The mixture was separated on a sheet of 3MM filter filter paper (solvent A), the corresponding sugars were eluted and estimated with appropriate standards by the Somogyi–Nelson method [11] for reducing sugars and that of Roe [12] for keto-hexoses.

The mixture consisted of 45% fructose, 5% mannose, 25% glucose, and 25% psicose. Sugar identification was confirmed by chromatography in solvents (A), (B), and (C).

Formation of D-*psicosazone.* Fructose (3 g.) and dicyclohexylcarbodi-imide (16 g.) were dissolved in methanol (160 ml.) and heated in a sealed tube at 85° for 16 hr. The reaction was stopped by adding 160 ml. of water. Three ether extractions were carried out on the mixture, and the extracts discarded. The neutral solution was shaken with charcoal (Norit A) in the cold for 2 hr. The suspension was filtered, and the clear filtrate evaporated to a syrup and dissolved in 0·01M-phosphate buffer (100 ml.).

Glucose, mannose, and fructose were removed from the mixture with baker's yeast. The cells were filtered off and the filtrate was deionized with Amberlite resin MB-3. Proteins were precipitated with 50% trichloroacetic acid and the excess of acid was eliminated by ether extraction. The aqueous layer was concentrated to a syrup (*ca.* 0·4 g.).

A solution of the syrup (0·3 g.) in water (7 ml.), phenylhydrazine (0·87 ml.), glacial acetic acid (1·06 ml.), and saturated sodium hydrogen sulphite solution (0·87 ml.) were heated on a water-bath for 30 min. On cooling, yellow crystals (0·22 g.) separated. After two recrystallizations from an aqueous ethanol, and a third from acetone–cyclohexane (7 : 11) they had m. p. 162—163°, undepressed on admixture with an authentic specimen of D-psicosazone (m. p. 163—164°) (Found: C, 60·1; H, 6·2; N, 15·5. Calc. for $C_{18}H_{22}O_4N_4$: C, 60·3; H, 6·2; N, 15·6%). When recrystallized from aqueous ethanol they showed $[\alpha]_D^{19}$ $-29°$ [c 0·51 in ethanol (2·5 ml.) and pyridine (0·1 ml.)] $\longrightarrow -20 \pm 3°$ (equilibn. 24 hr.) {lit.,[13] $[\alpha]_D^{19}$ $-30°$ [*c* 0·52 in ethanol (2·5 ml.) and pyridine (0·1 ml.)] $\longrightarrow -20 \pm 3°$ (equilibn. 24 hr.)}.

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[*Received, May 4th,* 1964.]

[11] Somogyi, *J. Biol. Chem.*, 1945, **160**, 61; Nelson, *ibid.*, 1944, **153**, 375.
[12] Roe, *J. Biol. Chem.*, 1934, **107**, 15.
[13] Hough, Jones, and Richards, *J.*, 1953, 2005.

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142. *Heterocyclic Polyfluoro-compounds. Part VII.*[1] *Direct Vapour-phase Fluorination of 2-Fluoropyridine.*

By R. E. BANKS and G. E. WILLIAMSON.

THE object of this work was to provide a better route to undecafluoropiperidine than electrochemical fluorination of pyridine.[2] This was not achieved: direct fluorination of 2-fluoropyridine at 150—160° gave a mixture of the compounds NF_3, CF_4, C_2F_6, C_3F_8, C_4F_{10}, n-C_5F_{12}, $CF_3{\cdot}CHF{\cdot}CF_3$, $C_2F_5{\cdot}CHF_2$, $CF_3{\cdot}NF_2$, $(CF_3)_2NF$, $(CF_3)_2NH$, $CF_3{\cdot}N{:}CF_2$, $CF_3{\cdot}N{:}CF{\cdot}CF_3$, $(CF_3)_2N{\cdot}N(CF_3)_2$, $CF_3{\cdot}[CF_2]_2{\cdot}CF{:}N{\cdot}CF_3$, $\overline{CF_2{\cdot}[CF_2]_3{\cdot}N}{\cdot}CF_3$, and $\overline{CF_2{\cdot}[CF_2]_4{\cdot}N}F$, together with unidentified material that probably contained perfluoro-1,1′-bipiperidyl.

[1] Part VI, Banks, Haszeldine, Latham, and Young, *J.*, 1965, 594.
[2] Banks, Ginsberg, and Haszeldine, *J.*, 1961, 1740.

Pure undecafluoropiperidine was isolated with difficulty in <0·1% yield; the estimated yield of this product was 3% [by gas–liquid chromatography (g.l.c.)].

Defluorination of undecafluoropiperidine with mercury at 320° gave perfluoro-2,3,4,5-tetrahydropyridine in 93% yield.

Experimental.—The fluorination apparatus was essentially the same as that used previously to study the halogenation of benzene with chlorine trifluoride.[3] Infrared spectra, used to identify most of the products, were recorded with Perkin-Elmer instruments (models 21 and 137) equipped with sodium chloride optics. A Perkin-Elmer Vapor Fraktometer (model 116) was used for g.l.c.

Fluorine (714 g.; 17·5 g./hr.), 2-fluoropyridine (262 g.; 6·4 g./hr.) diluted with nitrogen (7·5 l./hr.) and heated to 150°, and nitrogen (25·0 l./hr.) at 150° were fed simultaneously into the reactor, which was held at 150—160°, using a Bigelow "cool-flame" burner. A total of 537 g. of product condensed in Pyrex traps at −183°, and *ca.* 50 g. of a brown solid, which was discarded, collected in a steel trap at 100° that was attached directly to the exit from the reactor. A steel tube filled with sodium fluoride and heated to 100° was placed between the Pyrex and steel traps to remove hydrogen fluoride from the products. The fluorination product was evaporated at 23° *in vacuo*, to yield a gaseous fraction (40·83 l.), a volatile liquid (A) (*ca.* 110 ml.), and a residue (B) (213 g.) which consisted of a viscous yellow oil covered by a mobile colourless liquid. The gaseous fraction was shaken with mercury to remove compounds like $CF_2{:}NF$ which create difficulties during distillation processes by fouling mercury in manometers,[4] leaving 39·20 l. of material that was distilled and found to contain the compounds NF_3, CF_4, C_2F_6, COF_2, CO_2, SiF_4, $CF_3\cdot NF_2$ (these totalled 26·10 l.), C_3F_8 (a major component), C_4F_{10}, n-C_5F_{12}, $CF_3\cdot CHF\cdot CF_3$, $CF_3\cdot CF_2\cdot CHF_2$, $(CF_3)_2NF$ (a major component), $CF_3\cdot N{:}CF_2$, $(CF_3)_2NH$ (from $CF_3\cdot N{:}CF_2$ and HF [5]), $CF_3\cdot NCO$ (from $CF_3\cdot N{:}CF_2$ and H_2O encountered during work-up [6]), $CF_3\cdot N{:}CF\cdot CF_3$, $(CF_3)_2N\cdot N(CF_3)_2$, $CF_3\cdot COF$, and $C_2F_5\cdot COF$ (these last two presumably arose through ingress of oxygen into the reactor).

The liquid product (A) was heated under reflux with anhydrous sodium fluoride to remove any traces of hydrogen fluoride and to decompose any compounds that might readily release hydrogen fluoride before the material was introduced into expensive distillation equipment. The recovered material (93·7 g.), which was shown by g.l.c. to contain more than 20 components, was distilled through a 30 cm. × 8 mm. Podbielniak column packed with Heli-pak Hastelloy-B wire coils (0·036 × 0·07 × 0·07 in.), but no definite fractions were obtained. Material with b. p. 21—77° (42·8 g.) was separated by large-scale g.l.c. (18·5 ft. × 1·5 in., 30% w/w dinonyl phthalate on Celite, 70°, N_2, 600 ml./min.) to yield three fractions (I)—(III).

Fraction (I) (1·93 g.) was shown by infrared spectroscopy to be tetrakistrifluoromethylhydrazine (Found: *M*, 288. Calc. for $C_4F_{12}N_2$: *M*, 304) contaminated by impurities containing COF, C⁚N, and NF groups. These impurities were removed from a sample (1·75 g.) of the fraction by shaking it with aqueous 2N-sodium hydroxide (15 ml.) for 4 hr. at 23°; the organic residue (1·62 g., 93%) (Found: *M*, 304) was recovered by distillation *in vacuo*, dried (P_2O_5), and found to give an infrared spectrum that did not contain the bands at 5·32, 5·40 (COF), and 5·65 μ (C⁚N) that were present in the spectrum of (I).

A portion (0·38 g.) of the residue was shaken with 2N-hydriodic acid for 1 week at 80°; the aqueous phase became coloured by free iodine (0·045 g.), which was estimated by titration against 0·1N-sodium arsenite solution; the organic product (0·34 g., 90%), recovered by distillation *in vacuo* and dried (P_2O_5), was spectroscopically pure tetrakistrifluoromethylhydrazine (Found: C, 16·0; N, 9·3%; *M*, 300. Calc. for $C_4F_{12}N_2$: C, 15·8; N, 9·2%; *M*, 304). The impurity containing the NF group may have been $C_4F_9\cdot NF_2$, $CF_3\cdot NF\cdot C_3F_7$, or $(C_2F_5)_2NF$.

Fraction (II) (1·41 g.) was identified by infrared spectroscopy and g.l.c. as a mixture of perfluoro-(1-methylpyrrolidine) and perfluoro-(n-butylidenemethylamine).[7] A sample (1·20 g.) of this material was shaken with 2N-sodium hydroxide solution for 40 min. at 23°, and the organic residue was recovered by distillation *in vacuo* and dried (P_2O_5) to yield spectroscopically pure perfluoro-(1-methylpyrrolidine) (Found: *M*, 283. Calc. for $C_5F_{11}N$: *M*, 283). The hydrolysate,

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[3] Banks, Johncock, Mobbs, and Musgrave, *Ind. and Eng. Chem.* (*Process Design*), 1962, **1**, 262.

[4] Cuculo and Bigelow, *J. Amer. Chem. Soc.*, 1952, **74**, 710.

[5] Barr and Haszeldine, *J.*, 1955, 2532.

[6] Barr and Haszeldine, *J.*, 1956, 3428.

[7] Banks, Cheng, and Haszeldine, *J.*, 1962, 3407.

which gave positive tests for fluoride ions, was evaporated to dryness *in vacuo*, and the solid residue was extracted with absolute ethanol (15 ml.). The white solid obtained by evaporation of the extract was dissolved in water (5 ml.), and the solution (pH adjusted to 4 with hydrochloric acid) was treated with an aqueous solution of *S*-benzylthiouronium chloride, to yield *S*-benzylthiouronium heptafluorobutyrate (0·1 g.), m. p. 188° (from water) (lit.,[7] 187°) (Found: C, 38·1; H, 3·0; S, 8·7. Calc. for $C_{12}H_{11}F_7N_2O_2S$: C, 37·9; H, 2·9; S, 8·4%).

Fraction (III) (1·5 g.) showed four peaks on an analytical chromatogram, but it was resolved on a large-scale column (3 m. × 2·2 cm., 30% w/w didecyl phthalate on Celite, 20°) into spectroscopically pure undecafluoropiperidine (0·33 g.) (Found: C, 21·4; N, 5·2%; *M*, 283. Calc. for $C_5F_{11}N$: C, 21·2; N, 4·95%; *M*, 283) and a colourless liquid that was not identified.

A fraction (19·6 g.), separated from (A) by distillation, had an infrared spectrum similar to that reported [8, 9] for perfluoro-1,1′-bipiperidyl, but containing bands characteristic of C–H, C=C, and C=N bonds. The material had b. p. 77—105° (lit.,[8] 72°/51 mm.) (Found: C, 22·4; H, 0·4; N, 5·9. Calc. for $C_{10}F_{20}N_2$: C, 22·7; H, 0·0; N, 5·3%).

Residue (B) (213 g.), obtained by evaporation of the total product formed by fluorination of 2-fluoropyridine, was filtered through a plug of glass wool to yield a bright yellow viscous oil (130 g.), and a colourless involatile liquid (83 g.) that began to decompose with evolution of hydrogen fluoride when an attempt was made to distil it at atmospheric pressure. When this liquid was distilled at reduced pressure it boiled over the range 80°/400 mm.—75°/2 mm., and the Vigreux still used became severely etched; arbitrary fractions were collected, and they all had similar infrared spectra, reminiscent of that of perfluoro-1,1′-bipiperidyl but containing bands indicative of the presence of C=C and C=N bonds, and gave multi-peak gas–liquid chromatograms (2 m., didecyl phthalate on Celite, 130°).

Defluorination of undecafluoropiperidine with mercury. Undecafluoropiperidine was prepared by electrochemical fluorination of pyridine as described previously.[2, 7] A stream of nitrogen (600 ml./hr.) was passed for 8·25 hr. through undecafluoropiperidine (4·96 g.) held at 0°, and the gaseous mixture was bubbled through mercury (75 ml.) contained in a steel trap (39 cm. deep × 2·7 cm. i.d.) heated electrically to 320°, the outlet of which was connected to two Pyrex traps at −72° by way of a steel water-cooled reflux condenser. The apparatus was purged with nitrogen (1 l./hr.) for 1 hr., and then the product in the cold traps was separated by trap-to-trap fractional condensation *in vacuo*, to yield spectroscopically pure perfluoro-2,3,4,5-tetrahydropyridine [7] (4·13 g., 93%) (Found: *M*, 245. Calc. for C_5F_9N: *M*, 245).

The experiment was repeated at 150° and at 250°, when the yield of perfluoro-2,3,4,5-tetrahydropyridine (percentage recovery of undecafluoropiperidine in parenthesis) was 21% (71·5) and 50% (41), respectively. Neither perfluoro-(1-methylpyrrolidine) nor perfluoro-(n-butyldenemethylamine) was detected in the products from these defluorinations.

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[8] Simmons *et al.*, *J. Amer. Chem. Soc.*, 1957, **79**, 3429.

[9] Halpern and Goldenson, *Appl. Spectroscopy*, 1957, **11**, 173.

143. *The Reaction of Dimesitylenevanadium with Carbon Monoxide.*

By F. Calderazzo and R. Cini.

Hexacarbonylvanadium was briefly reported [1] to be obtained by the reaction of ditoluenevanadium with carbon monoxide. More recently [2] the reaction of diarenevanadium(0) complexes with carbon monoxide was claimed to yield dimeric carbonylarenevanadium compounds of formula $V_2(CO)_6arene_2$, which could be considered as arene-substituted derivatives of the hypothetical dodecacarbonyldivanadium and as such should be spin-paired complexes, with a metal–metal bond. The infrared bands of the terminal CO groups should be observed between 2000 and 1900 cm.$^{-1}$. However, it was shown [3] that $V(CO)_6$ undergoes the fast reduction (1).

$$V^0(C_6H_3Me_3)_2 + V^0(CO)_6 \longrightarrow [V^I(C_6H_3Me_3)_2][V^{-I}(CO)_6] \qquad (1)$$

It has now been found that the reaction of dimesitylenevanadium with carbon monoxide, in mesitylene as solvent, gives almost exclusively a microcrystalline solid, practically insoluble in the reaction medium, which is identical with dimesitylenevanadium(I) hexacarbonylvanadate(—I) obtained by reaction (1). Both compounds show only two infrared bands (tetrahydrofuran solution) on the low-frequency side, at 1894—1895s and 1859vs cm.$^{-1}$, due [3,4] to the anion $[V(CO)_6]^-$. Moreover, a metathetical reaction (2) with lithium iodide can be carried out in tetrahydrofuran in both cases.

$$[V(C_6H_3Me_3)_2][V(CO)_6] + LiI \longrightarrow [V(C_6H_3Me_3)_2]I + Li[V(CO)_6] \qquad (2)$$

In agreement with the proposed structure, reduction with sodium in tetrahydrofuran yields dimesitylenevanadium(0) and $Na[V(CO)_6]$:

$$[V(C_6H_3Me_3)_2][V(CO)_6] + Na \longrightarrow V(C_6H_3Me_3)_2 + Na[V(CO)_6] \qquad (3)$$

Finally, magnetic susceptibility measurements on $[V(C_6H_3Me_3)_2][V(CO)_6]$ and on the corresponding iodide have shown the presence of two unpaired electrons as expected for the cation $[V\ arene_2]^+$.

The formation of $[V(C_6H_3Me_3)_2][V(CO)_6]$ from the reaction of $V(C_6H_3Me_3)_2$ with carbon monoxide can be understood in terms of the gradual substitution (4) of the aromatic ligands on dimesitylenevanadium(0) by CO.

$$V(C_6H_3Me_3)_2 \xrightarrow{CO} \{V(CO)_3C_6H_3Me_3\} \xrightarrow{CO} V(CO)_6 \qquad (4)$$

The resulting $V(CO)_6$ then undergoes the fast oxidation–reduction (1). For this reason, hexacarbonylvanadium is only a transitory species in the reaction of dimesitylenevanadium with carbon monoxide. Therefore, the process used by Pruett and Wyman [1] to prepare $V(CO)_6$ must have involved the transformation $[V(CO)_6]^- \longrightarrow V(CO)_6$. By reaction (3), dimesitylenevanadium(I) hexacarbonylvanadate(I—) can be converted into $NaV(CO)_6$. From an aqueous solution of this salt, $V(CO)_6$ is obtained by known methods.[5]

Experimental.—All operations were performed in a nitrogen atmosphere. Dimesitylenevanadium was prepared as previously described.[3] Microanalyses are by Dr. K. Eder, Ecole de Chimie, Geneva.

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[1] Pruett and Wyman, *Chem. and Ind.*, 1960, 119.
[2] Pruett and Wyman, U.S.P. 3,091,624/1963.
[3] Calderazzo, *Inorg. Chem.*, 1964, **3**, 810.
[4] Hieber, Peterhans, and Winter, *Chem. Ber.*, 1961, **94**, 2572.
[5] Calderazzo and Ercoli, *Chimica e Industria*, 1962, **44**, 990.

Reaction of dimesitylenevanadium with carbon monoxide. Dimesitylenevanadium (2·35 g.) dissolved in mesitylene (50 ml.) was treated with carbon monoxide (100 atm.) at about 35° for 20 hr. The microcrystalline solid formed was filtered off, washed with heptane to eliminate the unreacted dimesitylenevanadium, and dried *in vacuo.* The filtered red mesitylene solution did not show any significant infrared band in the carbonyl stretching region, and in particular near 1975 cm.$^{-1}$ where hexacarbonylvanadium absorbs [6] strongly. After treatment with water to dissolve small amounts of unidentified hexacarbonylvanadates, the solid was dried, and crystallised by dissolution in tetrahydrofuran and precipitation with ether (52·5% yield). Similar results were obtained when hydrogen (20 atm.) was used [2] in the reaction in addition to carbon monoxide. The properties of the $[V(C_6H_3Me_3)_2][V(CO)_6]$ correspond to those already reported [3] (Found: C, 55·9, 56·15; H, 4·6, 4·8; V, 20·4, 20·3; CO, 32·35. Calc. for $C_{24}H_{24}O_6V_2$: C, 56·5; H, 4·75; V, 19·95; CO, 32·95%).

The metathetical reaction (2). This gave $[V(C_6H_3Me_3)_2]I$ (ref. 3) in almost quantitative yield (Found: C, 51·55; H, 5·75; I, 30·2; V, 12·15, 12·04. Calc. for $C_{18}H_{24}IV$: C, 51·7; H, 5·8; I, 30·35; V, 12·2%).

The reaction (3). $Na[V(CO)_6]$ and $V(C_6H_3Me_3)_2$ were identified spectroscopically, the latter also by m. p. 125—126° (lit.,[3] 126—127°), as the sole products of the reaction in tetrahydrofuran for 2 hr. at room temperature.

Magnetic susceptibilities. These were measured at 22° by the Faraday method using the equipment described elsewhere,[7] adapted to solids, and about 50 mg. of complex in each case.

		$10^6\chi_M$ (c.g.s.u.)	μ_{eff} (B.M.)
$[V(C_6H_3Me_3)_2][V(CO)_6]$	from $V(C_6H_3Me_3)_2$ + CO	3430 ± 30	$2{\cdot}8_6$
	from reaction (1)	3406 ± 30	$2{\cdot}8_5$
$[V(C_6H_3Me_3)_2]I$		3456 ± 30	$2{\cdot}8_7$

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[6] Calderazzo, unpublished results; Beck and Nitzschmann, *Z. Naturforsch.*, 1962, **17**b, 577.

[7] Cini and Sacconi, *J. Sci. Instr.*, 1954, **31**, 56.

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144. *Selective Reactivity of Dinitrogen Tetroxide with Water in Salt Hydrates.*

By C. C. ADDISON and D. J. CHAPMAN.

WATER present in salt hydrates may be bonded in a number of ways; in limiting cases, water molecules may be co-ordinated to a metal ion, or may merely occupy vacant sites in the crystal lattice. Present evidence for bonding in salt hydrates rests largely on their physical properties. We have now observed that liquid dinitrogen tetroxide behaves selectively towards water in many salt hydrates. Immersion of hydrates in the liquid results in the formation of lower hydrates, and analysis indicates that the water : salt ratios in the products are very near to whole numbers; in none of the salts examined was the anhydrous compound produced. Interpretation of the reactions on a structural basis is necessarily restricted, because crystal structures for only a few salt hydrates are known, but it appears justifiable to correlate the selectivity with the different types of bonding of water molecules. For example, when aluminium alum is immersed in liquid dinitrogen tetroxide, the liquid immediately penetrates the crystals, which collapse to a powder. Six molecules of water in $KAl(SO_4)_2,12H_2O$ (probably those that normally surround the potassium ion) are removed, whereas the remaining six (believed to be those co-ordinated to the aluminium ion) remain unchanged even after immersion for several days. Examples of other reactions are given in Table 1.

TABLE 1.

The reaction of liquid dinitrogen tetroxide with salt hydrates.

Reactant	Product	Reactant	Product
$KAl(SO_4)_2,12H_2O$	$KAl(SO_4)_2,6H_2O$	$NiSO_4,7H_2O$	$NiSO_4,3H_2O$
$KCr(SO_4)_2,12H_2O$	$KCr(SO_4)_2,9H_2O$	$Ni(NO_3)_2,6H_2O$	$Ni(NO_3)_2,4H_2O$
$Cr(NO_3)_3,9H_2O$	$Cr(NO_3)_3,6H_2O$	$Cu(NO_3)_2,3H_2O$	Reactant unchanged
$Fe(NO_3)_3,9H_2O$	$Fe(NO_3)_3,5H_2O$	$CuSO_4,5H_2O$	$CuSO_4,3{\cdot}5H_2O$
$Co(NO_3)_2,6H_2O$	$Co(NO_3)_2,4H_2O$	$Zn(NO_3)_2,6H_2O$	$Zn(NO_3)_2,3{\cdot}5H_2O$
		$MgSO_4,7H_2O$	$MgSO_4,2H_2O$

In these reactions, 1 g. of the finely powdered hydrate was immersed in 20 ml. of liquid dinitrogen tetroxide at room temperature. The liquid became green owing to the formation of dinitrogen trioxide, and was replaced by fresh tetroxide after 1 and 24 hours. The product was then filtered in a closed system and washed with liquid tetroxide, final traces of the latter being removed under vacuum. With all the compounds listed in Table 1, analyses of the products obtained after 1 and 24 hours were virtually identical; visual evidence also indicated that reaction occurred almost immediately, so that the water molecules present either react rapidly, or are inert to dinitrogen tetroxide over long periods. Although this note deals only with reactions of the pure tetroxide, it is noteworthy that related compounds such as nitric acid and dinitrogen pentoxide dissolve in liquid dinitrogen tetroxide, and it is probable that the study of selective reactions could be refined by the use of such solutions.

Sulphates.—Both aluminium alum [1] and chromium alum [2] have the α-alum structure, yet chromium alum is only reduced to the 9-hydrate by dinitrogen tetroxide. Both products showed the characteristic infrared absorption bands of water at 3400 and 1640 $cm.^{-1}$, and differences between the two were not significant. The difference in behaviour of the two alums may be related to the well-known stability of aquo-complexes of chromium.

It was of interest to examine some simple sulphates, since these often contain an odd number of water molecules. The thermal or vacuum dissociation of copper sulphate hydrates, for example, which proceeds in the order $5H_2O \longrightarrow 3H_2O \longrightarrow 1H_2O$, indicates that the " odd " molecules (even though they are not initially co-ordinated to the metal) are not easily removed. The fact that the products of reaction of hydrates of copper and nickel sulphates with dinitrogen tetroxide have odd numbers of water molecules suggests that these reactions follow a pattern similar to that observed in thermal dissociation. Co-ordination to the metal ions is not necessarily, therefore, the most important structural feature that renders water molecules inert to dinitrogen tetroxide. Thus, with the 7-hydrate of magnesium sulphate, where any such co-ordination will be weak, reaction does not proceed beyond the 2-hydrate stage.

Nitrates.—Change in the anion from sulphate to nitrate, which usually gives rise to different hydration numbers in the common salts, also influences the extent to which the products of reaction with dinitrogen tetroxide are hydrated (Table 1). Copper nitrate 3-hydrate is unusual in that this (the normal) hydrate is unattacked by dinitrogen tetroxide. In all other cases examined, some reduction in hydration number occurs, and with cobalt, nickel, and zinc nitrates the reaction provides a convenient route to the preparation of hydrates intermediate between the (normal) 6-hydrates, and the 2-hydrates prepared by reaction of the anhydrous chlorides with pure nitric acid.[3,4] Variation in hydration number results in interesting changes in the bonding of the nitrate groups (Table 2).

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[1] Lipson, *Nature*, 1935, **135**, 912.
[2] Klug, *J. Amer. Chem. Soc.*, 1940, **62**, 2992.
[3] Hathaway and Underhill, *J.*, 1960, 648.
[4] Hathaway, Holah, and Hudson, *J.*, 1963, 4586.

TABLE 2.

The infrared spectra of some metal nitrate hydrates.

Hydrate	Basis of assignment	Infrared spectrum (cm.$^{-1}$)				
	$NO_3^-(D_{3h})$		ν_3	ν_1	ν_2	
$Ni(NO_3)_2,6H_2O$			1383	1048	837	
	$ONO_2(C_{2v})$	ν_4	ν_1	ν_2	ν_6	ν_3/ν_5
$Ni(NO_3)_2,4H_2O$		1495	1320	1040	815	760
$(Ni(NO_3)_2,2H_2O$ [4]		1560 1540	1310	1061	810	760
$Co(NO_3)_2,4H_2O$ ...		1490	1330	1040	820	760
$Zn(NO_3)_2,3{\cdot}5H_2O$ ...		1495	1300	1040	815	750

The loss of two molecules of water from nickel nitrate 6-hydrate is sufficient to cause covalent bonding of both nitrate groups to the metal. The ν_4–ν_1 separation for the 2-hydrate is significantly larger than for the 4-hydrate, indicating a strengthening of the covalent bond in the 2-hydrate.

Oxalates.—Reactions of dinitrogen tetroxide with some oxalato-complexes are also selective; the reactions are less precise, but merit brief mention. After several successive treatments of the 2-hydrate of oxalic acid with the liquid tetroxide, pure anhydrous oxalic acid is produced. A similar reaction occurs with potassium tetraoxalate, $KH_3(C_2O_4)_2,2H_2O$. However, the product retains one molecule of nitric acid, and is formulated as $\{2H_2C_2O_4 + KNO_3\}$ rather than $KH_3(C_2O_4)_2,HNO_3$, since bands characteristic of the nitrate ion can be identified in the infrared spectrum. This behaviour is observed with potassium salts of oxalato-complexes also, the number of nitric acid molecules retained in the product being determined by the number of potassium ions present. Thus, when liquid dinitrogen tetroxide was added to the complex $K_3[Cr(C_2O_4)_3],3H_2O$ and allowed to evaporate at room temperature for 2 days, the chromium : oxalate ratio was unchanged, and analysis and physical properties indicated 80% conversion into $\{H_3[Cr(C_2O_4)_3] + 3KNO_3\}$. The preparation of oxalato–chromium(III) acid by another method has been reported.[5] The complexes *cis*-$K[Cr(C_2O_4)_2(H_2O)_2],2H_2O$ and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2],3H_2O$ were converted, during several days immersion, into $\{H[Cr(C_2O_4)_2(H_2O)_2] + KNO_3\}$, and the *cis*-reacts more readily than the *trans*-compound. This is attributed to differences in the reactivity of water molecules outside the co-ordination complex, which may be determined to some extent by the configuration of the complex ions.

Experimental.—The analyses recorded in Table 3 were carried out by standard methods on reaction products that had been immersed in liquid dinitrogen tetroxide for 24 hr. at 20°.

TABLE 3.

Analyses of reaction products (values in parentheses are calculated on the basis of the hydration numbers shown).

Product	Metal (%)	SO_4 (%)	Product	Metal (%)	N (%)
$KAl(SO_4)_2,6H_2O$	Al, 7·4 (7·4)	52·7 (52·4)	$Cr(NO_3)_3,6H_2O$ ...	14·5 (15·0)	11·8 (12·1)
$KCr(SO_4)_2,9H_2O$	Cr, 11·6 (11·7)	42·2 (43·1)	$Fe(NO_3)_3,5H_2O$ ...	17·0 (16·8)	12·6 (12·7)
$NiSO_4,3H_2O$	28·2 (28·1)	46·0 (46·0)	$Co(NO_3)_2,4H_2O$ ...	23·8 (23·1)	11·4 (11·0)
$CuSO_4,3{\cdot}5H_2O$ ...	27·9 (28·5)	43·9 (43·1)	$Ni(NO_3)_2,4H_2O$ ...	23·2 (23·0)	11·1 (11·0)
$MgSO_4,2H_2O$ ...	15·3 (15·6)	60·2 (61·4)	$Zn(NO_3)_2,3{\cdot}5H_2O$	25·8 (25·9)	11·0 (11·1)

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THE UNIVERSITY, NOTTINGHAM. [*Received, May* 27*th*, 1964.]

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[5] McCutcheon and Schnele, *J. Amer. Chem. Soc.*, 1953, **75**, 1845.

145. *The Reduction of Oximes by Hydrazine–Raney Nickel.*

By Douglas Lloyd, Ronald H. McDougall, and F. I. Wasson.

The use of hydrazine in the presence of metal catalysts for the reduction of nitro-compounds and esters of nitric and nitrous acids was described by Kuhn.[1] Balcom and Furst [2] showed that hydrazine in the presence of Raney nickel was an excellent and convenient reagent for the reduction of nitro-compounds; this reagent has also been applied to nitriles.[3] A report [4] of the reduction of an oxime to an amine led us to investigate the generality of the reaction with oximes. The results (see Table) show that saturated ketoximes are normally reduced under simple conditions, the yields of amines often being comparable with those obtained by reduction with lithium aluminium hydride.[5] Two typical aldoximes which were investigated were not reduced. In the case of αβ-unsaturated ketoximes a pyrazoline is produced instead of an amine, *e.g.*, 3,5,5-trimethylpyrazoline from the oxime of mesityl oxide. Biacetyl monoxime and pentane-2,4-dione dioxime formed nickel complexes instead of amines under the standard conditions, but 2,5-diaminohexane was obtained from hexane-2,5-dione dioxime.

Yields of amines from reduction of oximes.

Oxime	Amine (%)	Oxime	Amine (%)
Acetone	36	Propiophenone	24
Butan-2-one	76	Benzyl phenyl ketone	74
Pentan-2-one	42	Fluorenone	94
Undecan-2-one	9	3-Hydroxy-1,2-benzofluorenone	97
Cyclopentanone	27	Benzoin	0
Cyclohexanone	65	Mesityl oxide	*
Cycloheptanone	29	Isophorone	*
Menthone	90	Carvone	*
Carvomenthone	36	Biacetyl monoxime	†
Dihydrocarvone	8	Pentane-2,4-dione dioxime	†
Fenchone	6	Hexane-2,5-dione dioxime	31
Camphor	0	n-Heptanal	0
Benzophenone	45	Benzaldehyde	0

* Pyrazoline formed. † Nickel complex formed.

Experimental.—Reduction of oximes to amines. In a typical run the oxime (0·02 mole) and hydrazine hydrate (64%; 6 ml.) were dissolved in ethanol (50 ml.). Raney nickel sludge (W-4)[6] was added in portions to maintain a steady reaction. When reaction subsided, excess of hydrazine was decomposed by refluxing until evolution of ammonia ceased (*ca.* 4 hr.). The solution was filtered, and the amine was normally isolated by passing gaseous hydrogen chloride through the solution. Alternatively, the water-insoluble amines could be obtained directly by adding water to the ethanolic solution. The amines were characterised by suitable derivatives.

Attempted reduction of mesityl oxide oxime. To a mixture of mesityl oxide oxime (11·81 g.) and hydrazine (64%; 30 ml.) in ethanol (100 ml.) Raney nickel was added as above. After filtration and addition of hydrogen chloride, the solution was concentrated, water added, and the solution washed with ether. The aqueous solution was basified, extracted with ether, and the dried extract fractionally distilled, giving a colourless oil, b. p. 80—84°/45 mm., whose infrared spectrum was identical with that of 3,5,5-trimethylpyrazoline.

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[1] Kuhn, *J. Amer. Chem. Soc.*, 1951, **73**, 1510.

[2] Balcom and Furst, *J. Amer. Chem. Soc.*, 1953, **75**, 4334.

[3] Pietra and Trinchera, *Gazzetta*, 1956, **86**, 1045.

[4] Gilks, unpublished work quoted by Reed, *Roy. Inst. Chem. Lectures, Monographs, Reports*, 1957, No. 5, 38.

[5] Cf., *e.g.*, Smith, Maienthal, and Tipton, *J. Org. Chem.*, 1952, **17**, 294; Walter, *J. Amer. Chem. Soc.*, 1952, **74**, 5185.

[6] Tucker, *J. Chem. Educ.*, 1950, **27**, 489.

*Attempted reduction of pentane-*2,4-*dione dioxime.* Raney nickel was added to the dioxime (7·28 g.) and hydrazine (64%; 14 ml.) in ethanol (250 ml.) as above. On refluxing to decompose excess of hydrazine the solution became brown. After filtration it was boiled with decolourising charcoal, filtered, and concentrated, to give an orange nickel-containing solid, m. p. >300°.

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146. *Nucleophilic Displacements in Dimethyl-*1*-phenylethylsulphonium Ion.*

By H. M. R. Hoffmann.

'Onium salts, like alkyl halides, are alkylating agents but offer several sites for nucleophilic attack; *e.g.*, there are three sites in sulphonium and four sites in quaternary ammonium and phosphonium salts. The position of nucleophilic attack has long been recognised as dependent upon the mechanism, and on constitutional influences of the alkyl group.[1] In accord with these findings we here report an interesting switch in the site of nucleophilic displacement, when dimethyl-1-phenylethylsulphonium ion is the substrate and the strength of the nucleophile is varied.

Product distribution for nucleophilic displacements in dimethyl-1-phenylethylsulphonium ion.

Nucleophile	Solvent	Temp.	Rate constants k_1 (sec.$^{-1}$); k_2 (l. mole^{-1} sec.$^{-1}$)	% Substitution at MeCHPh	at Me	Ref.
EtOH	EtOH	59·8°	$k_1 = 3{\cdot}84 \times 10^{-5}$	100	—	—
$(H_2N)_2CS$	MeCN	59·8	$k_2 = 1{\cdot}02 \times 10^{-3}$	>99	<1	2
N_3^-	80% aq. EtOH	55·2	$k_2 = 1{\cdot}2 \times 10^{-3}$	>99	<1	3
EtO^-	EtOH	34·9	$k_2 = 7{\cdot}6 \times 10^{-4}$ *	84	16	4
MeS^-	EtOH	25·0	Large	41·9	58·1	

* For substitution at MeCHPh.

We have found that the ethanolysis of dimethyl-1-phenylethylsulphonium toluene-*p*-sulphonate occurs exclusively at the secondary carbon atom. Similarly, displacement of dimethyl sulphide is by far the fastest reaction with azide ion in 80% aqueous ethanol[3] or thiourea in acetonitrile.[2] With ethoxide ion in ethanol, however, attack at the methyl carbon atoms becomes noticeable,[4] and finally we have studied the reaction:

$$MeS^- + MeCHPh{\cdot}\overset{+}{S}Me_2 \longrightarrow MeCHPh{\cdot}SMe + Me_2S$$

Since the product, methyl 1-phenylethyl sulphide, can result from an attack of methyl sulphide ion on an *S*-methyl and/or phenyl-bearing carbon atom, the sites of nucleophilic displacement cannot be determined by conventional analytical techniques. Our results

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[1] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 318; Hughes, Ingold, *et al.*, *J.*, 1933, 70, 526, 1571.

[2] Hoffmann and Hughes, *J.*, 1964, 1259.

[3] Harvey, Hoye, Hughes, and Ingold, *J.*, 1960, 800.

[4] Banthorpe, Hughes, and Ingold, *J.*, 1960, 4054.

are based upon a stereochemical analysis. Since displacements by the strongly nucleophilic thiolate ion can be easily carried out stereospecifically,[5] an attack of this reagent at the secondary carbon atom will give methyl 1-phenylethyl sulphide with 100% inversion of configuration, whereas displacement at a methyl carbon leaves the asymmetric centre unaffected and therefore entails 100% retention of configuration. It follows from the optical rotation of the product that there is only 41·9% attack at 1-phenylethyl, but 58·1% displacement at the methyl carbon atoms.

These observations can be rationalised by considering the degree of bond-making and bond-breaking in the transition state. 1-Phenylethyl as the more stabilised alkyl structure will always take complete precedence over methyl for displacements in which bond-breaking in the transition state is advanced, *e.g.*, in all solvolyses. Indeed, the ethanolysis of 1-phenylethyl bromide at 50° is 296 times faster than that of methyl bromide.[6] Likewise, in the displacements using thiourea, considerable stretching of the $C-SMe_2^+$ bond in the transition state is indicated by the concurrent *E*1 reaction which could not be excluded.[2] However, as the attacking nucleophile becomes stronger, rates increase and the more accessible methyl carbon atoms can compete effectively with the activated secondary site where some steric hindrance to an attack from the rear develops. Accordingly, the very strongly nucleophilic methanethiolate ion [5] attacks the methyl carbon atoms in unprecedented proportion.

*Experimental.—The reaction of sodium methyl sulphide with dimethyl-*1*-phenylethylsulphonium toluene-*p*-sulphonate in ethanol at* 25°. The reaction was too fast for a kinetic investigation at room temperature. Dimethyl-1-phenylethylsulphonium toluene-*p*-sulphonate (2·76 g.), prepared with complete retention of configuration [2] from methyl 1-phenylethyl sulphide of α_D^{20} $-106{\cdot}1°$ (neat, *l* 1 dm.), was kept for 20 min. at 25° in a solution (55 ml.) of sodium methyl sulphide (0·216M) in ethanol. Methyl 1-phenylethyl sulphide was isolated and had α_D^{20} $-17{\cdot}2°$ (neat, *l* 1 dm.). The ethanolysis of the sulphonium salt at 59·8° was followed by titration of the acid liberated during the reaction.

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[*Received, June 2nd,* 1964.]

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[5] Hoffmann, *J.*, 1964, 1249.
[6] From the data of Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 1604, and Winstein, Grunwald, and Jones, *ibid.*, 1951, **73**, 2700.

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147. *Dehydrochlorination Reactions Involving Trifluoromethane.*

By G. Pass.

Trifluoromethane is characterised by its high thermal stability and is chemically inert except in reactions with halogens at high temperatures, although it is reported to be completely solvolysed in liquid ammonia.[1] Thus pyrolysis of trifluoromethane occurs above 800° to give fluoro-olefins, including hexafluoropropene,[2] while bromine will react with trifluoromethane at 680° to give a high yield of bromotrifluoromethane.[3]

It has now been found that chlorotrifluoroethylene will react with trifluoromethane at 700° to give hexafluoropropene in 60% yield on a 60% conversion of trifluoromethane. The pyrolysis of chlorotrifluoroethylene at this temperature gave a mixture of liquid

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[1] Jander, *Z. anorg. Chem.*, 1962, **315**, 91.
[2] U.S.P. 3,009,966.
[3] U.S.P. 2,875,254.

products similar to that reported by Miller,[4] and a trace of hexafluoropropene was found in the gaseous products. Addition of trifluoromethane to the chlorotrifluoroethylene gas stream caused a marked reduction in the quantity of liquid products with a corresponding increase in the amount of hexafluoropropene produced. The fact that this reaction occurs at a temperature where trifluoromethane is only slightly decomposed thermally and that an amount of hydrogen chloride equivalent to the hexafluoropropene is obtained suggests that the reaction can be represented as

$$CF_3H + Cl{\cdot}CF{=}CF_2 \longrightarrow CF_3{\cdot}CF{=}CF_2 + HCl$$

The reaction appears to be affected by the metal of the reaction tube and the highest yields of hexafluoropropene were obtained using a nickel tube.

Chlorotrifluoromethane was detected in the reaction products and, in view of the fact that no one-carbon compounds were isolated from the pyrolysis of chlorotrifluoroethylene,[4] can be attributed to a reaction of trifluoromethane with chlorotrifluoroethylene. A quantity of hydrogen fluoride, equivalent to $\sim$20% of the initial trifluoromethane, was also obtained but the reaction by which it is formed remains uncertain. It is unlikely to arise from simple thermal decomposition of trifluoromethane at this temperature.

An attempt to prepare hexafluoropropene under similar conditions by a dehydrochlorination reaction between chlorotrifluoromethane and trifluoroethylene was unsuccessful. The products obtained were identical with those from the pyrolysis of trifluoroethylene alone. Similarly trifluoromethane and chlorotrifluoromethane did not react below a temperature where decomposition of the trifluoromethane was appreciable. A recently reported reaction between chlorotrifluoromethane and ethylene at 950° indicates that higher temperatures are required for chlorotrifluoromethane to undergo dehydrochlorination.[5]

The presence of a chlorine atom in the chlorofluorocarbon which is labile at 650° and above appears to be a requirement for a dehydrochlorination reaction with trifluoromethane. Thus chloropentafluorobenzene was found to react with trifluoromethane at 700° to give a small quantity of octafluorotoluene. A complex mixture of products was obtained, owing primarily to thermal rearrangement of chloropentafluorobenzene, from which the octafluorotoluene was separated by g.l.c.

Experimental.—Trifluoromethane was prepared by the room-temperature disproportionation of chlorodifluoromethane,[6] chlorotrifluoroethylene by the dechlorination of 1,1,2-trichlorotrifluoroethane,[7] and trifluoroethylene by the catalytic reduction of chlorotrifluoroethylene.[8] Chlorotrifluoromethane, chlorodifluoromethane, and 1,1,2-trichlorotrifluorethane were products of Imperial Chemical Industries, Mond Division.

All reactions were carried out in a flow-tube reactor. The gas mixture, at measured flow-rates, was passed through a nickel tube (length, $\sim$25 cm.; inside diam., 4 mm.) kept between 650 and 750° by means of an electrically-heated tube furnace. Liquid reagents were injected at a measured rate into the trifluoromethane gas stream. The gaseous product was passed through a standard solution of sodium hydroxide to remove the acid gases and then collected in an evacuated flask. The quantity of hydrogen fluoride and hydrogen chloride in the product was determined by titration of the sodium hydroxide solution. The other gaseous products were determined quantitatively by g.l.c. and qualitatively by i.r. spectroscopy.

The column used for g.l.c. was packed with " Chromosorb " (Johns Manville Ltd.) on which silicone grease had been adsorbed.

Infrared spectra were recorded on a Perkin Elmer Infracord instrument.

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[4] Slesser and Schram, " Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," McGraw-Hill, New York, 1952, pp. 595—600.

[5] F.P. 1,334,300.

[6] B.P. 649,253.

[7] Lovelace, Rausch, and Postelnek, " Aliphatic Fluorine Compounds," Reinhold, New York, 1958, p. 104.

[8] Knunyants, Krasuskaya, and Mysov, *Bull. Acad. Sci. U.S.S.R.*, 1960, 1314.

Reaction of Trifluoromethane with Chlorotrifluoroethylene.—Trifluoromethane (0·5 l.) and chlorotrifluoroethylene (0·5 l.) were passed through the reaction tube at 700°, with an average residence time of 8 sec. The sodium hydroxide solution contained the equivalent of 0·21 l. of hydrogen chloride and 0·14 l. of hydrogen fluoride. The gas which passed through the sodium hydroxide scrubber (0·65 l.) was shown by g.l.c. to contain trifluoromethane (0·19 l.), hexafluoropropene (0·21 l.), chlorotrifluoroethylene (0·06 l.), and chlorotrifluoromethane (0·02 l.). Three other components were present in this gas but they were not identified.

Reaction of Trifluoromethane with Chloropentafluorobenzene.—Chloropentafluorobenzene (2·8 g.) was injected during 1 hr. into a stream of trifluoromethane (0·5 l.). The average residence time in the reaction tube at 700° was 10 sec. The sodium hydroxide solution contained the equivalent of 0·07 l. of hydrogen chloride and 0·12 l. of hydrogen fluoride. The remaining gaseous products (0·34 l.) were found to contain trifluoromethane (0·27 l.) and chlorotrifluoromethane (0·01 l.). The liquid products (2 g.) were separated by gas–liquid chromatography and found to contain mainly chloropentafluorobenzene but a small amount of a fraction identified as octafluorotoluene was obtained (Found: C, 36·0; F, 64·3. Calc. for C_7F_8: C, 35·6; F, 64·4%). The infrared spectrum had major peaks at 1661, 1538, 1522, 1356, 1242, 1201, 1177, 1010, 1005, 884, and 719 cm.$^{-1}$

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148. *A Convenient Preparation and Characterisation of Hypotaurine.*

By Terence C. Owen and A. C. Wilbraham.

Hypotaurine (2-aminoethanesulphinic acid) (I) occurs in biological systems.[1] It is an important product in the radiolysis of cystamine [2] and in the preparation of mixed disulphides by reaction of 2-aminoethyl 2-aminoethanethiolsulphonate (II) with thiols.[3] During recent investigations [4] we had occasion to prepare this compound, and, as existing procedures were rather tedious, we have developed a rapid preparation.

Hypotaurine results from dismutation of the thiolsulphonate (II) in alkaline medium when salts of (II) are treated with bases. Cavallini *et al.*[5] used sodium hydroxide as the base and separated the products by lengthy fractionation on a cation-exchange resin. We have found it convenient to use a moderate excess of a strongly basic anion-exchange resin (Amberlite IRA-400; hydroxide form) as the base. Cystamine (III) is washed out with water and the amphoteric hypotaurine is eluted with dilute acetic acid. Evaporation of the acetic acid eluate gives crystalline material directly and in good yield.

$$\underset{\text{(II)}}{3NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2} \longrightarrow \underset{\text{(I)}}{4NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2H} + \underset{\text{(III)}}{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2}$$

Useful derivatives of hypotaurine do not appear to have been reported. The dinitrophenyl derivative, *NS*-bis-2,4-dinitrophenylhypotaurine, is produced rapidly and quantitatively upon treatment of weakly alkaline solutions of hypotaurine with fluoro-2,4-dinitrobenzene. The product is virtually pure, is readily crystallized, is of relatively high molecular

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[1] Cavallini, Mondovi, and DeMarco, *J. Biol. Chem.*, 1955, **216**, 577.
[2] Shapiro and Eldjarn, *Radiation Res.*, 1955, **3**, 255, 393.
[3] Field, Owen, Crenshaw, and Bryan, *J. Amer. Chem. Soc.*, 1961, **83**, 4414.
[4] Field, Ferretti, and Owen, *J. Medicin. Chem.*, 1964, **7**, 39.
[5] Cavallini, DeMarco, and Mondovi, *Giorn. Biochim.*, 1953, **2**, 338; " Biochemical Preparations," Wiley, New York, 1963, Vol. X, p. 72.

weight, and possesses the characteristic *N*-alkyl-2,4-dinitroaniline chromophore [$\lambda_{max.}$ (in acetone) 3470 Å; ε 20,390] which permits quantitative determination of microgram quantities by ultraviolet spectrophotometry. The reaction with fluorodinitrobenzene occurs rapidly on paper chromatograms and is conveniently used for both detection and quantitative estimation of hypotaurine.[6]

Experimental.—*Hypotaurine* (I). A solution of the thiolsulphonate (II) hydrochloride [3] (2·58 g., 0·01 mole) in water (20 ml.) was added during 30 min. to a stirred suspension of (Amberlite IRA-400, hydroxide form; 50 ml., 0·041 equiv.) in water (100 ml.) at 20°. The suspension was transferred to a separatory funnel, drained, and washed with water (100 ml.). The aqueous washings were discarded. The resin bed was washed with 10% acetic acid (100 ml.; flow 10 ml./min.). Evaporation of the aqueous acetic acid under reduced pressure, and addition and similar evaporation of two successive portions of anhydrous ethanol, gave crystalline material which was again suspended in ethanol and filtered off (0·80 g., 73%), m. p. 180—180·5° after recrystallization from aqueous ethanol (m. p.s from 170 to 186° have been reported [5]) (Found: C, 22·3; H, 6·6; N, 12·7; S, 29·1. Calc. for $C_2H_7NO_2S$: C, 22·1; H, 6·5; N, 12·8; S, 29·4%), $\nu_{max.}$ (Nujol) strong bands at 6·17, 6·25, 7·1, 7·9, 8·07, 8·45, 8·95, 9·55, 10·05, 10·45, 11·35, and 11·97 μ.

NS-*Bis*-2,4-*dinitrophenylhypotaurine*. Sodium hydrogen carbonate (0·9 g.) and then fluoro-2,4-dinitrobenzene (2·4 g.) in warm (50°) propan-2-ol (100 ml.) were added to a stirred solution of hypotaurine (0·73 g.) in water (20 ml.) at 50°. Filtration of the cooled solution gave the bright yellow *dinitrophenyl derivative* (3·0 g., ~100%), m. p. 167—170°, unchanged by repeated recrystallization from acetone–propan-2-ol (Found: C, 37·9; H, 2·6. $C_{14}H_{11}N_5O_{10}S$ requires C, 38·1; H, 2·5%). The derivative was obtained directly from the thiolsulphonate (II) by treatment of its hydrochloride with sodium hydroxide (3·4 equiv. per mole), removal of cystamine by six extractions with chloroform, and treatment of the aqueous solution with sodium hydrogen carbonate and fluorodinitrobenzene.

Analyses are by courtesy of the Department of Chemistry, University of Liverpool.

Research grants from the D.S.I.R. and from N.A.T.O. are gratefully acknowledged.

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UNIVERSITY OF SOUTH FLORIDA, TAMPA, FLORIDA, U.S.A. (T. C. O.) [*Received, June 8th*, 1964.]

[6] Jason, Owen, and Wilbraham, *Analyst*, 1965, in the press.

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149. *Silicon Tetrafluoride as a Fluorinating Agent. Part II.*[1]

By K. O. CHRISTE and A. E. PAVLATH.

THE use of silicon tetrafluoride as a fluorinating agent has been described.[1] As it has been shown in this laboratory [2] that arsenic trifluoride is a useful fluorinating agent, and arsenic trioxide and silicon tetrafluoride are both waste products, the following reaction was studied:

$$2As_2O_3 + 3SiF_4 \rightleftharpoons 3SiO_2 + 4AsF_3$$

Arsenic trioxide was sublimed in a stream of silicon tetrafluoride through a hot quartz tube filled with quartz granules. Arsenic trifluoride was formed above 650°, the optimum range being 750—850°.

Attempts to cause sulphur trioxide to react with silicon tetrafluoride between 400 and 800° did not yield any sulphur–flourine compound.

[1] Part I, K. O. Christe and A. E. Pavlath, *J. Org. Chem.*, 1964, **29**, 3007.
[2] F.P. 1,298,198/1961.

An investigation of the equilibrium

$$4AsCl_3 + 3SiF_4 \rightleftharpoons 4AsF_3 + 3SiCl_4$$

showed that up to 750° arsenic trifluoride was not formed. At reflux temperature, fluorination of silicon tetrachloride with arsenic trifluoride results in the equilibrium being shifted completely towards the left.

Experimental.—Reaction of arsenic trioxide with silicon tetrafluoride. Arsenic trioxide (4·66 g.) in a small quartz boat was placed at the mouth of a quartz tube (diam. 2·5 cm.) filled with high-surface quartz granules. The tube was electrically heated to 800° along 33 cm. of its length in a tube furnace. The arsenic trioxide sublimed through the tube in a stream of silicon tetrafluoride (300 c.c./min. for a retention time of 5 sec.). Arsenic trifluoride was trapped at $-78°$, and fractionated in a vacuum line to give the pure compound (1·515 g.), b. p. 58·1° (lit., 57·8°) (Found: As, 54·2; F, 42·1. Calc. for AsF_3: As, 56·8; F, 43·2%), with the correct i.r. spectrum. Unchanged arsenic trioxide was recovered almost quantitatively (conversion of As_2O_3, 24·6%; yield of AsF_3, 95%).

Reaction of silicon tetrachloride with arsenic trifluoride. Arsenic trifluoride (528 g.) was placed in a three-necked flask fitted with a condenser, stirrer, and dropping funnel. Silicon tetrachloride (510 g.) was slowly added with stirring. The heat of reaction kept the mixture under reflux. When the reaction had finished the product (726 g.) was distilled. It was entirely arsenic trichloride.

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150. (+)-*Fisetinidol from* Afzelia xylocarpa.

By F. M. DEAN, STANG MONGKOLSUK, and VERAPONG PODIMUANG.

EXTRACTION of the heartwood of *Afzelia xylocarpa* with tetrahydrofuran gave a complex mixture which appeared to consist of condensed tannins and similar materials. From this mixture ether isolated a phenol, $C_{15}H_{14}O_5$, which formed a tetra-acetate. The trimethyl ether had hydroxylic absorption near 3μ while the derived acetate did not. The phenol contained no methoxyl groups and the infrared spectrum showed that no carbonyl groups were present, hence the existence of a heterocyclic ring was inferred. The green ferric reaction and other colour tests indicated the presence of a catechol nucleus, this appearing as veratric acid when the trimethyl ether was oxidised. Clearly, the third phenolic hydroxyl group had to be located on a second aromatic nucleus. As only the residue C_3H_4 remained, and the ^1H resonance spectrum of the acetate of the trimethyl ether showed that this did not include a *C*-methyl group, it seemed that a member of the catechin series was present, and a particularly close correspondence to fisetinidol was noted. The infrared spectrum was identical with that of an authentic, synthetic specimen of the dextrorotatory compound.[1] The hydroxyl stretching band ($\nu_{max.}$ 3590 cm.$^{-1}$) of the trimethyl ether in dilute solution in carbon tetrachloride was very similar to that for (+)-catechin tetramethyl ether,[2] and the optical rotations of this and other derivatives paralleled those in the (+)-catechin series. (+)-Fisetinidol therefore has the *trans*-configuration, already indicated by its synthesis by hydrogenation of (—)-fustin, and the absolute configuration 2*R*,3*S*. Although (—)-fisetinidol is known to be a constituent of *Acacia mollissima*,[1] the dextrorotatory isomer has not been found in plants before. The genera *Afzelia* and *Acacia* are related, in that both belong to the Leguminosae, though to different sub-families.

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[1] Weinges, *Annalen*, 1958, **615**, 203; 1959, **627**, 229.
[2] Dean and Locksley, *J.*, 1963, 393.

Experimental.—The powdered heartwood (200 g.) of *Afzelia xylocarpa* was extracted for 48 hr. with light petroleum (b. p. 40—60°), and then, under nitrogen, with tetrahydrofuran for 5 days. The latter extract was concentrated under nitrogen and *in vacuo* at 40° until a viscous liquid remained which was poured into ether (200 ml.; distilled from phosphorus pentoxide). The precipitate was partly soluble in ether, and the solute was recovered as a pale yellow powder (1·6 g.) by the addition of light petroleum (b. p. 40—60°). Crystallisation from water (charcoal) gave (+)-*fisetinidol* as plates (1·3 g.), m. p. 213—214°, $[\alpha]_D^{20}$ +8·0° (acetone–water, 1 : 1) (*c* 0·55), giving a bright red solution in warm sulphuric acid (Found: C, 65·0; H, 5·1. $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·2%).

With methyl sulphate and potassium carbonate in boiling acetone, (+)-fisetinidol (0·3 g.) gave the *trimethyl ether*, needles m. p. 119° (from aqueous methanol), $[\alpha]_D^{20}$ +29·5° (tetrachloroethane; *c* 0·57) [Found: C, 68·3; H, 6·3; OMe, 29·8. $C_{15}H_{11}O_2(OMe)_3$ requires C, 68·3; H, 6·4; OMe, 29·4%]. Acetylation of the trimethyl ether with acetic anhydride and pyridine gave the *acetate*, needles, m. p. 88—90° (from aqueous acetic acid), $[\alpha]_D^{20}$ +18·7° (tetrachloroethane; *c* 0·47) [Found: C, 67·0; H, 6·1; OMe, 25·7. $C_{17}H_{13}O_3(OMe)_3$ requires C, 67·0; H, 6·1; OMe, 26·0%]. *Fisetinidol tetra-acetate* could not be crystallised and was obtained only as a powder, m. p. 55—60°, $[\alpha]_D^{20}$ −1·0: (tetrachloroethane; *c* 0·76) [Found: C, 62·7; H, 5·1; Ac, 38·7. $C_{15}H_{10}O_2(OAc)_4$ requires C, 62·4; H, 5·0; OAc, 38·2%].

(+)-Fisetinidol trimethyl ether (0·3 g.) was treated with potassium permanganate (3 g.) in boiling acetone (50 ml.) for 1 hr. Addition of water (10 ml.), evaporation of the acetone, acidification with dilute sulphuric acid, clarification with sulphur dioxide, and extraction with ether gave a solution from which the acid fraction was isolated by means of aqueous sodium hydrogen carbonate and crystallised from water, yielding veratric acid, m. p. and mixed m. p. 110—112°, further identified spectroscopically.

The authors thank the British Government for financial assistance to one of them (V. P.) under the Colombo Plan, Dr. G. Eglinton for determining the hydroxyl stretching absorption of (+)-fisetinidol trimethyl ether, and Dr. D. G. Roux for the infrared spectrum of synthetic (+)-fisetinidol.

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151. *The Gas Constant and the Ideal Gram Molecular Volume of Gases.*

By (the late) F. Din.

The values for the gas constant, ***R***, and the ideal gram molecular volume of gases, which are most frequently quoted in text-books of physical chemistry are 82.057 cm.^{3} atm. (deg. K)$^{-1}$ mole^{-1} (or 8·3144 joules (deg. K)$^{-1}$ mole^{-1}) and 22,414·6 cm.^{3} mole^{-1}, respectively. However, closer scrutiny shows that these values are based on an ice-point of 0°C = 273·16°K, instead of the value recommended in 1954, 273·15°K.[1]

The U.S. National Academy of Sciences—National Research Council has very recently published a new list of " best values " for the physicochemical constants, and these have been accepted by the U.S. Bureau of Standards.[2] The unified $^{12}C = 12$ scale of atomic weights is used, and 0°C = 273·15°K. The gas constant becomes 8·3143 joules (deg. K^{-1}) mole^{-1}, and the ideal volume 22,413·6 cm.^{3} mole^{-1}, which corresponds to 22,414·6 cm.^{3} mole^{-1}, as before, on the old chemical scale, " natural " oxygen = 16.

The value of the gas constant is therefore based on that of the ideal gram molecular volume, and, by tradition, this volume is derived from the density of oxygen gas at standard temperature and pressure (0°C; 1 atm.), and the deviation from the perfect gas law is expressed by the equation:

$$(pV)_0/(pV)_1 = 1 + \lambda$$

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[1] 10th General Conference on weights and measures, 1954.

[2] *Nat. Bur. Stand. (U.S.), Tech. News Bull.*, 1963, **47**, No. 10.

If one accepts the modern physical methods of establishing atomic weights, or, for that matter, the limiting-pressure method, then density measurements on all gases contribute to the evaluation of the ideal volume. A review of the published data on this basis would, however, be quite a lengthy task. From a study of all the Papers published since 1921 on the density and compressibility of oxygen, the following Table has been prepared.

The normal density and compressibility of oxygen.

Density (g./l.)	1·42896	1·42899	1·42895	—	—	1·42905	1·42904	1·42894	1·42894
$1 + \lambda$	—	—	—	1·00085	1·00087	1·00097	1·00092	1·00097	1·00091
Ref.	3	4	5	6	7	8	9	10	11
Year	1921	1922	1922	1922	1925	1924	1926	1926	1936
Density (g./l.)	1·42895	1·42894	1·42895	1·42881	1·42881	—	—	—	
$1 + \lambda$	1·00094	1·00091	—	1·00086	1·00088	1·000956	1·000988	1·000972	
Ref.	12	13	14	15	16	17	18	19	
Year	1937	1938	1939	1950	1952	1923	1925	1954	

A reproducibility of the density measurements, if not an absolute accuracy, of 1 part in 10^5, as claimed by Moles and his co-workers, is probably not an exaggeration. Therefore, when comparing the results of different workers, it is essential that the values should be brought to a common reference standard, and minute differences in standardisation, which could be ignored with measurements of a lower order of precision, must be taken into account. The exact correlation of results, however, is not as simple as might at first be supposed. For instance, one may question whether the authors were using the correct values for the acceleration due to gravity (g) at their laboratories, instead of old unauthenticated values. Baxter and Starkweather corrected [9] their first published results [8] for precisely this reason. The volumetric calibration of glass globes is likewise open to question, since it usually depends on a careful assessment of the correct data for the density of water or of mercury. Research into matters such as these, which are not made sufficiently clear by the authors, can take one back several decades, and is often tedious, frustrating, and inconclusive. In the Table, the only correction that could be justifiably made was the adjustment, wherever appropriate, of the densities to the standard value of $g = 980{,}665$ cm./sec.^{2}, in place of the formerly much-used value of 980,616 cm./sec.^{2}. The factor is 1·000049, and it is perhaps worth mentioning, by way of illustration of the slight discrepancies which can creep into results of this kind, that Moles and Gonzalez incorrectly adjusted one of their values by 5 parts in 140,000, instead of by 7 parts.

It can be seen from the Table that the results of the schools of Baxter, Moles, and Batuecas are in somewhat better agreement amongst themselves than with the others, suggesting that the discrepancies are probably due to small systematic errors of calibration or standardisation. All the authors had much faith in the heating of potassium permanganate and in electrolysis as methods of preparation of oxygen, although, as Stock and

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[3] Moles and Gonzalez, *Compt. rend.*, 1921, **173**, 355.
[4] Moles and Gonzalez, *J. Chim. phys.*, 1922, **19**, 310.
[5] Moles and Crespi, *Anales real Soc. espãn. Fis. Quím.*, 1922, **20**, 190.
[6] Guye and Batuecas, *Helv. Chim. Acta*, 1922, **5**, 532.
[7] Batuecas, *J. Chim. phys.*, 1925, **22**, 101.
[8] Baxter and Starkweather, *Proc. Nat. Acad. Sci. U.S.A.*, 1924, **10**, 479.
[9] Baxter and Starkweather, *Proc. Nat. Acad. Sci. U.S.A.*, 1926, **12**, 699.
[10] Stock and Ritter, *Z. phys. Chem.*, 1926, **124**, 204.
[11] Moles and Toral, *Monatsh*, 1936, **69**, 342.
[12] Moles and Roquero, *Anales real Soc. espãn. Fis. Quim.*, 1937, **35**, 263.
[13] Moles and Escribano, *Compt. rend.*, 1938, **207**, 66.
[14] Moles, Toral, and Escribano, *Trans. Faraday Soc.*, 1939, **35**, 1439.
[15] Batuecas and Garcia Malde, *Anales real Soc. espãn. Fis. Quím.*, 1950, **46***B*, 517.
[16] Casado and Batuecas, *Anales real Soc. espãn. Fis. Quim.*, 1952, **48***B*, 5.
[17] Kuypers and Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, 1923, 165a.
[18] Holborn and Otto, *Z. Physik*, 1925, **33**, 1.
[19] Michels, Schamp, and de Graaff, *Physica*, 1954, **20**, 1209.

Ritter showed,[10] and as is now well established, these preparations appear to give rise to a little nitrogen, presumably occluded by the crystals, and, in the case of electrolysis, some hydrogen. It is interesting to note that Batuecas and his co-workers obtained slightly lower values for both the density and $(1 + \lambda)$ than did the other workers, suggesting that their oxygen may have contained some nitrogen or hydrogen. Rather conveniently, these two possible errors tend to cancel out when the ideal volume is calculated. Also, Batuecas and his co-workers used rather small flasks for their density measurements, which perhaps detracts from their results a little. Stock and Ritter's result for the density[10] is in excellent agreement with those of Moles and his co-workers, and, as will be shown below, their value for $(1 + \lambda)$ is undoubtedly very sound.

The last three values of $(1 + \lambda)$ given in the Table were derived from measurements of the pressure–volume isotherm at 0°C at pressures up to 100 atm. The usual procedure is to fit the experimental data, by least-squares methods, to the quadratic equation

$$pV = A + Bp + Cp^2$$

with the constraint $pV = 1$ at 0°C and 1 atm. (the Amagat system). The A constant is thus equivalent to $(1 + \lambda)$. In the opinion of Wild[20] and later of Cragoe,[21] this method yields values of $(1 + \lambda)$ at least as good as, if not better than, those obtained from density measurements in the range 0—1 atm. Cragoe has pointed out that Holborn and Otto[18] fell into error when calculating the coefficients, with the pressures in metres of mercury, but Cragoe's argument is extremely difficult to follow.

The former value, 22,414·6 cm.^{3} mole^{-1}, for the ideal volume, is that recommended by Birge[22] in an excellent article on the physical constants in 1941, and there does not appear to have been any published discussion since then on the ideal volume and the gas constant. Birge selected the density data of Baxter and Starkweather, and, for $(1 + \lambda)$, the value recommended by Cragoe[21] from a critical study of the isotherm measurements of oxygen, namely 1·0009535 (the inclusion of the last two figures seems excessively optimistic). Cragoe's review, however, was before the work of Michels, Schamp, and de Graaff.[19] The extreme precision of the measurements of the Amsterdam school is very well known. In the case of the oxygen data, two sets of coefficients were evaluated, one for the full pressure range 1—120 atm., and the other for the lower pressures only; precisely which these are is not stated. The authors consider that the latter are the true theoretical virial coefficients, which are not unduly influenced by the need to obtain a good least-squares fit at the higher pressures. In any case, the value of A is the same for both series, namely 1·000972, and, this should be accepted as the best available. For the density, excellent as the work of Baxter and Starkweather is, it seems, that to use their value alone nowadays is to ignore the very extensive and equally excellent work of Moles and his co-workers. A figure of 1·42900 g./l., or 1·42897 mg./cm.^{3}, can probably best be taken. Finally, if we accept 5 in 140,000 as the possible error in the density, and 2 in 100,000 for $(1 + \lambda)$, the ice-point being now fixed by definition, then we find:

$$\begin{aligned} V_{\text{ideal}} &= 22{,}414{\cdot}5 \pm 1{\cdot}2 \text{ cm.}^3 \text{ mole}^{-1} \\ \boldsymbol{R} &= 82{\cdot}059 \pm 0{\cdot}005 \text{ cm.}^3 \text{ atm. (deg. K)}^{-1} \text{ mole}^{-1} \\ &= 8{\cdot}3147 \pm 0{\cdot}0005 \text{ joules (deg. K)}^{-1} \text{ mole}^{-1} \\ (^{12}\text{C} &= 12) \qquad (0^\circ\text{C} = 273{\cdot}15^\circ\text{K}) \end{aligned}$$

This volume is almost identical with that recommended by Birge,[22] but it is based on the new unified scale of atomic weights, instead of the former, " natural " oxygen = 16.

THE BRITISH OXYGEN COMPANY LIMITED,
SCIENTIFIC CENTRE, LONDON S.W.19.

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[21] Cragoe, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 495.
[22] Birge, *Reports Progr. Phys.*, 1941, **8**, 90.

152. *Nuclear Methylation of Some 6-Substituted 4-Aminopyrimidines: A Correction.*

By D. J. BROWN and T. TEITEI.

WE recently described[1] products resulting from treatment of 4-methoxy- and 4-chloro-6-methylaminopyrimidine with methyl iodide. We have subsequently found that an earlier specimen, on which their structures were based, had been erroneously relabelled.

In fact, the first compound yielded 1,6-dihydro-1-methyl-4-methylamino-6-oxopyrimidine (m. p. 194°) identified by mixed melting point and ultraviolet spectrum [neutral molecule, $\lambda_{max.}$ (log ε): 260 (3·93), 223 (4·44)] with authentic material,[2] and 1,4-dihydro-6-methoxy-1-methyl-4-methyliminopyrimidine [hydriodide, m. p. 215—217°; $\lambda_{max.}$ as cation, 263 (4·20)]. The second compound gave 4-chloro-3,6-dihydro-3-methyl-6-methyliminopyrimidine [hydriodide, m. p. 223°; $\lambda_{max.}$ as cation, 263 (4·09) and 222 (3·99)]. The spectrum [270 (3·83), 237 (4·14) at pH 7] recorded[1] as that of 1,6-dihydro-1-methyl-4-methylamino-6-oxopyrimidine was that of its 4-methylthio-analogue.

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[1] D. J. Brown and T. Teitei, *J.*, 1963, 3535.

[2] D. J. Brown and J. S. Harper, *J.*, 1961, 1298.