

NOTES.

630. *A New Reaction of Sulphinic Acids.*

By W. V. FARRAR.

ADDITION of acetic acid to aqueous sodium toluene-*p*-sulphinic acid containing sodium cyanate causes brisk evolution of carbon dioxide, followed by precipitation of crystals. This substance, $C_8H_{10}O_2N_2S$, is believed to be (I; $R = p\text{-MeC}_6\text{H}_4$). Since both acid and alkaline hydrolyses regenerate the sulphinic acid, the alternative structure (II) is unlikely; this would be expected to give the sulphonamide. The infrared spectrum confirms the



presence of a C=N bond, and the absence of $C \equiv N$, so that the compound cannot be the cyanamide salt of the sulphinic acid. The amidine (I) is probably formed by addition of sulphinic acid to free carbodi-imide, transiently formed when sodium cyanate is acidified; a few seconds after acidification, sodium cyanate no longer gives the amidine (I) on addition

of sulphinate. Similar compounds (I; R = Ph and *o*-NO₂·C₆H₄) were made from benzene-sulphinic acid and *o*-nitrobenzenesulphinic acid.

Attempts to use these compounds (which are formally *C*-substituted formamidines) as starting materials for heterocyclic syntheses have been completely fruitless. At their melting points, or in hot solvents, they decompose into a mixture of diaryl disulphide and arenesulphonamide.

Experimental.—*C-Toluene-p-sulphonylformamidine*. A solution of sodium toluene-*p*-sulphinate dihydrate (20 g.) and sodium cyanate (20 g.) in water (200 c.c.) was treated with acetic acid (20 c.c.). Carbon dioxide was evolved, followed after a few minutes by deposition of a heavy precipitate (4–5 g.). Recrystallisation from a large volume of water gave needles, m. p. *ca.* 192° (decomp.; varying with rate of heating) (Found: C, 48.4; H, 5.3; N, 13.5; S, 16.0. C₈H₁₀O₂N₂S requires C, 48.4; H, 5.1; N, 14.1; S, 16.2%). 1 Hour with refluxing 2*N*-sodium hydroxide or hydrochloric acid caused complete hydrolysis to the sulphinic acid; the nature of the other products was not investigated.

The following compounds were made similarly in similar yields: *C-benzenesulphonylformamidine* (I; R = Ph), m. p. *ca.* 190° (decomp.), from water (Found: C, 46.0; H, 4.3; N, 15.3. C₇H₈O₂N₂S requires C, 45.7; H, 4.4; N, 15.2%); *C-o-nitrobenzenesulphonylformamidine* (I; R = *o*-NO₂·C₆H₄), m. p. *ca.* 195° (decomp.), from water (Found: C, 36.4; H, 3.3; N, 18.4; S, 14.6. C₇H₇O₄N₃S requires C, 36.7; H, 3.1; N, 18.3; S, 14.0%).

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631. Conductance in Triethyl Phosphite.

By C. M. FRENCH and P. B. HART.

DURING a study of the influence of solvent structure and size on conductance relationships, it was hoped to employ a series of trialkyl phosphites as solvents, which might then be compared with the corresponding phosphates studied previously.^{1,2} Unfortunately, the phosphites proved usually too readily oxidisable in the presence of the quaternary ammonium picrates commonly used as solutes (the system quoted below appeared to be an exception); and, of the many other salts examined, only the quaternary ammonium toluene-*p*-sulphonates were sufficiently soluble for any conductance measurements to be made. These solutes were extremely hygroscopic and had to be handled in dry-boxes, and considerable precautions were necessary to exclude all traces of moisture when preparing solutions of them. Work in these solvents was therefore not extended, but the results of measurements made in two systems by methods described earlier² have some features of interest and are now presented.

Experimental.—Triethyl phosphite was freed from traces of the dialkyl ester by storage over sodium until no more of the latter dissolved, filtering, and redistilling under reduced pressure; it had b. p. 50°/14 mm., d_4^{25} 0.9610, n_D^{17} 1.4140, η^{25} 0.650 cp., ϵ^{25} 5.01, κ^{25} 2×10^{-9} ohm⁻¹ cm.⁻¹ (lit., b. p. 48°/12.5 mm.,⁴ d_4^{25} 0.96,⁵ $n_D^{17.5}$ 1.4140⁵). Tetrabutylammonium toluene-*p*-sulphonate was prepared by neutralising the quaternary ammonium hydroxide with recrystallised toluene-*p*-sulphonic acid in ethanol. The latter was evaporated off, and the salt recrystallised from ethyl acetate. Tetrapentylammonium picrate was prepared as described earlier.³

Equivalent conductivities at different concentrations in triethyl phosphite at 25° of the two

¹ French and Muggleton, *J.*, 1957, 5064.

² French, Hart, and Muggleton, *J.*, 1959, 358.

³ French and Hart, *J.*, 1960, 1671.

⁴ Ford-Moore and Williams, *J.*, 1947, 1465.

⁵ McCombie, Saunders, and Stacey, *J.*, 1945, 380.

systems studied here are as tabulated. In both cases the graphs of Λ against \sqrt{c} were steep curves with minima at about $3 \times 10^{-3}N$. These indicated extensive ion-pair and triple-ion formation as expected from the low dielectric constant of the solvent. As commonly occurs with such

Tetrapentylammonium picrate

| | | | | | | | | | |
|---------------------|-----|------|------|------|------|------|------|------|------|
| $c \times 10^4$ | ... | 76.8 | 40.6 | 29.0 | 18.3 | 10.1 | 5.79 | 3.21 | 1.88 |
| $\Lambda \times 10$ | ... | 1.97 | 1.88 | 1.92 | 2.07 | 2.72 | 3.18 | 4.05 | 4.78 |

Tetrabutylammonium toluene-*p*-sulphonate

| | | | | | | | | | | | |
|---------------------|-----|------|------|------|------|------|------|-------|-------|-------|--------|
| $c \times 10^4$ | ... | 89.8 | 60.0 | 34.8 | 23.2 | 6.14 | 1.43 | 0.646 | 0.453 | 0.108 | 0.0327 |
| $\Lambda \times 10$ | ... | 2.33 | 2.38 | 2.22 | 2.16 | 2.52 | 5.26 | 12.2 | 15.4 | 23.7 | 33.8 |

solvents also, Shedlovsky plots failed to become linear over the concentration range examined, and extrapolation to Λ_0 was not therefore possible. It may be observed, however, that at finite concentrations the equivalent conductances of both tetra-alkylammonium salts are of the order of 100 times less in triethyl phosphite than at the same concentrations of the picrates of these quaternary ammonium ions in triethyl phosphate² but resemble values in other solvents with dielectric constant of approximately 5. The differences in conductance between the phosphite and phosphate systems may thus apparently be accounted for by the somewhat higher viscosity and considerably lower dielectric constant of the phosphorous than the phosphoric acid esters, but not otherwise related to structural differences between the two solvents.

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632. *The Systems Water-Chlorine-Calcium Chloride and Water-Chlorine-Barium Chloride.*

By K. W. ALLEN.

IN the course of a study of chlorine hydrate,¹ it was necessary to investigate the equilibria between water, chlorine, and calcium chloride and also between water, chlorine, and barium chloride—all at a temperature of 0° and under a pressure of 1 atm. The results for the system including calcium chloride are represented in the Figures. The compositions of the fixed points are: Invariant liquid *A*, Cl_2 , 0.45 ± 0.05 ; CaCl_2 , 15; H_2O , 84.6%. Invariant liquid *B*, Cl_2 , 0.15; CaCl_2 , 34.19; H_2O , 65.66%. Chlorine hydrate solid, Cl_2 , $35.15 \pm 0.54\%$. Saturated solution of chlorine in water,² Cl_2 , 0.5%. Saturated solution of calcium chloride in water³ Cl_2 , 37.3%.

The system including barium chloride is similar except that no region of equilibrium between gaseous chlorine and solution alone was detected. Thus the system could be represented by a figure similar to that given but with the invariant points *A* and *B* coincident. The compositions of the fixed points are: Invariant liquid Cl_2 , 0.3; BaCl_2 , 21.9; H_2O , 77.8%. Saturated solution of barium chloride in water⁴ BaCl_2 , 23.5%.

Experimental.—The details of the method used for the analysis of the system water-chlorine-calcium chloride have been described.¹ Precisely similar methods were used for the system including barium chloride except that the barium was determined gravimetrically as sulphate.

¹ Allen, *J.*, 1959, 4131.

² Seidell, "Solubilities of Inorganic and Metal-organic Compounds," Van Nostrand Co. Inc., New York, 1940, Vol. I, p. 396.

³ *Op. cit.*, p. 280.

⁴ *Op. cit.*, p. 155.

FIG. 1. The system water-chlorine-calcium chloride at 0° and 1 atm.

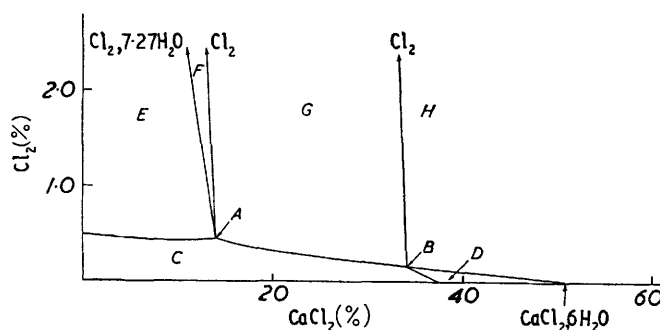
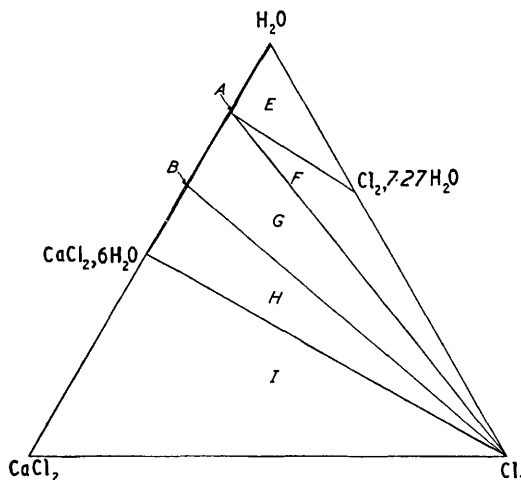


FIG. 2. Enlargement of the water corner of the diagram for the system water-chlorine-calcium chloride at 0°, drawn on rectangular co-ordinates with unequal scales.

A, Invariant liquid. B, Invariant liquid. C, Unsaturated solutions. D, Solutions plus solid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. E, Solutions plus solid chlorine hydrate, $\text{Cl}_2 \cdot 7 \cdot 27\text{H}_2\text{O}$. F, Invariant liquid A plus solid chlorine hydrate plus gaseous chlorine. G, Solutions plus gaseous chlorine. H, Invariant liquid B plus solid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ plus gaseous chlorine. I, Solid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ plus solid CaCl_2 (anhyd.) plus gaseous chlorine.

The author thanks Dr. J. E. Garside, Dr. J. Leicester, and Dr. G. H. Cheeseman for their help in the work.

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633. Preparation of Some Potential Schistosomicidal Agents.

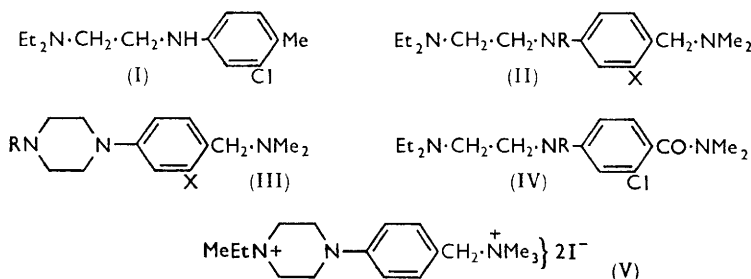
By D. E. AMES.

It has been claimed¹ that substituted *p*-toluidines, *e.g.*, (I), possess activity against schistomia infections of mammals. In the present work, the synthesis of triamines of types (II) and (III), having an additional basic substituent in the methyl group, was examined in the hope of preparing compounds showing more effective schistosomicidal activity.

4-Amino-2-chloro-*NN*-dimethylbenzamide was condensed with diethylaminoethyl chloride to give 2-chloro-4-diethylaminoethylamino-*NN*-dimethylbenzamide (IV; R = H) but this could not be reduced satisfactorily to the triamine (II; R = H, X = Cl) with lithium

¹ Farbenfabr. Bayer A.-G., B.P. 729,332/1952.

aluminium hydride. Duff and Furness² have shown that condensation of dialkylanilines with hexamine in formic acid yields *NN*-dimethyl-4-dialkylaminobenzylamines. Application of this procedure to *N*-diethylaminoethyl-*N*-methylaniline gave the required triamine (II; R = Me, X = H) in low yield provided that a large excess of hexamine was used. 1-Ethyl-4-phenylpiperazine was similarly converted into the triamine (III; R = Et, X = H) which, with excess of methyl iodide, gave a dimethiodide, presumably (V) in



which the less hindered terminal amino-groups have been quaternised. Further compounds of type (III; X = Cl or OMe) were also prepared in very low yield by the same procedure.

Dr. P. E. Thompson (Parke, Davis and Co., Detroit) has studied the effects of these compounds on mice infected with *S. mansoni*, but none of them showed promising activity.

Experimental.—The *NN*-dimethylamides all gave low values for nitrogen in microanalyses.

*2-Chloro-*NN*-dimethyl-4-nitrobenzamide.*

 2-Chloro-4-nitrobenzoic acid³ (22 g.) was refluxed for 1·5 hr. with thionyl chloride (50 c.c.); toluene (100 c.c.) was added and the solution evaporated at the water-pump. The residue was taken up in ether-benzene (200 c.c.; 1 : 1) and stirred while excess of dimethylamine was passed in. After the mixture had been cooled and filtered, the solid was washed with water and recrystallised from benzene, to give the *amide* (17·3 g.) as prisms, m. p. 117—118·5° (Found: C, 47·0; H, 4·1. C₉H₆O₃N₂Cl requires C, 47·3; H, 4·0%).

*4-Amino-2-chloro-*NN*-dimethylbenzamide.*

 The foregoing nitro-*amide* (85 g.), suspended in ethanol (400 c.c.), was hydrogenated in the presence of platinised charcoal⁴ (ca. 2 g.) until absorption ceased (3·0 mol.). The solution was filtered at the b. p.; prisms of the *amino-amide* (63·5 g.), m. p. 167—169°, separated on cooling (Found: C, 54·8; H, 4·7; Cl, 17·6. C₉H₁₁ON₂Cl requires C, 54·4; H, 5·6; Cl, 17·8%).

*2-Chloro-4-(2-diethylaminoethylamino)-*NN*-dimethylbenzamide.*

 A mixture of the foregoing *amino-amide* (33 g.), 2-diethylaminoethyl chloride hydrochloride (36 g.), and potassium carbonate (32 g.) in xylene (240 c.c.) with water (27 c.c.) was refluxed for 3 hr. and then water was removed azeotropically. After addition of sodium hydrogen carbonate solution, the mixture was filtered and the separated aqueous layer was extracted with ethyl acetate. The insoluble solid and the combined organic layers were extracted with 2*N*-hydrochloric acid (250 c.c., then 2 × 150 c.c.). Basification of the extracts gave an oil which was isolated with ethyl acetate and distilled at 190—205°/0·3 mm. This was dissolved in ether and a seed of 4-amino-2-chloro-*NN*-dimethylbenzamide added. After the solution had been kept at 0° for 3 days, it was filtered and distilled to give the *diamino-amide* (14 g.), b. p. 196—200°/0·3 mm., *n*_D²⁰ 1·5628 (Found: C, 61·0; H, 8·2; Cl, 11·6. C₁₅H₂₄ON₃Cl requires C, 60·5; H, 8·1; Cl, 11·9%).

Preparation of Triamines (II) and (III).

 A mixture of the diamine (0·25 mol.), hexamine (180 g.), and 85% formic acid (450 c.c.) was warmed cautiously until the vigorous reaction which soon occurred had subsided and was then refluxed (bath 140°) for 12 hr. Water (1 l.) was added and the solution strongly basified with 10*N*-sodium hydroxide and extracted

² Duff and Furness, *J.*, 1952, 1159.

³ Albert and Linnell, *J. Soc. Chem. Ind.*, 1936, 54*r*.

⁴ Baltzly, *J. Amer. Chem. Soc.*, 1952, **74**, 4589.

repeatedly with ethyl acetate. The washed and dried (MgSO_4) extracts were fractionally distilled and the high-boiling fraction redistilled to give the triamine.

N-Diethylaminoethyl-*N*-methyl-4-(dimethylaminomethyl)aniline, thus prepared from *N*-diethylaminoethyl-*N*-methylaniline⁶ in 27% yield, had b. p. $137\text{--}139^\circ/0.5\text{ mm.}$, n_D^{20} 1.5230 (Found: C, 72.9; H, 11.2; N, 15.4. $\text{C}_{16}\text{H}_{23}\text{N}_3$ requires C, 73.0; H, 11.1; N, 16.0%). Its trihydrochloride formed needles, m. p. 195° (decomp.), from ethanolic hydrogen chloride (Found: C, 50.4; H, 8.7; N, 11.0; Cl, 28.3. $\text{C}_{16}\text{H}_{23}\text{N}_3\text{Cl}_3 \cdot 0.5\text{H}_2\text{O}$ requires C, 50.3; H, 8.7; N, 11.0; Cl, 27.9%)

1-Ethyl-4-(4-dimethylaminomethylphenyl)piperazine, prepared from 1-ethyl-4-phenylpiperazine⁶ in 27% yield, had b. p. $110\text{--}113^\circ/0.2\text{ mm.}$, n_D^{20} 1.5470 (Found: C, 72.6; H, 10.1; N, 17.4. $\text{C}_{15}\text{H}_{25}\text{N}_3$ requires C, 72.8; H, 10.2; N, 17.0%). The trihydrochloride, prisms from ethanolic hydrogen chloride, had m. p. $226\text{--}228^\circ$ (decomp., sealed capillary) (Found: C, 49.4; H, 7.9; N, 11.3; Cl, 29.0. $\text{C}_{15}\text{H}_{25}\text{N}_3\text{Cl}_3 \cdot 0.5\text{H}_2\text{O}$ requires C, 49.2; H, 8.0; N, 11.5; Cl, 29.1%).

Methyl iodide (10 c.c.) was added to this triamine (5.5 g.) in 2-methoxyethanol (50 c.c.); a white precipitate which had been formed after 20 min. at room temperature did not dissolve on refluxing for 30 min. (bath 130°). The cooled mixture was filtered and the solid washed with methanol, leaving the dimethiodide (9.7 g.), presumably (V), m. p. $255\text{--}258^\circ$ (decomp.) (Found: C, 38.8; H, 5.9; N, 7.5; I, 48.3. $\text{C}_{17}\text{H}_{31}\text{N}_3\text{I}_2$ requires C, 38.4; H, 5.9; N, 7.9; I, 47.8%).

1-*m*-Chlorophenyl-4-methylpiperazine. *N*-Methyldiethanolamine⁷ (200 g.) and *m*-chloroaniline (200 g.) were treated gradually with concentrated hydrochloric acid (320 c.c.), and the mixture was distilled until the bath-temperature reached 300° (cf. Pollard and Wicker⁸). The hot mass was poured into water (1 l.), basified with 5*N*-sodium hydroxide, and extracted with ethyl acetate. The extracts were washed with aqueous sodium hydroxide and water and then distilled, to give the piperazine (105 g.), b. p. $120\text{--}125^\circ/0.8\text{ mm.}$, n_D^{20} 1.5792 (Found: C, 62.2; H, 7.2; Cl, 17.0. $\text{C}_{11}\text{H}_{15}\text{N}_2\text{Cl}$ requires C, 62.7; H, 7.2; Cl, 16.8%).

1-(3-Chloro-4-dimethylaminomethylphenyl)-4-methylpiperazine. Prepared by the general procedure as above in 12% yield, the triamine was an oil, b. p. $142\text{--}146^\circ/0.6\text{ mm.}$, n_D^{20} 1.5658 (Found: C, 62.4; H, 8.0; Cl, 13.5. $\text{C}_{14}\text{H}_{22}\text{N}_3\text{Cl}$ requires C, 62.8; H, 8.3; Cl, 13.2%). The hydrochloride formed prisms, m. p. 240° (decomp.), from ethanolic hydrogen chloride (Found: C, 43.4; H, 6.9; Cl, 36.3. $\text{C}_{14}\text{H}_{22}\text{N}_3\text{Cl} \cdot 3\text{HCl} \cdot 0.5\text{H}_2\text{O}$ requires C, 43.6; H, 6.8; Cl, 36.7%).

1-*m*-Methoxyphenyl-4-methylpiperazine. *N*-Methyl-di-(2-chloroethyl)amine hydrochloride⁷ (184 g.), *m*-anisidine (123 g.), anhydrous potassium carbonate (350 g.), and 2-butoxyethanol (750 c.c.) were stirred under reflux (bath 160°) for 7 hr. After addition of water (3 l.), the separate aqueous layer was extracted with ethyl acetate (500 c.c.), and the combined organic layers were washed with 5*N*-sodium hydroxide and water (twice each). Fractional distillation through a short Fenske column afforded the piperazine (100 g.), b. p. $106\text{--}108^\circ/0.3\text{ mm.}$, n_D^{20} 1.5598 (Found: C, 69.6; H, 8.7; N, 13.4. $\text{C}_{12}\text{H}_{18}\text{ON}_2$ requires C, 69.9; H, 8.8; N, 13.6%).

1-(4-Dimethylaminomethyl-3-methoxyphenyl)-4-methylpiperazine, prepared by the general procedure in 8% yield, had b. p. $131\text{--}135^\circ/0.3\text{ mm.}$, n_D^{20} 1.5330 (Found: C, 68.1; H, 9.9; N, 16.3. $\text{C}_{15}\text{H}_{25}\text{ON}_3$ requires C, 68.4; H, 9.6; N, 16.0%).

The author is indebted to Dr. R. E. Bowman for helpful discussions and to Mr. F. Oliver for the microanalyses.

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⁵ Dewar, *J.*, 1944, 615.

⁶ Forsee and Pollard, *J. Amer. Chem. Soc.*, 1935, **57**, 1788.

⁷ Hanby and Rydon, *J.*, 1947, 516.

⁸ Pollard and Wicker, *J. Amer. Chem. Soc.*, 1954, **76**, 1854.

634. *Deacetylation of Glycoside Polyacetates.*

By D. H. LEABACK.

SINCE the publications by Zémplen and his co-workers,¹ deacetylation of glycoside polyacetates is usually carried out in dry methanol containing a catalytic amount of sodium. When working up the products it is often possible to ignore the small amount of sodium present; nevertheless, some workers prefer to employ barium or potassium methoxide and remove the cations as the sulphate² or perchlorate³ respectively.

Bonner and Koehler³ pointed out how convenient it is when the deacetylated product crystallises from the medium; a method by which this may be achieved with most acetylated glycosides is described here. On addition of catalytic amounts of sodium, a wide range of acetylated glycosides dissolve in a very small volume of methanol and within a short time the deacetylated glycoside crystallises. Since many deacetylations are carried out on a boiling-water bath, this solubilising effect of sodium methoxide on glycoside acetates is often missed. Bonner and Koehler³ selected phenyl β -D-glucoside as an example of a compound that did not crystallise from a deacetylation mixture; however, crystallisation did take place under the following conditions.

2N-Sodium methoxide (0.5 ml.) was added to a suspension of phenyl 2,3,4,6-tetra-*O*-acetyl- β -D-glucose (4.5 g.) in dry methanol (5 ml.), in a stoppered flask. The mixture was shaken until dissolution was complete; after 15–20 min. the deacetylated glycoside started to crystallise, and the mixture was left for 18 hr. at 5° before the flask was inverted (to drain away the methanol). The residue was recrystallised, to give 2.1 g. (79%) of phenyl β -D-glucoside, m. p. 172–173°, $[\alpha]_D^{25} - 71^\circ$ (c 1 in H₂O).

The procedure seems to be general (acetylated glycuronic esters may be an exception⁴) and has been employed in this laboratory for deacetylation of ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucose and a wide range of acetylated aryl glycosides in the β -D-glucose, β -D-galactose, and 2-acylamino-2-deoxy- β -D-glucose series. The best proportion of acetylated glycoside to methanol must be established by a preliminary experiment, since the solubility of deacetylated glycosides in methanol varies considerably. The advantages of the procedure are: (i) Only small volumes of dry methanol are required for deacetylations and, even with poorly soluble glycoside polyacetates, addition of other solvents (to effect solution) is unnecessary.⁵ (ii) The onset and course of the reaction are observable. (iii) Heating is unnecessary since deacetylation takes place rapidly at room temperature; this is particularly convenient when elevated temperature causes liberation of troublesome amounts of aglycone. (iv) Crystallisation from the deacetylation medium brings about some purification.

On the basis of a mechanism advanced for catalytic deacetylation,¹ the process described here could be explained by assuming that one or more of the partly deacetylated intermediates (or their sodium complexes) is more soluble in methanol than the fully acetylated or deacetylated glycoside.

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¹ Cf. Zémplen and Kunz, *Ber.*, 1923, **56**, 1705.

² Weltzien and Singer, *Annalen*, 1925, **443**, 71.

³ Bonner and Koehler, *J. Amer. Chem. Soc.*, 1948, **70**, 314.

⁴ F. B. Anderson, personal communication.

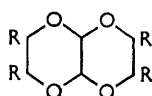
⁵ Cf. Leaback and Walker, *J.*, 1957, 4754.

635. *Interaction of trans-2,3-Dichloro-1,4-dioxan and Sulphuric Acid.*

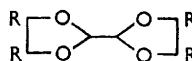
By L. A. CORT.

trans-2,3-DICHLORO-1,4-DIOXAN dissolves in concentrated sulphuric acid; the solution evolves hydrogen chloride without change in temperature, and crystalline material separates which is readily purified to give a compound A, $C_6H_6Cl_4O_4$.

Compound A exhibits no selective absorption between 2840 and 1460 cm^{-1} , and is inert towards a large number of reagents. With dilute mineral acids it yields up to 3 mol. of glyoxal and no detectable amounts of carboxylic acids or alcohols, and it is slowly converted into glyoxal and glycollic acid by boiling aqueous ethanolic potassium hydroxide (2 mol.). (In this reaction it is impossible to tell whether the glycollic acid arises from a complex series of changes first involving dehydrohalogenation, or whether it arises simply as a transformation product of the glyoxal.) These facts indicate that compound A is either 2,3,6,7-tetrachloro-1,4,5,8-tetraoxadecalin (I; $R = Cl$) or 4,5,4',5'-tetrachlorobis-1,3-dioxolan-2-yl (II; $R = Cl$), but do not distinguish between them.



(I)



(II)

Although a compound with either of these structures might have been expected to react with one or more of the following reagents, compound A was recovered substantially quantitatively in each case: (i) aluminium lithium hydride (cf. 2-chlorotetrahydrofurans¹); (ii) phosphorus pentachloride (cf. 1,4,5,8-tetraoxadecalin²); and (iii) dimethylaniline (cf. 2,3-dichloro-1,4-dioxan³). Other experiments from which compound A was recovered are noted in the Experimental Section.

Theoretically, either of the structures here suggested for compound A can be considered as being derived from the corresponding hydroxy-compounds (I and II; $R = OH$, respectively), by replacement of hydroxyl with chlorine. Now the former of these hydroxy-compounds has the structure previously postulated⁴ for "trimeric glyoxal." [It seems equally possible that "trimeric glyoxal" could be 4,5,4',5'-tetrahydrobis-1,3-dioxolan-2-yl (II; $R = OH$), but this alternative does not seem to have been considered.] However, although treatment of "trimeric glyoxal" with phosphorus pentachloride resulted in a vigorous reaction, no organic compound could be isolated containing chlorine which did not also contain phosphorus.

Experimental.—*trans*-2,3-Dichloro-1,4-dioxan (200 g.), m. p. 31° [prepared according to Kucera and Carpenter⁵ (cf. Summerbell and Lunk³)], was added slowly at 40° to well-stirred concentrated sulphuric acid (1 l.), and stirring continued for 24 hr. (until effervescence had ceased). The mixture was poured on crushed ice (3 kg.), and the solid product (93 g.), m. p. 129—135°, isolated. By recrystallisation from benzene or acetone there was obtained compound A, rhombs, m. p. 143—144° (shrinking at 137—139°) [Found: C, 25.35; H, 2.2; Cl, 49.9%; M (Rast), 272. $C_6H_6Cl_4O_4$ requires C, 25.4; H, 2.1; Cl, 50.0%; M , 284]. The m. p. was unchanged by further crystallisation from a number of solvents, or by sublimation, and material recovered from attempted reactions always showed shrinking at about 137—139° before melting.

¹ Crombie, Gold, Harper, and Stokes, *J.*, 1956, 136.

² Fiessmann and Hörndler, *Chem. Ber.*, 1954, **87**, 911.

³ Summerbell and Lunk, *J. Amer. Chem. Soc.*, 1957, **79**, 4802.

⁴ Raudnitz, *J.*, 1948, 763.

⁵ Kucera and Carpenter, *J. Amer. Chem. Soc.*, 1935, **57**, 2346.

In the preparation of compound A, neither orthophosphoric acid nor trichloroacetic acid could replace the sulphuric acid.

Hydrolysis of compound A. The compound (0.1019 g.) was boiled with aqueous 1% sulphuric acid (100 ml.) for 6 hr. Isolation through the use of an excess of the reagent in the usual manner gave glyoxal bis-*p*-nitrophenylhydrazone (0.3408 g., 96% of theory), m. p. 330—332° (decomp.). After crystallisation from acetone the m. p. and mixed m. p. were 332—334° (decomp.) (Found: C, 51.1; H, 3.7; N, 25.2. Calc. for $C_{14}H_{12}N_6O_4$: C, 51.2; H, 3.7; N, 25.6%).

After similar hydrolyses with hydrochloric acid, neither carboxylic acids nor alcohols could be detected (with *S*-benzylthiuronium hydrochloride and *p*-nitrobenzoyl chloride, respectively).

Reaction of compound A with aqueous ethanolic potash. To a suspension of compound A (35 g.) in boiling 95% ethanol (100 ml.) was added dropwise a solution of potassium hydroxide (13.8 g.) in water (25 ml.) so as to maintain gentle boiling. After boiling had been continued for a total of 4 hr. the mixture was concentrated (water-pump) to 35 ml. and then cooled. There separated compound A (19.7 g.), m. p. and mixed m. p. 141—143°, after crystallisation. From the filtrate, after 12 hours' storage, there was deposited potassium chloride (2.1 g.). From the remaining liquid there was isolated in the usual manner the *S*-benzylthiuronium salt (6.4 g.) of glycollic acid, m. p. and mixed m. p. 148—150°, after crystallisation from water (Found: C, 49.4; H, 5.7; N, 11.9; S, 13.0. Calc. for $C_{10}H_{14}N_2O_3S$: C, 49.6; H, 5.8; N, 11.6; S, 13.2%).

From another similar experiment the final liquid was treated to yield glyoxal bis-*p*-nitrophenylhydrazone, m. p. and mixed m. p. 329—332° (decomp.).

Attempted reactions with compound A. The compound was recovered in >95% yield in each case on treatment with the following reagents in the boiling solvents indicated: magnesium or phenylmagnesium bromide (diethyl ether), sodium or sodamide (toluene), potassium ethoxide or thiourea (ethanol), bromine or *N*-bromosuccinimide (carbon tetrachloride, with irradiation). Compound A sublimed quantitatively on fusion with potassium carbonate. There appeared to be a reaction between compound A and sodium iodide in acetone, but no olefinic product was obtained and the recovery after 70 hr. was 60%.

Reaction of "trimeric glyoxal." An aqueous solution of glyoxal was stored over sodium hydroxide until the weight became constant (2.1 g.). The gummy solid was ground with phosphorus pentachloride (8.3 g.), and the mixture extracted once with boiling benzene (25 ml.). Evaporation of the solvent left only a trace of material. The main solid residue contained chlorine and phosphorus and was almost completely soluble in cold water.

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636. Reactivity of Tri-*n*-butyl Borate with Certain Chlorides.

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TETRA-*n*-BUTOXYSILANE undergoes ready mutual replacement of alkoxy and halogen with boron trichloride,¹ $BuO\cdot Si(Obu)_3 + BCl_3 \longrightarrow BuO\cdot BCl_2 + ClSi(Obu)_3$, subsequent replacements being slower, but with a drift always towards the formation of tributyl borate. A similar pattern characterises the tributyl phosphite-boron trichloride,² and triphenyl phosphite-boron trichloride³ (or bromide)³ systems. Triethyl phosphate forms a complex $(EtO)_3P=O, BCl_3$,⁴ which gradually extrudes ethyl chloride and forms a network of $-P-O-B-O-$ links. Triphenyl phosphate gives a complex, $(PhO)_3P=O, BCl_3$, which is much more stable thermally and either dissociates into the initial compounds or decomposes into a number of compounds, mainly unidentified, when the temperature and pressure are suitably adjusted.³

¹ Gerrard and Strickson, *Chem. and Ind.*, 1958, 860.

² Gerrard and Lindsay, *Chem. and Ind.*, 1960, 152.

³ Frazer, Gerrard, and Patel, *Chem. and Ind.*, 1959, 90, 728; *J.*, 1960, 726.

⁴ Gerrard and Griffey, *Chem. and Ind.*, 1959, 55.

There was no reaction of tri-*n*-butyl borate with silicon tetrachloride, thionyl chloride, or phosphorus trichloride at the b. p. In the presence of ferric chloride, however, *n*-butyl chloride, butene, hydrogen chloride, and degeneration products such as sulphur dioxide, boric oxide, silica, and phosphorous oxide, were formed according to the system. No chloro-esters were observed.

Results described for non-catalysed systems are in accordance with the low nucleophilic reactivity of oxygen in the borate, owing probably to the low electron-density clearly shown by the low solubility of hydrogen chloride in *n*-butyl borate,^{5,6} and to the weak electrophilic function of boron, caused by back-co-ordination from oxygen.⁷

Although phosphorus oxychloride forms a complex with boron trichloride,⁸ it could be separated from *n*-butyl borate at 15°/1 mm., showing again the weak acceptor power of boron in the ester.

A mixture of 3 mols. of phosphorus pentachloride and 2 mols. of *n*-butyl borate gave hydrogen chloride, butene, *n*-butyl chloride, phosphorus oxychloride, and a residue containing all the boron, whereas when 5 mols. of borate were used, and the temperature was raised to 120°, the same products were obtained, except that the oxychloride reacted in its own right as described.

Acetyl chloride (3 mols.) did not react with *n*-butyl borate (2 mols.) at the temperature of reflux; but in the presence of ferric chloride, *n*-butyl chloride, *n*-butyl acetate, and a residue containing all the boron were obtained.

Trimethyl borate appeared to behave similarly to the *n*-butyl ester; but volatility factors made separations very difficult.

Experimental.—Easily hydrolysed halogen is designated e.h. and vapour-phase chromatography was used to assist in identification of volatile products.

Silicon tetrachloride system. Tri-*n*-butyl borate (18.9 g., 4 mols.) was heated with silicon tetrachloride (10.0 g., 3 mols.) at 80–85° (16 hr.) under reflux. The tetrachloride (9.1 g., 90%) (Found: Cl, 82.5. Calc. for Cl₄Si: Cl, 83.5%) was then removed at 18°/10 mm. and condensed at –80°; the residue gave butyl borate (17.8 g., 94%), b. p. 108–110°/10 mm., n_D^{20} 1.4090 (Found: B, 4.67. Calc. for C₁₂H₂₇O₃B: B, 4.7%). There was difficulty in completely removing the tetrachloride from the borate. When the borate (19.75 g., 4 mols.) and tetrachloride (11.4 g., 3 mols.) were similarly heated (6 hr.) in the presence of ferric chloride (0.15 g.), butene (1.47 g., 10%) was condensed at –80° and converted into dibromobutane (5.0 g.), b. p. 53–54°/18 mm., n_D^{20} 1.5110, d_4^{20} 1.785. The residue afforded *n*-butyl chloride (17.8 g., 75%), b. p. 77°, n_D^{20} 1.4045, d_4^{20} 0.887 (Found: Cl, 37.9. Calc. for C₄H₉Cl: Cl, 38.2%), and a final residue (8.84 g.) containing all the boron (B₂O₃, 3.00 g.) and silica (3.80 g., 95%). It was difficult to remove the remaining butyl chloride from the final residue.

Thionyl chloride system. A mixture of thionyl chloride (8.65 g., 3 mols.) and the borate (11.1 g., 2 mols.) was heated (18 hr.) at 130° under reflux. Thionyl chloride (7.55 g., 87%), b. p. 78° (Found: Cl, 58.5. Calc. for OCl₂S: Cl, 59.6%), was removed at 18°/16 mm. and condensed at –80°. Tri-*n*-butyl borate (10.81 g., 97%), b. p. 107–110°/10 mm. (Found: B, 4.69%), was obtained from the residue, and a brown liquid (0.21 g.) remained. The lower recovery of thionyl chloride was due to its slow decomposition under the conditions. In the presence of ferric chloride (0.24 g.), the mixture (borate, 9.77 g.) evolved sulphur dioxide at 20°. The temperature was slowly (3 hr.) raised to 80°. Sulphur dioxide (3.20 g., 77%) was condensed at –80°; the remainder gave *n*-butyl chloride (8.75 g., 73%), b. p. 77–78° (Found: Cl, 37.7%), and the final residue (4.32 g.) contained all the boron (0.47 g.).

Phosphorus trichloride system. A mixture of phosphorus trichloride (4.88 g., 1 mol.) and *n*-butyl borate (8.27 g., 1 mol.) was heated for 12 hr. at 95° under reflux. Phosphorus trichloride (4.22 g., 86.5%) (Found: Cl, 76.5. Calc. for Cl₃P: Cl, 77.4%) was removed at 18°/25 mm. and condensed at –80°. The residue gave the borate (7.28 g., 87%), b. p. 112–115°/15 mm. (Found: B, 4.7%). Ferric chloride catalysed the reaction, but it had to be added in

⁵ Gerrard and Macklen, *J. Appl. Chem.*, 1956, **6**, 241; 1959, **9**, 85; *Chem. and Ind.*, 1959, 1549.

⁶ Gerrard, Mincer, and Wyvill, *J. Appl. Chem.*, 1959, **9**, 89.

⁷ Abel, Gerrard, Lappert, and Shafferman, *J.*, 1958, 2895.

⁸ Burg and Ross, *J. Amer. Chem. Soc.*, 1943, **65**, 1637.

batches (0.1 g. every 2 hr.) because it became coated with degeneration products. The mixture (borate, 7.31 g.) was heated for 20 hr. at 95° under reflux. *n*-Butyl chloride (5.96 g., 67%), b. p. 78° (Found: Cl, 37.6%), was withdrawn at 15°/20 mm., and the residue (5.62 g.) comprised ferric chloride and degeneration products, boric oxide (*B*, 0.324 g., 94%), yellow phosphorus, and oxides of phosphorus (*P*, 1.08 g., 97%).

Phosphorus oxychloride. After a mixture of phosphorus oxychloride (12.43 g., 1 mol.) and *n*-butyl borate (18.68 g., 1 mol.) had been stored at 18° for 24 hr., the oxychloride (11.96 g., 96%) (Found: Cl, 68.8. Calc. for OCl_2P : Cl, 69.5%) was withdrawn at 15°/1 mm. (1 hr.), finally at 30°/1 mm. (15 min.) (mechanical shaking), and condensed at -80°. The residue gave butyl borate (18.65 g.), b. p. 73–75°/0.8 mm. (Found: B, 4.65%), which contained chlorine (0.5%) and 8% more acidic material than for the borate. The infrared spectrum conformed with the standard for the borate. There was a final residue (0.27 g.). When the mixture (borate, 8.1 g.) was heated to 130°, a vigorous evolution of gas ensued. After 90 min. the trap (-80°) contained hydrogen chloride (1.70 g., 46%), butene (3.2 g., 54%) and *n*-butyl chloride (0.55 g., 6%) (Found: Cl, 37.6%). The residue (5.55 g.) was a solid (Found: *P*, 1.042 g.; *B*, 0.370 g. Calc. for the system: *P*, 1.12 g.; *B*, 0.382 g.). Chlorine (e.h.) (0.69 g.) was also present. Small amounts of solid had been dispersed over the reflux condenser by the vigour of reaction.

Phosphorus pentachloride. The pentachloride (13.56 g., 3 mols.) slowly disappeared from its mixture with *n*-butyl borate (9.91 g., 2 mols.) as the system was heated to 70° (held for 4 hr.). There was a vigorous evolution of butene (2.08 g.) (dibromobutane, 7.2 g.; d_4^{20} 1.7815, n_D^{20} 1.5125) and hydrogen chloride (2.05 g.), manipulated by a cold trap and an alkali trap. The residue afforded *n*-butyl chloride (7.1 g., 60%) and phosphorus oxychloride (2.5 g.), b. p. 100–106°, by a tedious separation, and the final residue (4.91 g.) contained all the boron (0.467 g.). When 5 mols. of the borate (18.26 g.) were used for 3 mols. of the pentachloride, and the mixture was warmed slowly to 120° (held for 2 hr.), the cold-trap contents (11.86 g.) were separated into butene (5.62 g., 43%), hydrogen chloride (3.86 g., 45.2%), *n*-butyl chloride (1.98 g.), and a residue (0.2 g.) of boron trioxide and phosphorus pentoxide. The reaction residue afforded *n*-butyl chloride (3.97 g.), b. p. 78.5° (Found: Cl, 37.8%), and a final residue (9.19 g.) (Found: *P*, 1.36 g., 94%; *B*, 0.832 g., 96% of amount in the system; e.h. Cl, 0.84 g.).

Acetyl chloride. After a mixture of acetyl chloride (4.75 g., 3 mols.) and *n*-butyl borate (9.52 g., 2 mols.) had been heated for 17 hr. at 90° under reflux, acetyl chloride (4.36 g., 92%), b. p. 52° (Found: Cl, 44.5. Calc. for $\text{C}_2\text{H}_3\text{OCl}$: Cl, 45.3%), was removed at 18°/25 mm. and condensed at -80°. *n*-Butyl borate (9.14 g., 96%), b. p. 112–115°/15 mm. (Found: B, 4.76%), was obtained from the residue. In the presence of ferric chloride (0.62 g.) the mixture (borate, 20.91 g.) was heated at 60° for 2 hr. *n*-Butyl chloride (8.2 g., 66%), b. p. 78–80° (Found: Cl, 37.5%), *n*-butyl acetate (11.1 g., 71%), b. p. 122°, n_D^{19} 1.3950 (Found: Ac, 37.3. Calc. for $\text{C}_4\text{H}_{10}\text{O}_2$: Ac, 37.0%), and a middle fraction (8.0 g.), b. p. 80–120°, comprising a mixture of *n*-butyl acetate and *n*-butyl chloride, were obtained. The residue (4.17 g.) contained all the boron (0.971 g.).

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637. *Interaction of Trialkyl Phosphates with Boron Trichloride.*

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INTERACTION of boron trichloride with each of eight trialkyl phosphates (alkyl = Me, Et, Prⁿ, Prⁱ, Buⁿ, Bu^s, Bu^t, *n*-pentyl) first involves the formation of a complex $(\text{RO})_3\text{P}=\text{O}, \text{BCl}_3$, at temperatures below 0°, and then elimination of alkyl chloride, olefin, and hydrogen chloride and formation of a network of $-\text{P}-\text{O}-\text{B}-\text{O}-$ links giving a substance identical with or closely related to the so-called boron phosphate, $[\text{BPO}_4]_n$. The elimination occurred approximately stepwise as the temperature was raised to 300° by stages (a technique based on many preliminary experiments), 120° (1 hr.), 180° (1 hr.), and 300° (1 hr.). The residue was heated in an open crucible to about 1000°, and the final

residue (except when $R = \text{Me}$) contained practically all the boron and phosphorus in the system.

Evidence of formation of the 1 : 1 complex was the constancy of weight at $15^\circ/20 \text{ mm}$. Evolution of hydrogen chloride was accompanied by olefin, but the latter was not estimated quantitatively.

Table 1 shows the overall results in terms of chlorine, the fate of boron, and phosphorus. Table 2 shows the fate of the chlorine at the different stages of heating to 300° : the

TABLE 1.

| R in (RO) ₃ P=O | Produced up to 300° | | | BPO ₄ produced at 1000° | | | |
|-------------------------------|----------------------------|------------|-----------------------------|---|---------------|----------------|----------------|
| | RCl (%) | HCl (%) | Residue e.h. Cl ‡ (%) | Found (g.) | Calc. (g.) | B (%) Found | P (%) Found |
| Me | 88.2 | 1.2 | 6.4 | 4.68 | 6.01 | 11.5 | 30.2 |
| Et | 85.3 | 12.0 | —* | 7.71 | 7.84 | 10.3 | 29.4 |
| Pr ^a | 76.5 | 15.0 | 6.3 | 8.05 | 8.63 | 9.7 | 31.4 |
| Pr ⁱ | 73.7 | 13.6 | 6.3 | 3.79 | 3.86 | 10.8 | 30.4 |
| Bu ^a | 71.8 | 19.3 | 6.3 | 4.97 | 5.24 | 10.6 | 31.0 |
| Bu ^s | 49.9 | 40.8 | 9.3 | 4.08 | 4.37 | 9.6 | 27.5 |
| Bu ⁱ | 73.6 | 19.1 | 4.9 | 6.00 | 6.24 | 10.45 | 30.8 |
| n-Pentyl ... | 74.8 | 17.0 | 7.4 | 6.00 | 6.09 | 10.2 10.2 † | 30.9 29.3 † |

* Heated to 1000° in silica flask; no part was removed. † Calc. ‡ e.h. = easily hydrolysed.

TABLE 2.

| R | (RO) ₃ P=O (g.) | Approx. m. p. of complex | Produced up to 120° | | | Produced, $120-180^\circ$ | | | Produced, $180-300^\circ$ | | |
|----------------------------------|-------------------------------|--------------------------------|----------------------------|------------|-----------------------------|---------------------------|------------|-----------------------------|---------------------------|------------|---------------------------|
| | | | RCl (%) | HCl (%) | Residue e.h. Cl (%) * | RCl (%) | HCl (%) | Residue e.h. Cl (%) * | RCl (%) | HCl (%) | Residue e.h. Cl (%) |
| Me | 7.95 ^a | 62° | 57.7 | — | 27.1 | 17.9 | — | 15.6 | 12.6 | 1.2 | 6.4 |
| Et | 13.52 | 0 | 68.6 | — | — ^b | 11.6 | 0.1 | — ^b | 5.1 | 5.4 | — ^b |
| Pr ^a | 18.28 | 11—13 | 60.3 | — | 19.2 | 16.2 ^c | 9.3 | 10.3 | — | 5.7 | 6.3 |
| Pr ⁱ | 8.18 | 26—28 | 64.5 | 5.2 | 16.7 | 7.9 | 5.5 | 10.2 | 1.3 | 2.9 | 6.3 |
| Bu ^a | 13.19 | — | 49.1 | — | 16.4 | 22.7 ^d | 12.8 | 10.1 | — | 6.5 | 6.3 |
| Bu ^s ^e ... | 10.29 | −6° to +1° | 41.4 | 23.4 | 12.5 | 8.5 | 13.6 | 10.4 | — | 3.8 | 9.3 |
| Bu ⁱ | 15.72 | −4° to +3° | 56.9 ^f | 0.14 | 16.8 | 16.7 ^g | 14.1 | 8.7 | — | 4.6 | 6.2 |
| n-Pentyl | 17.75 | — | 1.9 ^h | 0.8 | 10.3 ⁱ | 72.9 | 9.7 | 11.2 | — | 6.5 | 7.4 |

^a In CH_2Cl_2 , 25 ml. ^b In silica flask, no part removed. ^c Pr^a 73%, Prⁱ 27%. ^d Bu^a 94%, Bu 6%. ^e In n-pentane, 15 ml. ^f Buⁱ 76%, Bu^s 24%. ^g Buⁱ 47, Bu^s 47, Bu^a (?) 6%. ^h Much more formed but did not distil. ⁱ Larger residue due to undist. RCl, therefore % of e.h. Cl, is lower.

* Cl as % in residue.

bulk of the elimination of chlorine and alkyl group occurs during the first stage of heating. During the elimination of alkyl group, some rearrangement, where possible, in that group occurs especially during the second and third stage of heating. Olefin and hydrogen chloride are formed mainly in the second stage, except in the example of $R = \text{Bu}^s$. Thus the formation of a carbonium ion is indicated. The nature of the intermediate residues, and the absence of evidence of the formation of chloro-esters containing only boron or

phosphorus, and not both, point to a gradual development of a network such as —B—O—P—O— .

Final heating at 1000° gives a hydrolytically stable residue approximating to boron phosphate, $[\text{BPO}_4]_n$.

Behaviour in this system is in marked contrast to that of related ester-halide systems such as alkoxyasilane-boron trichloride,¹ tri-n-butyl phosphite-boron trichloride,² and

¹ Gerrard and Strickson, *Chem. and Ind.*, 1958, 860.

² Gerrard and Lindsav. *Chem. and Ind.*. 1960. 152.

triphenyl phosphite-boron trihalide,³ in which mixtures of chloro-esters are produced, and the two non-metals do not appear together in any molecule. There is resemblance to the triaryl phosphate-boron trihalide system⁴ in so far that an insoluble complex is formed; but the thermal properties of the aryl complexes, $(\text{ArO})_3\text{P}^+\text{O}^-\text{BX}_3$ are very different. There is however strong resemblance to the trialkyl phosphate-silicon tetrachloride system,⁵ which gives silicon phosphate by a similar extrusion of alkyl and chlorine.

Experimental.—The trialkyl phosphate (1 mol.) was added to boron trichloride (1 mol.) at -70° . The 1:1 complex was allowed to warm to room temperature. Preliminary experiments showed that further heating caused the initial elimination of alkyl and chlorine and formation of a solid, further elimination becoming more difficult and requiring a higher temperature to maintain the rate. The technique adopted comprised heating the system stepwise to 120° , 180° , 300° and holding it at each of these temperatures for 1 hr. Volatile matter was collected at -80° and identified by usual analyses, vapour-phase chromatography, and infrared spectroscopy. Olefin was not quantitatively determined, but may be equated to the hydrogen chloride evolved. An aliquot part from each stage residue was removed for analysis, and for this reason, amounts of products produced to and during each stage are corrected to results for an undisturbed system. The residue was finally heated to about 1000° in an open crucible.

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³ Frazer, Gerrard, and Patel, *Chem. and Ind.*, 1959, 90, 728.

⁴ Frazer, Gerrard, and Patel, *J.*, 1960, 726.

⁵ Gerrard and Jeacocke, *Chem. and Ind.*, 1959, 704.