

1121. *Elimination-Addition. Part VII.*¹ *Nucleophilic Displacement in 2-Chloro-3-phenylsulphonylpropene.*

By C. J. M. STIRLING.

NUCLEOPHILIC displacement of halogen from halogeno-olefinic sulphones has been extensively studied by Modena and his collaborators² and, in certain instances, the reactions have been considered to involve elimination followed by addition. The chloride (III) appeared to be a particularly favourable case for the operation of an elimination-addition mechanism *via* the allene (IV). As the structures of the products obtained with a series of nucleophiles from this allene, as well as from the acetylenic isomers (I) and (VI), have already been established,^{1,3} the reactions of the same nucleophiles with the chloride (III) have now been examined in order to discover which of a number of possible alternative reaction paths is indicated by the products obtained.

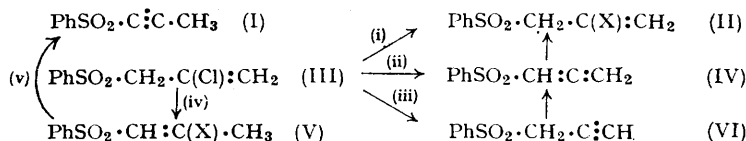
¹ Part VI, D. S. Campbell and C. J. M. Stirling, *J.*, preceding Paper.

² S. Gheretti, G. Modena, P. E. Todesco, and P. Vivarelli, *Gazzetta*, 1961, **91**, 620, and previous Papers.

³ C. J. M. Stirling, *J.*, 1964, 5856.

Five alternative reaction paths are indicated in the scheme: (i) direct substitution; (ii) elimination with formation of the allene and subsequent addition; (iii), elimination to give the acetylene (VI) and subsequent addition; (iv) isomerisation⁴ to the chloride (V; X = Cl) with subsequent displacement or addition-elimination;² (v) addition to the acetylene (I) formed by elimination from the isomeric chloride (V; X = Cl).

With methoxide, path (ii) is the major one; in reactions with a slight excess of the chloride, 65% of the allene is obtained, which with a slight excess of methoxide, gives the enol-ether (II; X = OMe).¹ Isolation of the allene does not exclude path (iii), as the terminal acetylene (VI) is rapidly isomerised³ by bases to the allene. Removal of the proton adjacent to the sulphonyl group and direct formation of the allene is, however, much more probable. Elimination is very rapid; the half-life of the chloride in 0.02N-methanolic sodium methoxide is less than 30 sec. at 20°. The slow subsequent addition step emphasises the low nucleophilicity: basicity ratio of this reagent.



With thiophenoxide and benzenesulphinate, the compounds (II; X = SPh and SO₂Ph, respectively) were obtained. The latter product reacts further to give 1,2,3-trisphenylsulphonylpropane.³ Formation of these products excludes paths (iv) and (v); addition of these reagents to the acetylene (I) gives the compounds (V; X = SPh and SO₂Ph, respectively). As sulphones (IV) and (VI) give the same products as the chloride, a distinction between paths (i), (ii), and (iii) cannot be made. None of the allene was detected in partial reactions, but this was expected as addition to the allene, in contrast with the methoxide reactions, is much faster than the overall reaction with the chloride. Thiophenoxide is a powerful nucleophile in displacement reactions and the direct path (i) is observed with related halides.²

The chloride reacts with dibenzylamine to give the enamine [V; X = N(CH₂Ph)₂]. No differentiation between alternative reaction paths can be made with this reagent as the sulphones (I), (IV), and (VI) all give this same adduct¹ faster than the amine reacts with the chloride. No intermediates could be found in the products of partial reactions.

Experimental.—2-Chloro-3-phenylsulphonylpropene. Thiophenol (25 g.), in 1.5N-ethanolic sodium ethoxide (150 ml.), was added with stirring to 2,3-dichloropropene (26 g.) in ethanol (50 ml.) at such a rate that the temperature of the mixture did not exceed 35°. The mixture was set aside at 25° for 105 min., diluted with water, and extracted with dichloromethane. Removal of the solvent and distillation of the residue gave 2-chloro-3-phenylthiopropene (36 g.), b. p. 122°/12 mm., *n*_D²² 1.5825 (Found: C, 58.8; H, 5.0. C₉H₉ClS requires C, 58.5; H, 4.9%). The sulphide (36 g.) was kept with 30% aqueous hydrogen peroxide (80 ml.) in acetic acid (165 ml.) for 1 hr. at 100°. Addition of water and extraction with chloroform gave the sulphone (32 g.), m. p. 45–50° raised to 57–58° (from benzene–light petroleum) (Found: C, 50.1; H, 4.3. C₉H₉ClO₂S requires C, 49.9; H, 4.2%).

Reactions with methoxide. 0.04N-Methanolic sodium methoxide (250 ml.) was added dropwise during 20 min. to the sulphone (2.16 g., 0.01 mole) in methanol (250 ml.). The neutral solution was evaporated to dryness under reduced pressure and water was added to the residue. Extraction with ether gave an oil (1.67 g.) whose infrared spectrum (7% solution in benzene) showed the presence of not more than 5% of recovered chloride. A portion (0.67 g.) of this product, in methanol (7 ml.), was treated with acetic acid (0.43 ml.) and sodium benzenesulphinate (1.82 g.). The mixture was set aside for 54 hr. at 20° and then filtered. The residue, after being washed with water, methanol, and benzene, was 1,2,3-trisphenylsulphonylpropane [1.17 g.; ≡ 0.455 g. (68%) of phenylsulphonylpropadiene], m. p. and mixed m. p. 240–242°. The filtrate and

⁴ Cf. A. T. Kader and C. J. M. Stirling, *J.*, 1962, 3686.

washings were extracted with dichloromethane and the extracts gave a residue (100 mg.) which, on treatment with isopropyl ether, gave 2-methoxy-3-phenylsulphonylpropene, m. p. and mixed m. p. 63°. This compound was recovered (72%) after 7 days when treated with sodium benzenesulphinate (3 mol.) and no trisulphone was obtained.

The allene content ($63 \pm 3\%$) of the remainder of the product was determined by infrared spectroscopy (of benzene solutions), by using the doublet at 1980 and 1940 cm^{-1} , and the allene was isolated (m. p. and mixed m. p. 43—44°) by chromatography on alumina. When the product mixture was subsequently treated with 0.04N-methanolic sodium methoxide, its infrared spectrum rapidly changed to that of 2-methoxy-3-phenylsulphonylpropene.

Reactions with thiophenoxide. The chloride (750 mg.) in methanol (51 ml.) was added to thiophenol (0.34 ml., 0.95 mol.) in 0.22N-methanolic sodium methoxide (15 ml.). The mixture was evaporated after 16 hr. and water was added to the residue. Extraction with ether gave 3-phenylsulphonyl-2-phenylthiopropene (940 mg., 94%), m. p. and mixed m. p. 55—56.5°. The reaction was repeated with a three-fold excess of the chloride. The infrared spectrum of the crude product showed no allenic or acetylenic absorptions.

Reactions with benzenesulphinate. The chloride (500 mg.) and sodium benzenesulphinate (0.82 mol.), in methanol (10 ml.) were refluxed for 5 hr. The mixture was filtered and the residue, after being washed with benzene, methanol, and water, gave 1,2,3-triphenylsulphonylpropane (45 mg., 10%), m. p. and mixed m. p. 240—242°. Extraction of the filtrate and washings with dichloromethane gave a residue, which, on treatment with isopropyl ether, gave crude 2,3-diphenylsulphonylpropene (395 mg., 65%), m. p. 120—122°, raised to 127—128° (270 mg.) alone or mixed with an authentic specimen. Evaporation of the isopropyl ether washings gave a residue whose infrared spectrum showed no allenic absorption and which, on crystallisation from light petroleum (b. p. 60—80°), gave recovered chloride (105 mg., 21%), m. p. 47—52° raised to 55—57° (and mixed m. p.).

When the reaction was repeated with sodium benzenesulphinate (3.5 mol.), and refluxing was continued for 16 hr., the trisulphone (86%) was obtained.

Reactions with dibenzylamine. The chlorosulphone (500 mg.) and dibenzylamine (0.98 ml., 2.2 mol.) in methanol (5 ml.) were set aside in the dark for 7 days at 20°. Evaporation of the mixture and extraction of the residue with 2:1 benzene-ether left dibenzylamine hydrochloride (420 mg., 79%), m. p. and mixed m. p. 273—275°. Evaporation of the extracts gave crude *trans*-2-dibenzylamino-1-phenylsulphonylpropene (685 mg., 78%), m. p. 92—104°, raised to 103—104° (600 mg., 68%) alone or mixed with an authentic specimen.

When the reaction was repeated with dibenzylamine (0.8 mol.), infrared-spectroscopic examination of the crude product revealed no allenic or acetylenic intermediates.

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1122. *The Polysaccharides of Enteromorpha Species.*

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THE polysaccharides in many marine algae have already been studied, especially those from the *Rhodophyceae* and *Phaeophaeceae*, but the only detailed results for polysaccharides of marine *Chlorophyceae* are on extracts from *Enteromorpha compressa*¹ and *Ulva lactuca*.²

The weeds in the present investigations were of *Enteromorpha torta* containing various amounts of *E. compressa* and *E. intestinales*. Because of the physical nature of the algae, it was not possible to collect one species only, or to separate the different species. All the samples contained two neutral glucosans and a sulphated polysaccharide. One of the glucosans (glucosan A), which is present in very small quantity, behaves similarly to insoluble laminarin in that it is soluble in water at 70° and slowly comes out of solution on cooling. The other (glucosan B) is extracted from the weed by hot aqueous solutions and remains in solution on cooling, together with the sulphated polysaccharide.

¹ J. P. McKinnell and E. Percival, *J.*, 1962, 3141; J. Love, W. Mackie, J. W. McKinnell, and E. Percival, *J.*, 1963, 4177.

² J. W. E. Brading, M. M. T. Georg-Plant, and D. M. Hardy, *J.*, 1954, 319.

From the dried milled weed a water-soluble polysaccharide mixture was obtained, the major component of which was the sulphated polysaccharide. Most complete extraction was obtained with hot dilute mineral acid. The neutral sugars obtained on hydrolysis were D-glucose, D-xylose, L-rhamnose, and 3-O-methyl-L-rhamnose. The presence of uronic acid was shown by a naphthoresorcinol test³ on the acidic portion of a hydrolysate.

The action of alkali on the polysaccharide led to progressive breakdown as the sulphate groups were removed, and in no case could a sulphate-free product be obtained.

A portion of the polysaccharide was methylated with dimethyl sulphate and sodium hydroxide in a nitrogen atmosphere to a final methoxyl content of 25.4%. The product was fractionated by solvent extraction. Part of it (fraction 1) was soluble in chloroform, and the residue was further subdivided into a methanol-soluble portion (fraction 2) and a methanol-insoluble portion (fraction 3). Hydrolysis and paper-chromatographic investigation, and demethylation experiments⁴ indicated that fraction 1 was a partially methylated glucosan. Chromatographic mobilities showed the presence of di-O-methylglucose as the main component, together with tri- and tetra-O-methylglucose. A methylated glucosan had previously been extracted from a methylated seaweed polysaccharide mixture.²

Paper-chromatographic investigation of hydrolysates of fractions 2 and 3 revealed the same constituents in each case. From the hydrolysate of fraction 2 were separated 2,3,4-tri-O-methyl-L-rhamnose, 2,3- and 2,4-di-O-methyl-L-rhamnose, 2,3-di-O-methyl-D-xylose, 2-O-methyl-L-rhamnose, 3-O-methyl-D-xylose, and L-rhamnose. The isolation of both rhamnose and tri-O-methylrhamnose from the methylated polysaccharide points to a highly branched structure for this component.

It was not found possible to isolate a uronic acid or an aldobiuronic acid by hydrolysis of the unmethylated polysaccharide because of the extreme conditions required for hydrolysis. Reduction with lithium aluminium hydride of an acidic residue obtained from a vigorous hydrolysis gave a product containing predominantly glucose units, indicating that the uronic acid was glucuronic acid.

The indications from the methylation studies that the soluble polysaccharide mixture as extracted contained about 20–25% of a neutral glucosan led to further experiments on the separation of the two components. At low temperatures the sulphated polysaccharide was extracted more rapidly from the weed than was the glucosan (glucosan B), so that by successive extractions at 25°, 50°, and 70° a considerable degree of separation was achieved. The ratio of glucosan to sulphated polysaccharide varied from 1:8 in the 25° extract to 8:3 in the 70° extract.

Experimental.—Paper chromatography was done on Whatman No. 1 paper by the descending-front technique with the solvent system butan-1-ol-ethanol-water (4:1:5). The chromatograms were developed by spraying with benzidine trichloroacetate or aniline hydrogen phthalate.

Paper ionophoresis was done on Whatman No. 1 paper under potential gradients of 25–40 v/cm., with borate buffer (pH 10) or phosphate buffer (pH 10). The glucosan was located with iodine, and the sulphated polysaccharide with Toluidine Blue (0.25% in water). Optical rotations are for aqueous solutions unless otherwise stated.

The weed samples were collected at North Berwick in September 1954, April 1955, and August 1955. On collection, the weed was immediately washed in several changes of sea water to remove as much as possible of the adhering sand, dried at 60° for 48 hr., and milled to pass a 48-mesh sieve.

Extraction of the polysaccharides. The weed was first extracted with cold methanol to remove the bulk of the colouring matter, terpenes, etc. In a typical procedure the dried weed was then extracted in portions (500 g.) with 0.1N-hydrochloric acid for 1 hr. at 70°. The extract was filtered through muslin, cooled to 20°, set aside for 2 days, clarified, and the insoluble material worked up for glucosan A. The clarified solution was worked up for the soluble polysaccharide mixture.

Purification of the polysaccharide mixture. A sample of the mixture was purified for analysis

³ B. Tollens, *Z. physiol. Chem.*, 1909, **61**, 95.

⁴ L. Hough, J. K. N. Jones, and W. H. Wadman, *J.*, 1950, 1702.

by dialysis against distilled water and treatment with charcoal. The product was a white powder which was slightly reducing to Fehling's solution, and gave a violet coloration with iodine solution, $[\alpha]_{\text{D}}^{20} - 47.5^{\circ}$ (c 1.0) [Found: S, 5.0; N, 1.2; ash (direct), 22.7, (as sulphate), 23.6; SO_4^{2-} , 16.4; uronic anhydride (by decarboxylation), 16.4%]. The reducing power (by reaction with hypiodite) was equivalent to one reducing group in 3922 g.; the equivalent weight (by titration of the free acid form) was 382.

Hydrolysis of the polysaccharide and separation of the hydrolysate. The polysaccharide (1 g.) was hydrolysed with *N*-sulphuric acid for 6 hr. at 100° , and the solution worked up in the usual manner, to give a syrup (0.61 g.) whose components were separated on a cellulose column.

Fraction P1. The syrup (0.024 g.) crystallised on standing, R_{G} 0.55, $[\alpha]_{\text{D}}^{20} + 24^{\circ}$ (c 2.5) (Found: OMe, 10.0%). A recrystallised portion had $[\alpha]_{\text{D}}^{20} + 28^{\circ}$ (c 4.4), *m. p.* 113—114°. A sample obtained from a further hydrolysis had chromatographic and electrophoretic (borate buffer) mobilities corresponding to 3-*O*-methyl-L-rhamnose, but different from 2-*O*-methyl-L-rhamnose, and was methylated to give 2,3,4-tri-*O*-methyl-L-rhamnose. Fraction P1 is therefore 3-*O*-methyl-L-rhamnose.

Fraction P2. The syrup (0.33 g.) crystallised. Recrystallisation from water gave a product with R_{G} 0.30, moving identically with L-rhamnose, $[\alpha]_{\text{D}}^{20} + 9.25^{\circ}$ (c 5.6), *m. p.* and mixed *m. p.* (with L-rhamnose hydrate) 90—94°. The diphenylhydrazone had *m. p.* 131°, mixed *m. p.* (with L-rhamnose di-*N*-phenylhydrazone, *m. p.* 136°) 133°. The *p*-nitrophenylhydrazone had *m. p.* and mixed *m. p.* [with L-rhamnose *N*-(*p*-nitrophenyl)hydrazone] 185° (Found: C, 48.1; H, 5.5; N, 14.0. Calc. for $\text{C}_{12}\text{H}_{17}\text{NO}_6$: C, 48.1; H, 5.7; N, 14.0%).

Fraction P3. The syrup (0.05 g.) crystallised, R_{G} 0.15, moving identically with xylose, $[\alpha]_{\text{D}}^{20} + 18^{\circ}$ (c 1.5), *m. p.* and mixed *m. p.* (with D-xylose) 143°. The di-*O*-benzylidene dimethyl acetal had *m. p.* and mixed *m. p.* (with di-*O*-benzylidene-D-xylose dimethyl acetal) 211° (Found: C, 67.35; H, 6.65. Calc. for $\text{C}_{21}\text{H}_{24}\text{O}_6$: C, 67.7; H, 6.5%).

Fraction P4. The syrup (0.067 g.) crystallised, R_{G} 0.09, moving identically with glucose, $[\alpha]_{\text{D}}^{20} + 50.5^{\circ}$ (c 3.35), *m. p.* and mixed *m. p.* (with D-glucose hydrate) 90°. The *p*-nitrophenylhydrazone had *m. p.* and mixed *m. p.* [with D-glucose *N*-(*p*-nitrophenyl)hydrazone] 183° (Found: C, 45.85; H, 5.1; N, 13.1. Calc. for $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_7$: C, 45.7; H, 5.4; N, 13.3%).

Identification of the uronic acid. The polysaccharide was given successive hydrolyses with increasing strengths of acid up to 3*N*-sulphuric acid. The acidic portion of the hydrolysate was converted into the glycosides and reduced with lithium aluminium hydride. Hydrolysis of the product, and chromatography, showed the presence of glucose with a trace of rhamnose, indicating that the polysaccharide contained glucuronic acid.

Methylation of the polysaccharide. The polysaccharide (50 g.) was given seven methylations with dimethyl sulphate and sodium hydroxide in a nitrogen atmosphere. The product (45 g.) was a brown gummy solid (Found: OMe, 25.4; SO_4^{2-} , 9.0; ash, 19.0%).

Fractionation of the methylated polysaccharide. The material (17.1 g.) was extracted with chloroform, to give a white solid, fraction 1 (5.4 g.), $[\alpha]_{\text{D}}^{25} + 160^{\circ}$ (in CHCl_3) (Found: OMe, 40.5%; ash, nil; SO_4^{2-} , nil). The chloroform-insoluble portion was extracted with boiling methanol, to give a brown solid, fraction 2 (6.9 g.), $[\alpha]_{\text{D}}^{25} - 80^{\circ}$ (in methanol) (Found: OMe, 21.2; SO_4^{2-} , 20.1; ash, 22.5%), and a methanol-insoluble residue, fraction 3 (4.8 g.).

Hydrolysis of methylated fraction 2, and separation of the hydrolysate. The material (4.35 g.) was hydrolysed and the hydrolysate separated into an acidic portion (0.71 g.) and a neutral portion (1.7 g.). The neutral portion was separated on a cellulose column and 9 fractions were characterised.

Fraction M1. The syrup (0.3000 g.) had $[\alpha]_{\text{D}}^{25} + 27.7^{\circ}$ (c 2.96) (Found: OMe, 44.5%). Chromatography showed two components, R_{G} 1.01 (strong) and 0.95 (faint). The major component was characterised as 2,3,4-tri-*O*-methyl-L-rhamnose by the preparation of the anilide, *m. p.* and mixed *m. p.* (with 2,3,4-tri-*O*-methyl-*N*-phenyl-L-rhamnopyranosylamine) 123°.

Fraction M2. The syrup had $[\alpha]_{\text{D}}^{20} + 10.0^{\circ}$ (c 4.2) (Found: OMe, 31.8%), and on chromatography and electrophoresis moved identically with 2,4-di-*O*-methyl-L-rhamnose. The anilide had *m. p.* 141—142°.

Fraction M3. The syrup had $[\alpha]_{\text{D}}^{20} + 20^{\circ}$ (c 2.5), and on chromatography and electrophoresis moved identically with 3,4-di-*O*-methyl-L-rhamnose.

Fraction M4. The syrup had R_{G} 0.80, $[\alpha]_{\text{D}}^{25} + 45.3^{\circ}$ (c 2.87) (Found: OMe, 32.0%). The anilide had *m. p.* and mixed *m. p.* (with 2,3-di-*O*-methyl-*N*-phenyl-L-rhamnopyranosylamine) 138°.

Fraction M5. The syrup (0.0478 g.) had R_G 0.75, $[\alpha]_D^{25} + 27.2^\circ$ (c 4.7) (Found: OMe, 34.6%), and on chromatography and electrophoresis moved identically with 2,3-di-*O*-methyl-D-xylose. The anilide had m. p. 125°, mixed m. p. (with 2,3-di-*O*-methyl-*N*-phenyl-D-pyranosylamine) 126°.

Fraction M6. The syrup (0.4100 g.) had R_G 0.62, $[\alpha]_D^{25} + 16.9^\circ$ (c 3.8) (Found: OMe, 17.4%), and on chromatography and electrophoresis moved identically with 2-*O*-methyl-L-rhamnose. The anilide had m. p. and mixed m. p. (with 2-*O*-methyl-*N*-phenyl-L-rhamnopyranosylamine) 150°.

Fraction M7. The syrup (0.0342 g.) had R_G 0.45, $[\alpha]_D^{25} + 30.6^\circ$ (Found: OMe, 18.4%). The osazone had m. p. 168—169°, mixed m. p. (with 3-*O*-methyl-*N*-phenyl-D-xylosazone, m. p. 172°) 170—172°.

Fractions M8 and M9. The syrups (0.1952 g. and 0.0158 g.) crystallised and were characterised as L-rhamnose and D-xylose, respectively, by the same means as for the hydrolysate of the unmethylated polysaccharide.

Fractional extraction of the weed. In a typical procedure the weed (100 g.) was extracted three times at 23°, three times at 50°, and once at 70°, with 0.1*N*-hydrochloric acid. The 70° extract deposited glucosan A (0.1 g.) on cooling. The other polysaccharides were isolated in the usual manner and analysed for constituent monosaccharides:

Temp. of extraction	No. of extractions	Yield (%)	Ash (direct) (%)	Ratio in hydrolysate glucose:xylose:rhamnose
23°	3	19.3	16.9	1:3:5
50	2	2.6	10.0	3:1:3
50	1	0.9	8.4	5:1:1
70 (glucosan A)	1	0.1	—	5:trace:trace
70 (cold-soluble material)	1	2.1	3.2	8:1:2

After treatment with Cetavlon⁵ the final fraction had a glucose:xylose:rhamnose ratio of 10:1:2.

Electrophoresis of glucosan B. Paper electrophoresis in a borate buffer left the glucosan at the base-line whilst the sulphated polysaccharide impurity migrated as a streak running from the base line. When phosphate buffer was used, the sulphated polysaccharide migrated as a discrete spot to give a much cleaner separation. A preparative separation by paper electrophoresis gave a product in which the only sugar detectable on chromatographic examination of a hydrolysate was glucose.

Glucosan A had a low negative rotation, contained no sulphur, and left no ash on ignition. With iodine it gave a blue-grey colour which disappeared on heating and reappeared on cooling. Hydrolysis gave glucose as the only sugar detectable on a chromatogram.

Glucosan B had a very low positive rotation and gave a blue-grey colour with iodine, which disappeared on heating and reappeared on cooling.

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⁵ B. C. Bera, A. B. Foster, and M. Stacey, *J.*, 1955, 3788.

1123. *Reduction of Hindered Nitriles to Aldehydes.*

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WE reported¹ that Raney nickel and sodium hypophosphite in aqueous acetic acid-pyridine reduced nitriles to aldehydes; good yields were obtained (the method has since been tested by

¹ O. G. Backeberg and B. Staskun, *J.*, 1962, 3961: Errata were published in *J.* 1962. In addition, in line 2 of Experimental, for 29 c.c. read 20 c.c., and in Table, column 1, entry 12, for 2-Cyanopyridine read 3-Cyanopyridine.

Guth *et al.*²) except with hindered nitriles such as *o*-toluonitrile and α -naphthonitrile. Similar results were reported for these compounds by Stephen³ and were ascribed to steric³ and solubility factors.⁴ Nevertheless, high conversions into the aldehydes have been achieved by using reagents such as lithium triethoxyaluminium hydride⁵ and also by hydrogenation of the nitriles over Raney nickel in the presence of hydrazine.⁶

We have found that, by stirring the hindered nitriles in formic acid solution with moist Raney nickel at 75–80°, the aldehydes are formed in 60–75% yield and this method accordingly supplements that previously reported.¹ The formic acid serves as a source of hydrogen⁷ and the Raney nickel catalyses both the decomposition of the acid and the reduction of the nitrile, and is gradually deactivated. Variations in time and temperature, volume of formic acid, and in the proportion and activity of the catalyst influence the yield, but were not studied in detail.

The following yields were obtained by reducing 1 g. of the nitrile in 15 c.c. of formic acid with moist Raney nickel (prepared from 1.5 g. of alloy) at 75–80° for 30 minutes.

Nitrile	Yield ^a (%)	Nitrile	Yield ^a
Ph	72	α -C ₁₀ H ₇	21 ^f , 39–53, 60–75 ^b
<i>o</i> -Me·C ₆ H ₄	65–75	β -C ₁₀ H ₇	55
<i>o</i> -Cl·C ₆ H ₄	70–83 ^b	PhCH:CH	64 ^g
<i>p</i> -Cl·C ₆ H ₄	82 ^c	<i>m</i> -NO ₂ ·C ₆ H ₄	trace ^h
<i>o</i> -MeO·C ₆ H ₄	80	5-HO-2,4-Me ₂ ·C ₆ H ₂ ^f	77 ⁱ
<i>p</i> -MeO·C ₆ H ₄	75–85	3-Cyanopyridine ^k	50
2,6-(MeO) ₂ ·C ₆ H ₃	45–55 ^d , 60–65 ^e	<i>n</i> -C ₃ H ₇	35–40 ^l
<i>p</i> -H ₂ NSO ₂ ·C ₆ H ₄	50	<i>n</i> -C ₅ H ₁₁	40–50

^a Determined as the 2,4-dinitrophenylhydrazone; *m. p.s.* agree with reported values. ^b 30 c.c. formic acid. ^c 20 c.c. formic acid. ^d *M. p.* 252°. ^e For 1 hr. ^f 3 g. Raney nickel alloy. ^g The double bond is not reduced. ^h Most of the nitrile was recovered unchanged. ⁱ We thank Prof. F. Wessely for a sample of this nitrile. ^j *M. p.* 305° (decomp.) (Found: N, 16.3. C₁₅H₁₄N₄O₅ requires N, 17.0%), *semicarbazone*, *m. p.* 238–239° (Found: N, 20.4. C₁₀H₁₃N₃O₂ requires N, 20.3%). ^k This nitrile was incorrectly described as the 2-isomer in ref. 1. ^l At 70°.

Experimental.—The general procedure is illustrated by the preparation of *o*-formyltoluene: Raney nickel alloy (50–50; 7.5 g.; a suitable weight was 1.5 g./1 g. nitrile; use of 0.5 g. or 3 g. alloy per 1 g. nitrile gave lower yields) was stirred (magnetically) with 2*N*-NaOH (150 c.c.) for 30–40 min., the temperature being allowed to rise, after which the alkaline solution was decanted and the nickel washed twice with water. A solution of *o*-toluonitrile (5 g.) in formic acid (98–100%; 75 c.c.; addition of 5 c.c. water did not significantly affect the yield; however, water was not added in the general procedure but if the water was removed from the moist catalyst by washing with formic acid, the yield of aldehyde was lower) was added to the moist catalyst and the mixture stirred at 75–80° for 30 min.; the yield of aldehyde was less at 40–50°. The mixture was diluted with alcohol–water (2:1, v/v; ca. 70 c.c.) and filtered, the nickel being washed with a little warm alcohol. For quantitative determination, an aliquot portion of the filtrate was treated with 2,4-dinitrophenylhydrazine⁸ (yield 73%); in the absence of catalyst no aldehyde was formed. The remainder of the filtrate was diluted with water, extracted with ether, the extracts washed with dilute sodium hydrogen carbonate solution, and evaporated to furnish the crude aldehyde (3.6 g., 70%). If required, this product was purified by conversion into the semicarbazone (5.2 g., 68%) which, on hydrolysis with dilute sulphuric acid, furnished the aldehyde (2.8 g., 56%).

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² V. Guth, J. Leitich, W. Specht, and F. Wessely, *Monatsh.*, 1963, **94**, 1262.

³ H. Stephen, *J.*, 1925, 1874.

⁴ L. Turner, *J.*, 1956, 1686.

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⁷ K. Tamaru, *Trans. Faraday Soc.*, 1959, **55**, 824.

⁸ A. I. Vogel, "Practical Organic Chemistry," Longmans, Green & Co., London, 1959, 3rd edn., p. 1061.

1124. The Reaction of Ethoxy-radicals with Ethylene.

By J. C. J. THYNNE.

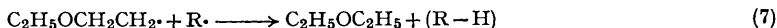
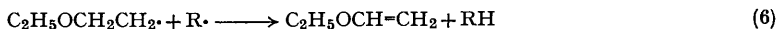
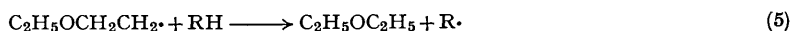
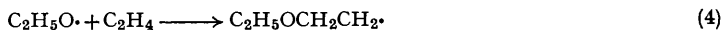
THE reaction of methyl radicals with various olefins in the gas^{1,2} and liquid^{3,4} phases has received much attention, and reaction by addition has been established as an important feature of such reactions. For alkoxy-radicals the situation is much less well documented. Kharasch, Arimoto, and Nudenburg⁵ have established that, in the liquid phase, t-butoxy-radicals react by addition to conjugated dienes, such as butadiene, and the resulting radical is sufficiently stable to dimerise, yielding a diether. There has been no report of an addition reaction between alkoxy-radicals and olefins in the gas phase. If such a reaction occurred, an alkoxyalkyl radical would be produced; little information regarding such radicals has been published,⁶ and it would be of interest to observe the extent to which typical alkyl-radical reactions such as disproportionation, combination, and abstraction are modified by the presence of an alkoxy-substituent in the radical. Accordingly, the gas-phase reaction of ethoxy-radicals with ethylene has been studied.

Experimental.—Apparatus. Reactions were performed in a cylindrical quartz cell housed in a heavy aluminium block furnace. Experimental details and technique were similar to those described previously.^{7,8} Mixtures of diethyl peroxide and ethylene in approximately 1:1 amounts were made up in a 1-litre bulb before reaction. Total pressures of between 100 and 200 mm. reaction mixture were normally used. Two methods for the production of ethoxy-radicals were used: (i) thermal decomposition of diethyl peroxide at 160°; (ii) photochemical decomposition of diethyl peroxide at 70°.

After reaction, the products were separated by low-temperature distillation and analysed by means of gas chromatography and mass spectrometry. Major products observed were diethyl ether, ethyl vinyl ether, ethanol, and acetaldehyde, the first two being produced in larger yield than the second two. Minor products included ethane, propane, and a product tentatively identified as ethyl methyl ether. In the experiments performed at 160° the extent of formation of these minor products was considerably greater than when the reactions were carried out at 70°.

Materials. Diethyl peroxide was prepared by the addition of diethyl sulphate to 30% hydrogen peroxide as described by Rebbert and Laidler.⁹ The peroxide was twice redistilled and then stored in the vacuum line in a bulb normally kept at -78°. Mass-spectrometric and gas-chromatographic analysis of the peroxide showed no ether impurity. Ethylene was obtained from the National Chemical Laboratory and had a stated purity of 99.92%.

Results and Discussion.—The following mechanism is suggested to account for the reaction products observed:



¹ Landers and Volman, *J. Amer. Chem. Soc.*, 1957, **79**, 2996.

² Brinton, *J. Chem. Phys.*, 1958, **29**, 781.

³ Levy and Szwarc, *J. Amer. Chem. Soc.*, 1954, **76**, 5981.

⁴ Buckley and Szwarc, *Proc. Roy. Soc.*, 1957, *A*, **240**, 396.

⁵ Kharasch, Arimoto, and Nudenburg, *J. Org. Chem.*, 1951, **16**, 1556.

⁶ Srinivasan, *J. Amer. Chem. Soc.*, 1962, **84**, 2475.

⁷ Thynne, *Trans. Faraday Soc.*, 1962, **58**, 676.

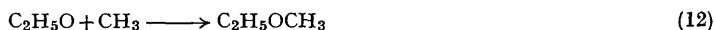
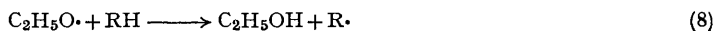
⁸ Thynne and Gray, *Trans. Faraday Soc.*, 1963, **59**, 1149.

⁹ Rebbert and Laidler, *J. Chem. Phys.*, 1950, **20**, 574.

[1964]

Notes.

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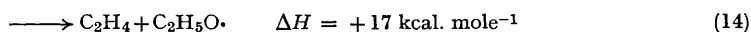
[In this mechanism R· can be C₂H₅O·, C₂H₅OCH₂CH₂·, or CH₃·.]

The presence of diethyl ether and ethyl vinyl ether in such large quantities among the reaction products can only reasonably be explained by the extensive addition of an ethoxy-radical to ethylene yielding an ethoxyethyl radical which is sufficiently stable¹⁰ to react by abstraction [reaction (5)], auto-disproportionation, and cross-disproportionation [reactions (6) and (7)]. The observation that diethyl ether and ethyl vinyl ether are produced in larger quantities than are acetaldehyde and ethanol suggests that, in the presence of high concentrations of ethylene, ethoxy-radicals react very readily by addition. The work reported here does not permit a quantitative evaluation of rate constants so that a direct comparison may not be made with, say, methyl radical attack on olefins. However, the greater reactivity of alkoxy-radicals, compared with that of methyl radicals, regarding hydrogen atom abstraction has been noted by several workers^{8, 11-13} and it appears that addition to olefins is similarly easy.

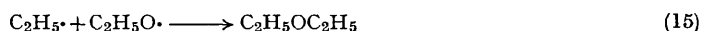
The presence of minor products such as ethane, propane, and possibly ethyl methyl ether is explained by the decomposition of the ethoxy-radical by carbon-carbon bond fission, producing a methyl radical, the minor products being formed by the subsequent reactions of the methyl radical. The fact that, even at 70°, some such products are formed suggests the formation of "hot" ethoxy-radicals during the photolysis of diethyl peroxide. Similar conclusions have been drawn by McMillan¹⁴ from studies of the photolysis of other peroxides.

Thermochemistry of the ethoxyethyl radical, C₂H₅OCH₂CH₂·. Addition of an ethoxy-radical to ethylene is exothermic. Using the method of group-energy terms¹⁵ a value of -13 kcal. mole⁻¹ may be calculated for the heat of formation of the radical C₂H₅OCH₂CH₂·, so that Δ*H* for reaction (2) is -17 kcal. mole⁻¹. This may be compared with the Δ*H* value of -22 kcal. mole⁻¹ for the addition of a methyl radical to ethylene [reaction (9)].

The chemistry of such alkoxyalkyl radicals is potentially very interesting, not only because of the influence of substituting groups on radical reactivity but also because such radicals have two possible modes of decomposition:



Some of the diethyl ether formed in this work may have been produced by decomposition of the ethoxyethyl radical by reaction (13), yielding an ethyl radical, and subsequent combination of an ethoxy- and an ethyl-radical to produce the ether [reaction (15)].



The fact that smaller amounts of acetaldehyde than of diethyl ether are formed, indicates that it is not likely to have been a major source in this work.

The following thermochemical data have been used in this work. Heats of formation (kcal. mole⁻¹): CH₃·, 31.5; C₂H₅·, 24.5; C₃H₇·, 22; C₂H₅O·, -8.5; C₂H₄, 12.5; CH₃CHO,

¹⁰ Long and Skirrow, *Trans. Faraday Soc.*, 1962, **58**, 1403.

¹¹ Thynne and Gray, *Proc. Chem. Soc.*, 1962, 295.

¹² Shaw and Trotman-Dickenson, *J.*, 1960, 3210.

¹³ Berces and Trotman-Dickenson, *J.*, 1961, 348.

¹⁴ McMillan, *J. Amer. Chem. Soc.*, 1961, **83**, 3018.

¹⁵ Franklin, *J. Chem. Phys.*, 1953, **21**, 2029.

–39.8. The following numerical values of the group-energy terms for the contribution of various groups to the heat of formation have been used: CH_3^- , –10.1; $-\text{CH}_2^-$, –5.0; $-\text{O}^-$, –27.2; $-\text{CH}_2^+$, 34.0.

My thanks are due to Professor Peter Gray for many interesting discussions.

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1125. Site of Basicity in Cinnoline.

By MARVIN CHARTON.

It has recently been suggested¹ that the basic centre of cinnoline is at N-2. The evidence on which this suggestion is based is that alkylation of 3- or 4-hydroxycinnoline occurs at N-2. We have correlated $\text{p}K_a$ values for 4-substituted cinnolines extant in the literature with the Hammett equation,

$$Q_X = \rho\sigma_X + Q_H$$

using the σ_I , σ_m , and σ_p constants. The correlations were made as described by Jaffé.² The σ_m and σ_p constants used are from McDaniel and Brown,³ the σ_I constants are from our recent compilation.⁴ The data used are given in Table 1, the results of the correlations in Table 2.

TABLE 1.
Data used in correlations.

1. Ionization constants of 4-substituted cinnolines in water at 20°.*

X	H	MeO	MeS	NH ₂
$\text{p}K_a$	2.42	3.21	3.13	6.84

2. Ionization constants of 4-substituted cinnolines in 50% ethanol–water at 21–22°.†

X	Cl	H	MeO	NH ₂
$\text{p}K_a$	2.08	2.51	2.71	6.26‡

* From ref. 6. † A. Albert, *J.*, 1949, 1356. The value for X = PhO has not been included in this series, as we believe the σ_p constant given by ref. 3 for this substituent (–0.320) to be in error. From the value given by ref. 3 for σ_m , PhO and the value reported by ref. 4 for σ_I , PhO, using the equation $\sigma_p = 3\sigma_m - 2\sigma_I$ (R. W. Taft, jun. and I. C. Lewis, *J. Amer. Chem. Soc.*, 1958, 80, 2436) a value of –0.02 for σ_p , PhO can be calculated. Using our method for estimation (M. Charton, *J. Org. Chem.*, 1963, 28, 3121) a value of –0.14 is obtained. Ref. 2 gives a value of –0.028. ‡ At 25°.

TABLE 2.
Results of correlations.

Series		ρ	r	s	t	Q_H
1	I	–1.58	0.097	2.42	0.138	4.14
	m	–11.4	0.797	1.47	1.865	4.20
	p	–6.01	0.941	0.823	3.948	2.51
2	I	–3.98	0.421	2.14	0.657	4.21
	m	–6.79	0.789	1.45	1.817	3.95
	p	–4.61	0.910	0.982	3.096	2.58

r , s , and t are the correlation coefficient, standard deviation, and "Student t " test, respectively.

These results show clearly that the σ_p constants give decidedly the best correlation. Although both series studied are limited to four the members, substituents involved differ widely in properties and are sufficient for differentiating σ_m and σ_p substituent effects. These

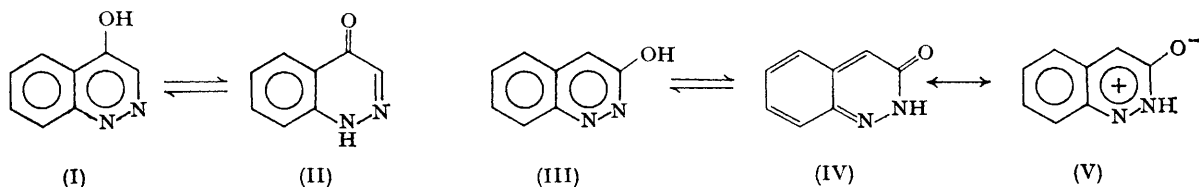
¹ D. E. Ames and H. Z. Kucharska, *J.*, 1964, 282.

² H. H. Jaffé, *Chem. Rev.*, 1953, 53, 191.

³ D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, 23, 420.

⁴ M. Charton, *J. Org. Chem.*, 1964, 29, 1222.

results are explicable only if N-1 is the site of protonation, at least for those cases in which the substituent is a donor by the resonance effect. This result is in accord with the calculations of Longuet-Higgins and Coulson⁵ on cinnoline. The pK_a values of 4-hydroxycinnoline for proton lost and gained (9.27 and -0.35 respectively)⁶ seem to indicate that 4-hydroxycinnoline (I) exists primarily as its keto-tautomer, (II).⁷ Thus its behaviour in alkylation reactions would not constitute evidence for the location of the basic centre in cinnolines. An almost analogous situation exists for 3-hydroxycinnoline (III) in its keto-tautomer form, (V) (pK_a values for proton lost and gained are 8.61 and 0.21 respectively).⁸



It is of interest to compare the ρ values for the 4-substituted cinnolines with those for 4-substituted quinolines. The ρ values are given in Table 3. The values for quinolines and cinnolines differ by about 10% in water and 25% in ethanol-water. This closeness suggests that molecular geometry has its greatest effect in determining the magnitude of ρ in these series, and thus the effect of the second nitrogen atom in cinnolines on ρ is comparatively small.

TABLE 3.

ρ Values for 4-substituted quinolines and cinnolines.

	$\rho(\text{H}_2\text{O})$ (20°)	Ref.	$\rho(50\% \text{ EtOH-H}_2\text{O})$ (21-22°)	Ref.
4-Substituted quinolines	-5.72	*, †	-6.15	*
4-Substituted cinnolines	-6.01	This work	-4.61	This work

* M. Charton, *J. Amer. Chem. Soc.*, 1964, **86**, 2033. † At 25°.

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⁵ H. C. Longuet-Higgins and C. A. Coulson, *J.*, 1959, 971.

⁶ A. Albert, "Physical Methods in Heterocyclic Chemistry," vol. I, ed. A. R. Katritzky, Academic Press, New York 1963, pp. 76, 83.

⁷ A. R. Osborn and K. Schofield, *J.*, 1956, 4207.

⁸ E. J. Alford and K. Schofield, *J.*, 1953, 1811.

1126. Soya Bean Saponins. Part V.¹ Soyasapogenol E.

By D. WILLNER, B. GESTETNER, D. LAVIE, Y. BIRK, and A. BONDI.

ACID hydrolysis of the saponin fraction obtained from the soya bean yields a mixture of triterpenoid alcohols, out of which four soyasapogenols, A, B, C, and D, have been identified.² Structures for these compounds had been suggested by Meyer *et al.*³ and were subsequently revised.⁴ The possibility, however, for other unidentified aglycones to occur in this fraction was not excluded.^{2,3} We report now the isolation of a fifth substance called soyasapogenol E, the structure of which has been identified as (Ia).

¹ Part IV, Ishaaya and Birk, *J. Food Sci.*, in the press.

² Ochiai, Tsuda, and Kitagawa, *Ber.*, 1937, **70**, 2083.

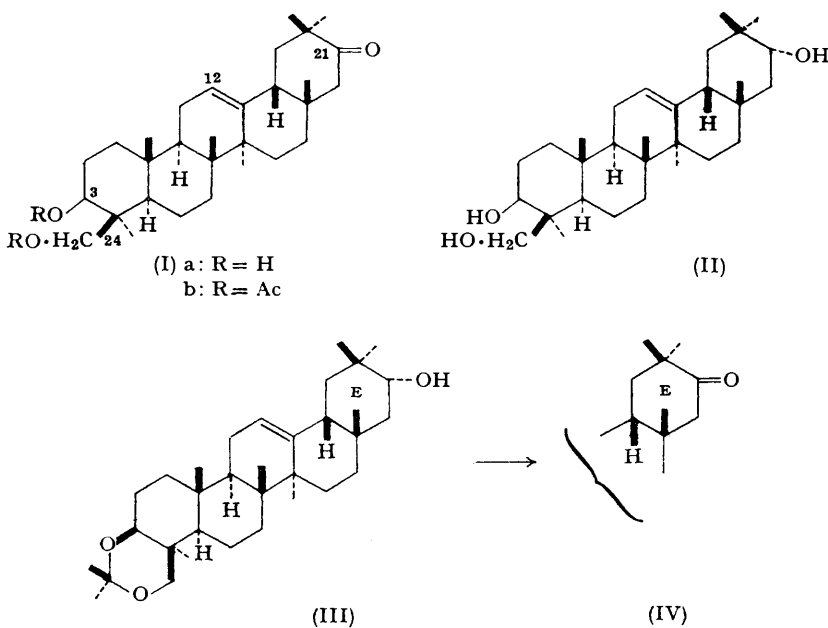
³ Meyer, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 672, 687, 1835.

⁴ Smith, Smith, and Spring, *Tetrahedron*, 1958, **4**, 111.

In a previous Paper⁵ the rapid separation and the identification of the various soyasapogenols of the soya bean by a circular paper chromatographic method have been described. When this method was applied to an acid hydrolysate of soya bean saponins a fifth substance, differing in its R_F value from the other sapogenols, was detected. The new substance stained green with antimony trichloride, whereas the known sapogenols developed a violet colour. An attempt to isolate the new substance by chromatography, using the procedure which was previously described^{2,3} for the four sapogenols, *i.e.*, by eluting the column with benzene and benzene-ether, proved ineffective. Substitution of methanol for the ether, however, yielded a mixture of the new compound and soyasapogenol C. By acetylating the mixture and chromatographing, pure soyasapogenol E diacetate (Ib) was obtained, m. p. 234—236°, $[\alpha]_D + 31^\circ$. The aglycone was prepared by the hydrolysis of the acetate but could not, however, be induced to crystallise.

The acetate (Ib) gave analytical figures for $C_{34}H_{52}O_5$, and was therefore a diacetate of the aglycone, $C_{30}H_{48}O_3$. The latter formula differs from soyasapogenols B (II) and D,³ both $C_{30}H_{50}O_3$, by two hydrogens. The infrared spectrum of the aglycone (Ia) revealed in the carbonyl region a band at 1706 cm.^{-1} (six-membered-ring ketone) while the diacetate (Ib) had additional bands at 1733 and 1739 cm.^{-1} for the two acetate esters at C-3 and C-24. It should be noted here that the band at 1706 cm.^{-1} is absent in all the soyasapogenols referred to above.³ Furthermore, since no absorption was recorded at about 1100 cm.^{-1} for the ether linkage occurring in soyasapogenol D,⁴ the possibility that the new product was a derivative of this sapogenol was ruled out.

The nuclear magnetic resonance spectrum of the diacetate showed a wide unresolved signal at $\tau 4.67$ for a vinylic proton (at C-12), a set of lines centred at $\tau 5.4$ related to one proton



(at C-3) adjacent to the acetoxy-group of a secondary alcohol, and two doublets formed by an AB system centred respectively at $\tau 5.58$ and 5.88 ($J_{AB} = 11\text{ c./sec.}$) due to two protons of the acetylated primary alcohol. A sharp peak at $\tau 7.95$ accounting for 6 protons is related to the methyl of the acetoxy-groups occurring in the molecule. The n.m.r. spectrum of the aglycone showed at high field a cluster of sharp peaks accounting for seven methyl groups (located at

⁵ Gestetner, *J. Chromatog.*, 1964, **13**, 259.

53, 55, 58, 61×2 , 75×2 c./sec.)* which are in agreement with the suggested structure for soyasapogenol E. Summing up, the new compound is a pentacyclic triterpene accommodating a primary and a secondary alcohol, a trisubstituted double bond, and one carbonyl group.

It seemed possible that soyasapogenol E, certainly closely related to soyasapogenol B, was derived from the latter by oxidation of the 21-hydroxyl group to a keto-group. In order to verify this possibility the dioxolan of soyasapogenol B (III) was prepared⁴ and subsequently oxidised with CrO_3 in pyridine to yield the 21-oxo-derivative (IV),⁴ which upon hydrolysis in methanolic HCl yielded soyasapogenol E (Ia). The synthetic product was found to be identical with the natural compound in all respects; both have identical infrared spectra throughout the whole range, the same R_F values on chromatoplates as well as on paper chromatograms, and both stained green with antimony trichloride. The acetylation product of the synthetic compound was also identical with the natural soyasapogenol E diacetate.

Experimental.—Melting points were taken on a Kofler hot-stage microscope and are corrected. All optical rotation measurements were carried out in chloroform solution. Infrared spectra were recorded on a Perkin-Elmer Infracord model 137 spectrophotometer. The nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer in deuterated chloroform solutions of about 5–10% concentration with tetramethylsilane as internal standard. Thin-layer chromatography was done on chromatoplates of silica gel G (Merck), the developing solvent being benzene-ethyl acetate 7:3. The spots were detected with iodine vapour.

Isolation of soyasapogenol E diacetate (Ib). Soya bean saponins were prepared from defatted soya bean flour,⁶ Lincoln variety, and a 0.1% solution of the saponin in 1*N*-sulphuric acid (in dioxan-water 1:3) was hydrolysed under reflux for 5 hr. The liberated saponinins were precipitated by addition of water. A sample (800 mg.) of the dried precipitate was dissolved in a small amount of benzene and chromatographed on alumina (100 g.) (ALCOA F-20), previously treated with a 10% solution of acetic acid.⁷ Elution was performed with benzene and then with benzene containing 0.75% and 1% of methanol (430 mg.). Eluate fractions (20 ml.) were examined by circular paper chromatography.⁵ Soyasapogenol E (Ia) accompanied soyasapogenol C in the fractions eluted with benzene containing 1% of methanol. Rechromatography was ineffective for separation between C and E which could be separated only through their acetates. The mixture was acetylated in pyridine-acetic anhydride (1:1) at room temperature overnight. The reaction product (150 mg.) was chromatographed on alumina (25 g.). Eluate fractions were examined by circular paper chromatography, using as solvent the upper phase of light petroleum-ethanol-water (40:1:9) and developing the chromatograms with antimony trichloride. Only soyasapogenol C acetate (90 mg.) was eluted with benzene, whereas the E acetate (Ib) (45 mg.) appeared in fractions eluted with 0.75% methanol-benzene. *Soyasapogenol E diacetate (Ib)*, crystallised from ethanol, had m. p. 234–236°, $[\alpha]_D + 31^\circ$ (*c* 0.65); ν_{max} 1706 (six-membered-ring ketone), 1739, 1733, and 1260 (acetates) cm^{-1} (Found: C, 75.1; H, 9.65. $\text{C}_{34}\text{H}_{52}\text{O}_5$ requires C, 75.5; H, 9.7%).

Soyasapogenol E (Ia). Soyasapogenol E diacetate (Ib) (50 mg.) was refluxed for 3 hr. in a 5% solution (25 ml.) of potassium hydroxide in methanol. The mixture was diluted with water and extracted with ether. The ether solution was washed with water and dried and the solvent was evaporated. The residue failed to crystallise and had ν_{max} 1706 cm^{-1} . It gave a green colour with antimony trichloride on a paper chromatogram.

Preparation of soyasapogenol E diacetate. 3 β ,24-Isopropylidenedioxyolean-12-en-21-one (IV) (170 mg.), prepared from soyasapogenol B,⁴ was dissolved in a mixture of methanol (50 ml.) and concentrated hydrochloric acid (7.5 ml.). The clear solution was refluxed for 15 min., and, after cooling, was diluted with water and extracted with ether. The ether solution was washed, dried over sodium sulphate, and the solvent evaporated. The residual solid did not crystallise; however it had the same infrared spectrum as that of the natural soyasapogenol E described above. Upon

* The use of c./sec. values for the methyl group signals is in accordance with previous studies in the triterpenes, cf. Lavie, Shvo, and Glotter, *Tetrahedron*, 1963, **19**, 2255, and Lavie, Benjaminov, and Shvo, *ibid.*, 1964, **20**, 2585.

⁶ Birk, Bondi, Gestetner, and Ishaaya, *Nature*, 1963, **197**, 1089.

⁷ Walter, Van Atta, Thompson, and Maclay, *J. Amer. Chem. Soc.*, 1953, **76**, 2271.

acetylation by the usual procedure, soyasapogenol E diacetate (130 mg.), m. p. 233—236°, was obtained which crystallised from ethanol. A mixture with the natural compound had the same m. p., and its infrared spectrum was identical throughout the whole range with the spectrum of the natural compound. On chromatoplate and paper chromatography⁵ both compounds behaved in a similar way.

Part of this work was supported by the U.S. Department of Agriculture. Thanks are due to Dr. Y. Shvo for the n.m.r. measurements and for contributing to their interpretation, and also to Mrs. S. Khalef for skilful technical assistance.

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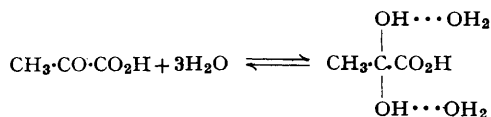
1127. *The Hydration of Pyruvic Acid.*

By V. GOLD, G. SOCRATES, and (in part) M. R. CRAMPTON.

THE presence of a significant proportion of hydrated pyruvic acid [2,2-dihydroxypropanoic acid, $\text{CH}_3\text{C}(\text{OH})_2\text{CO}_2\text{H}$] in aqueous solutions of pyruvic acid ($\text{CH}_3\text{CO}\cdot\text{CO}_2\text{H}$) has recently been inferred.^{1,2} The present study deals with this equilibrium and the rate of its attainment by n.m.r. measurements.

The n.m.r. spectrum of liquid pyruvic acid consists of two sharp lines at 10.6 and 2.6 p.p.m. downfield from internal tetramethylsilane, in the expected intensity ratio 1:3. A concentrated solution of pyruvic acid (*ca.* 4M) in water or deuterium oxide shows the methyl resonance in the same position and, in addition, a signal 0.86 p.p.m. upfield from it which is attributed to the methyl group of the hydrate. This attribution is supported by (a) the fact that the separation of this resonance from that of the methyl group of pyruvic acid is almost the same as that between the methyl signals of acetaldehyde and its hydrate (0.91 p.p.m., in agreement with earlier measurements³) and (b) by the variation of the relative intensities of the two methyl resonances with concentration such as to decrease the intensity of the new (*i.e.*, hydrate) signal as the concentration of pyruvic acid is raised and that of water falls.

The extrapolated limiting ratio of the peak areas of the hydrate methyl peak to the pyruvic acid methyl peak at zero acid concentration is *ca.* 2.4 at 31° (cf. 2.38 reported by Strehlow² for 25°). The ratio of these peak areas varies approximately with the third power of the concentration of water in the pyruvic acid–water mixture. In 4M-pyruvic acid its value is 0.68. Whilst the interpretation of the dependence of any chemical or physical property on a certain power of concentration of a major component of the medium is always questionable, the results clearly do indicate the stabilisation of pyruvic acid hydrate by water. Very tentatively (ignoring association between acid molecules) the third-power dependence could be rationalised in terms of hydrogen-bonding as



The movement of the methyl resonance to higher field on hydration of the carbonyl group implies more effective screening of the methyl protons in the hydrate. This effect is expected to be accompanied by a similar influence on the carboxyl group, and hence to a decrease in the acid dissociation constant. The correctness of this inference and the weakness

¹ M. Becker and H. Strehlow, *Z. Elektrochem.*, 1960, **64**, 813.

² H. Strehlow, *Z. Elektrochem.*, 1962, **66**, 392.

³ E. Lombardi and P. B. Sogo, *J. Chem. Phys.*, 1960, **32**, 635.

of 2,2-dihydroxypropanoic acid compared with pyruvic acid are more convincingly shown by the observation that the pyruvate anion in aqueous solution is entirely in the unhydrated form.⁴

On addition of hydrochloric acid to the solutions the methyl resonances broaden in a manner consistent with the occurrence of a rapid hydration-dehydration reaction. This phenomenon was systematically examined by observations on the more intense signal (that due to the unhydrated form) in 4M-pyruvic acid, signal/noise considerations being responsible for the choice of the high concentration.

Values of the parameter τ_A were calculated from the equation

$$\tau_A^{-1} = (T_{2A}')^{-1} - (T_{2A})^{-1}$$

where $2/T_{2A}'$ is the half-width of the signal at a particular catalyst concentration and $2/T_{2A}$ the corresponding half-width in the absence of catalyst. When defined in this way τ_A^{-1} does not relate to the total rate of the reaction but only to the catalysed portion. The distinction is made since, by analogy with the hydration of acetaldehyde,⁵ some "spontaneous" reaction is expected in this case. Values of τ_A^{-1} thus obtained increase linearly with the concentration of hydrochloric acid added. The corresponding graph passes nearly, but not quite, through the origin: the small discrepancy is attributed to slight uncertainty in the measurements of T_{2A} . From the slope the catalytic coefficient of the hydrochloric acid-catalysed hydration of pyruvic acid at 37.5° is obtained as 8.3 l. mole⁻¹sec.⁻¹. These findings are tabulated. The result is of the same order of magnitude as Strehlow's values but, because of the difference in conditions, cannot be compared exactly. The general agreement corroborates the correctness of the analysis of the data in both studies.

The kinetic work was discontinued on publication of Strehlow's detailed study.²

Financial support by the Air Research and Development Command, U.S. Air Force, through its European office, and by the United Kingdom Atomic Energy Authority is gratefully acknowledged. We also thank Dr. J. Carlidge for help with instrumentation.

Summary of n.m.r. rate measurements of hydration of pyruvic acid (4M) at 37.5°.

[HCl] (M)	τ_A^{-1} (obs.) (sec. ⁻¹)	τ_A^{-1} * (calc.) (sec. ⁻¹)	[HCl] (M)	τ_A^{-1} (obs.) (sec. ⁻¹)	τ_A^{-1} * (calc.) (sec. ⁻¹)	[HCl] (M)	τ_A^{-1} (obs.) (sec. ⁻¹)	τ_A^{-1} * (calc.) (sec. ⁻¹)
0.064	1.8	1.5	1.04	10.4	9.6	1.99	17.5	17.5
0.41	4.5	4.4	1.24	10.6	11.3	2.48	21.7	21.6
0.62	7.1	6.1	1.65	12.8	14.7	3.10	26.3	26.8
0.83	8.2	7.9						

* Calculated from $\tau_A^{-1} = 1.0 + 8.3[\text{HCl}]$.

KING'S COLLEGE, STRAND, LONDON, W.C.2.

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⁴ W. P. Jencks and J. Carriuolo, *Nature*, 1958, **182**, 598.

⁵ R. P. Bell, M. H. Rand, and K. M. A. Wynne-Jones, *Trans. Faraday Soc.*, 1956, **52**, 1093.

1128. *Hydroaromatic Steroid Hormones. Part XII.*¹

By A. J. BIRCH, G. A. HUGHES, G. KRUGER, and G. S. R. SUBBA RAO.

WHEN most of the present work was carried out² no œstrone derivatives with groups other than OR at position 3 had been reported. More recently,³ a number have been made containing 17 β -hydroxyl or -ester functions, starting from the 3-amino-analogue of œstradiol. Our own work leads directly to the 17-ketones and can also yield dihydro-aromatic derivatives.

¹ Part XI, A. J. Birch and J. B. Siddall, *J.*, 1965, 1552.

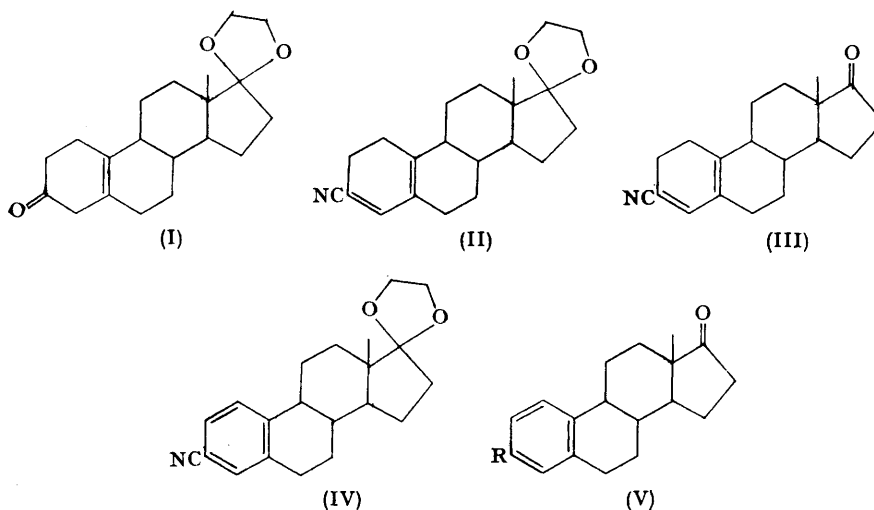
² G. A. Hughes, Ph.D. Thesis, Manchester, 1959.

³ E. Hecker, *Chem. Ber.*, 1962, **95**, 977.

The ketone (I) was prepared by controlled hydrolysis of 1,4-dihydro- α -estrone methyl ether 17-ethylene ketal; addition of hydrogen cyanide, and dehydration, gave (II). Removal of the ketal then yielded (III), whose assigned formula is supported by spectra, particularly λ_{\max} . 305 μ . (ϵ 9200) which accords with the *cis*-diene structure. It reacted with lithium acetylide at the 17-keto-group in the usual manner, to give the 17 α -ethynyl-carbinol.

Dehydrogenation of (II) with palladium-charcoal gave (IV) which was reduced with lithium aluminium hydride, followed by acid hydrolysis, to yield (V; R = CH₂•NH₂), and converted into the acetyl derivative (V; R = CH₂•NHAc). Mild acid hydrolysis of (IV) produced (V; R = CN), which reacted with lithium acetylide to give the 17 α -ethynyl-carbinol. Hydrolysis of (V; R = CN) with alkali gave the acid (V; R = CO₂H) which, on reduction with sodium borohydride and esterification with diazomethane, gave a methyl ester identical with that reported by Hecker.³

Compared with standard α -estrogens, some of these compounds show considerable dissociation of activity as antagonists of follicular stimulating hormone from uterotrophic activity. The results will be reported in detail elsewhere.



Experimental.—17,17-Ethylenedioxy α -estr-5(10)-*en*-3-one. The 17-ethylene ketal of 1,4-dihydro- α -estrone methyl ether (3 g.) in tetrahydrofuran (50 c.c.) and methanol (250 c.c.) was added to oxalic acid (5 g.) in water (50 c.c.). After 1 hr., a saturated solution of sodium hydrogen carbonate was added, and the gummy product (2.32 g.) extracted with ether and chromatographed on neutral alumina in benzene, elution being with benzene-light petroleum (1:1). The *product* had m. p. 104–106° (from light petroleum) (Found: C, 76.0; H, 8.85. C₂₀H₂₈O₃ requires C, 75.9; H, 8.9%), ν_{\max} . (Nujol) 1715 cm.⁻¹.

3-Cyano-17,17-ethylenedioxy α -estr-3,5(10)-*diene*. To the foregoing keto-ketal (2 g.) in acetone cyanohydrin (45 c.c.) was added a drop of saturated methanolic potassium hydroxide. After leaving overnight, water (300 c.c.) was added and the gum separated by centrifugation; it did not crystallise, but its spectrum accorded with the expected cyanohydrin structure (ν_{\max} . 3400, 2240, 1100, 1030 cm.⁻¹). It was dissolved in pyridine (5 c.c.) and phosphorus oxychloride (1 c.c.) added. After 15 hr., water (100 c.c.) was added and the *product* (650 mg.) extracted into chloroform, m. p. 143–144° (from methanol) (Found: C, 77.3; H, 8.2. C₂₁H₂₇NO₂ requires C, 77.5; H, 8.4%), λ_{\max} . 305 μ . (ϵ 9000), ν_{\max} . 2200, 1640, 1580, 1100, 1030 cm.⁻¹. Hydrolysis of the ketal (500 mg.) in aqueous acetone (10 c.c.) and concentrated hydrochloric acid (0.2 c.c.) for 2 hr. and working up in the usual way gave 3-cyano- α -estr-3,5(10)-*dien*-17-one (410 mg.), m. p. 261–263° (from methanol) (Found: C, 80.95; H, 8.05. C₁₉H₂₃NO requires C, 81.1; H, 8.2%), λ_{\max} . 305 μ . (ϵ 9200), ν_{\max} . 2180, 1724, 1575, 1640 cm.⁻¹.

3-Cyano-17 α -ethynyl-17 β -hydroxy α -estr-3,5(10)-*diene*. The above cyano-ketone (300 mg.) in pure tetrahydrofuran (20 c.c.) was treated for 12 hr. with lithium acetylide prepared by passing

acetylene through lithium aluminium hydride (500 mg.) in tetrahydrofuran. Worked up as usual, the pale yellow solid (205 mg.) gave the *product*, m. p. 172—174° (from methanol) (Found: C, 81.9; H, 8.3. $C_{21}H_{25}NO$ requires C, 82.1; H, 8.1%), ν_{\max} . 3400, 3250, 2180, 1640, 1580 cm^{-1} .

3-Cyano-17,17-ethylenedioxyæstra-1,3,5(10)-triene. 3-Cyano-17,17-ethylenedioxyæstra-3,5(10)-diene (100 mg.) was refluxed with palladium-charcoal (30%; 10 mg.) in 2-methylnaphthalene for 45 min. The solution was cooled, poured on to a column of Florex, and the 2-methylnaphthalene removed by elution with light petroleum. Elution with benzene-light petroleum (1:1) gave the *product* (52 mg.), m. p. 104—106° (Found: C, 77.2; H, 7.8. $C_{21}H_{25}NO_2$ requires C, 77.9; H, 7.8%), λ_{\max} . 270, 277, 286 $m\mu$ (ϵ 1230, 1482, 1360), ν_{\max} . 2225, 1605, 1110, 1050 cm^{-1} . The above ketal (100 mg.), in acetone (10 c.c.) and concentrated hydrochloric acid (0.5 c.c.), was refluxed for 10 min. Addition to water and extraction with ether gave 3-cyano-æstra-1,3,5(10)-trien-17-one (60 mg.), m. p. 262—263° (from acetone) (Found: C, 81.4; H, 7.5; N, 5.4. $C_{19}H_{21}NO$ requires C, 81.7; H, 7.6; N, 5.0%), λ_{\max} . 265 $m\mu$ (ϵ 6740), ν_{\max} . 2225, 1730, 1630, 1605, 1500 cm^{-1} ; n.m.r. absorption at τ 2.67 corresponding to 3 aromatic protons.

3-Carboxyæstra-1,3,5(10)-trien-17-one. The above cyano-ketone (100 mg.), potassium hydroxide (0.5 g.), and aqueous ethanol (5 c.c.; 10%) were heated in a sealed tube at 100° for 16 hr. Acidification gave the *product*, needles, m. p. 318—320° (from methanol) (Found: C, 76.6; H, 7.35. $C_{19}H_{22}O_3$ requires C, 76.5; H, 7.4%), λ_{\max} . 242, 270 $m\mu$ (ϵ 10,700, 6750), ν_{\max} . 2640, 2550, 1738, 1670, 1620, 1600 cm^{-1} . The acid (50 mg.) in ethanol (10 c.c.) was left overnight with sodium borohydride (50 mg.). The product had m. p. 285—288° (from methanol), λ_{\max} . 247, 277 $m\mu$ (ϵ 15,800, 1345), ν_{\max} . 3420, 1680 cm^{-1} . Rapid reaction with ethereal diazomethane gave the methyl ester, plates, m. p. 185—187° (from methanol), λ_{\max} . 244, 280 $m\mu$ (ϵ 15,200, 1550), ν_{\max} . 3480, 1710 cm^{-1} (lit., m. p. 185—187°, λ_{\max} . 244, 280 $m\mu$).

3-Cyano-17 α -ethynyl-17 β -hydroxyæstra-1,3,5(10)-triene. 3-Cyano-æstratrienone (100 mg.) was treated as above with lithium acetylide in tetrahydrofuran. The *product* had m. p. 140—143° (Found: C, 82.5; H, 7.6. $C_{21}H_{23}NO$ requires C, 82.6; H, 7.5%), ν_{\max} . 3400, 3250, 3180, 2210, 1600, 1062 cm^{-1} .

3-Aminomethylæstra-1,3,5(10)-trien-17-one. The cyanoethylenedioxyæstratriene (200 mg.), in dry ether (50 c.c.), was refluxed with lithium aluminium hydride (500 mg.) in ether and left for 16 hr. Worked up as usual, the gum (180 mg.) was refluxed with methanol (10 c.c.) containing concentrated hydrochloric acid, basified, and extracted. The *product* formed plates, m. p. 142—143° (from methanol) (142 mg.) (Found: C, 80.4; H, 8.9. $C_{19}H_{25}NO$ requires C, 80.6; H, 8.8%). Acetylation with acetyl chloride in pyridine gave a gum; chromatography in light petroleum-benzene (8:2) on Florex yielded 3-acetamidomethylæstra-1,3,5(10)-trien-17-one, m. p. 128—132° (from methanol) (Found: C, 77.2; H, 8.5. $C_{21}H_{27}NO_2$ requires C, 77.5; H, 8.3%), ν_{\max} . 3250, 1730, 1650, 1550, 1540, 1510 cm^{-1} .

We are indebted to the D.S.I.R. for a Scholarship (to G. A. H.), and to Syntex S.A. for financial assistance and a gift of œstrone.

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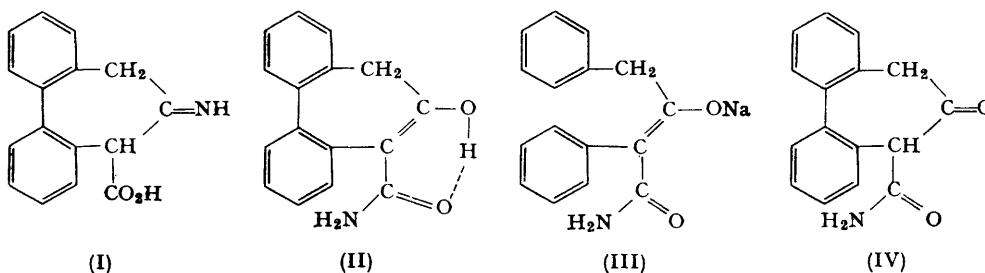
1129. A Re-examination of the Thorpe Reactions with 2,2'-Di(cyanomethyl)biphenyl and Benzyl Cyanide.

By F. BELL and K. R. BUCK.

WE find that the compound obtained by Kenner¹ from 2,2'-di(cyanomethyl)biphenyl, and assigned structure (I), is not a true carboxylic acid; it does not form alkaloidal salts, is insoluble in sodium carbonate, and dissolves only slowly in sodium hydroxide. The properties, in particular the n.m.r. spectrum, show that structure (II) is more correct, and this is broken by sodium hydroxide to give (III).

¹ J. Kenner and E. G. Turner, *J.*, 1911, **99**, 2101.

This result led us to re-examine the Thorpe reaction as applied to benzyl cyanide. As an alternative to the products previously described,²⁻⁵ β -oxo- α - γ -diphenylbutyramide (IV)^{6,7} was produced in considerable amount. This has a close formal similarity to (II), and the possibility of enolisation is indicated from the colour with ferric chloride. The n.m.r. spectrum showed, however, that (IV) is a more correct structure than one analogous to (II).



We also examined benzoylacetamide,⁸ and again our results favour a ketonic non-hydrogen-bonded structure; we consider structure (II) to be sterically favoured by the seven-membered carbon ring.

Experimental.—Infrared spectra are for the solid compounds. N.m.r. spectra (60 Mc./sec.) are for solutions in deuteriochloroform, with tetramethylsilane as internal standard.

Kenner's "1-imino-3,5-dibenzocyclohepta-3,5-diene-2-carboxylic acid" was obtained as stated.¹ After several recrystallisations from ethanol it formed needles, m. p. 188° (decomp.). It was sparingly soluble in carbon tetrachloride and carbon disulphide, and more soluble in chloroform (Found: C, 76.7; H, 5.0. Calc. for C₁₆H₁₃NO₂: C, 76.5; H, 5.2%). N.m.r.: complex band at τ 2.3—2.7 (8 aromatic ring protons), 2 protons at τ 6.75 (unsplit) (PhCH₂·C=), 2 protons at τ 4.4 (broad band) (CO·NH₂), 1 proton at τ -4.9 (unsplit) (enol form of β -diketone). ν_{\max} . 3300 and 3450 cm.⁻¹ (NH₂), 1620vs, vbr (shoulders at 1700 and 1570 cm.⁻¹) (chelated β -diketone, enol form).

Lesslie and Turner's process⁵ was applied to benzyl cyanide (150 g.). β -Oxo- α - γ -diphenylbutyramide (3.5 g.) was isolated, plates, m. p. 162—163° (from ethanol) (Found: C, 75.5; H, 5.7. Calc. for C₁₆H₁₅NO₂: C, 75.8; H, 5.9%); it gave a dark violet colour with ferric chloride, and dissolved in warm sodium hydroxide with evolution of ammonia. ν_{\max} . 3150 and 3360 (NH₂), 1635 (amide C=O), 1700 cm.⁻¹ (C=O). N.m.r.: 1 proton at τ 6.2 (unsplit) (PhCH), 2 protons at τ 6.63 (unsplit) (PhCH₂·CO·R), broad band at τ 4.8 (CO·NH₂), 10 protons, complex band τ 2.6—2.8 (aromatic ring hydrogens).

Benzoylacetamide, conveniently prepared by Guareschi's method,⁸ was recrystallised from benzene. N.m.r., complex band at τ 1.9—2.55 (5 aromatic ring protons), 2 protons at τ 6.01 (unsplit) (CO·CH₂·CO), τ 4.4 (CO·NH₂). ν_{\max} . 3180 and 3400 (NH₂), 1640 (amide C=O), 1680 cm.⁻¹ (C=O).

The authors are indebted to Mr. B. Semple, B.Sc., for the n.m.r. spectra.

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² E. F. J. Atkinson and J. F. Thorpe, *J.*, 1906, **89**, 1906.

³ N. Lees and J. F. Thorpe, *J.*, 1907, **91**, 1282.

⁴ C. S. Gibson, W. S. Kentish, and J. L. Simonsen, *J.*, 1928, 2131.

⁵ M. S. Lesslie and E. E. Turner, *J.*, 1929, 1512.

⁶ R. Walther and P. G. Schickler, *J. prakt. Chem.*, 1897, [2] **55**, 354.

⁷ H. Staudinger, *Ber.*, 1911, **44**, 533.

⁸ J. Guareschi, *Chem. Z.*, 1904, II, 905.

1130. Synthesis of Bistrifluoromethylaminosulphenyl Chloride.

By H. J. EMELÉUS and B. W. TATTERSHALL.

THE synthesis of bistrifluoromethylaminosulphenyl chloride (b. p. 49.5—51°, yield ca. 21%) by heating *N*-chlorobistrifluoromethylamine with sulphur in a metal bomb at 225°, or by

the reaction of bistrifluoromethylamine with sulphur dichloride, has been described.¹ The present Note describes two alternative methods of preparation which were developed independently. In the first, sulphur dichloride is allowed to react at room temperature with mercuric bistrifluoromethylamide, $[(CF_3)_2N]_2Hg$. The required compound, $(CF_3)_2NSCl$, was isolated in about 50% yield by fractionation *in vacuo*, the other major products being *N*-chlorobistrifluoromethylamine, perfluoro-2-azapropene ($CF_3 \cdot N : CF_2$), and sulphur chlorides unseparated from further bistrifluoromethylaminosulphenyl chloride. This reaction contrasts with that of phosphorus trichloride, which is fluorinated by the mercurial to phosphorus trifluoride, with the formation of perfluoro-2-azapropene.²

In the second method a mixture of disulphur dichloride with *N*-chlorobistrifluoromethylamine [λ_{max} . 246 $m\mu$ (ϵ 116)] was irradiated in a quartz bulb with a mercury-arc lamp. An almost quantitative yield of bistrifluoromethylaminosulphenyl chloride was formed, but this proved difficult to separate on a small scale from traces of sulphur chlorides. This reaction was also carried out using the mixture of by-products from the mercurial reaction described above. Thus, the *N*-chlorobistrifluoromethylamine was utilised and the overall yield of the sulphenyl chloride from the mercurial was increased to 82%.

The photochemical reaction is to be expected since *N*-chlorobistrifluoromethylamine should dissociate under ultraviolet irradiation, like the *N*-bromo-derivative,³ to give $(CF_3)_2N \cdot$ radicals. Disulphur dichloride is thought to dissociate under these conditions to $SCl \cdot$ radicals,⁴ and the appropriate recombinations to give the sulphenyl chloride are likely to follow.

In the reaction of mercuric bistrifluoromethylamide with sulphur dichloride, the by-product, *N*-chlorobistrifluoromethylamine, is produced in a competing reaction of the mercurial with chlorine, formed by the known dissociation of sulphur dichloride (15% dissociated to disulphur dichloride and chlorine at room temperature).⁵

Bistrifluoromethylaminosulphenyl chloride is a pale yellow liquid, the vapour pressure of which (-28° to $+45^\circ$) is represented by $\log_{10} p(\text{mm.}) = -1458/T + 7.43$, giving an extrapolated boiling point of 47.3° and a Trouton constant of 20.8. A sample underwent hydrolysis in cold water, to sulphur, bistrifluoromethylamine, and its hydrolysis products.⁶ A small fraction (4%) appeared as the sulphide $[(CF_3)_2N]_2S$ ⁷ which was identified spectroscopically.

The infrared spectrum of the sulphenyl chloride confirmed the presence of the bistrifluoromethylamino-group. A shoulder at 530 cm.^{-1} is probably associated with an S-Cl stretching vibration, which has been identified in this region for related molecules (CF_3SCl , 535;⁸ CCl_3SCl , 532;⁹ SCl_2 , 525;¹⁰ CH_3SCl , 524 cm.^{-1}). All bistrifluoromethylamino-compounds studied in the present work show a very intense absorption in the ultraviolet region at about 200 $m\mu$. In addition to this, the sulphenyl chloride has λ_{max} . 313 $m\mu$ (ϵ 28.9). This may be attributed to the S-Cl bond, since a similar absorption is found in related compounds¹¹ (CF_3SCl , λ_{max} . 333 $m\mu$, ϵ 25; CCl_3SCl , λ_{max} . 322 $m\mu$, ϵ 10).

Experimental.—*N*-Chlorobistrifluoromethylamine³ and mercuric bistrifluoromethylamide² were prepared as previously described. Disulphur dichloride and sulphur dichloride were purified by vacuum-fractionation.

Bistrifluoromethylaminosulphenyl chloride. The mercurial (5.46 g., 10.83 mmoles) and SCl_2 (2.235 g., 21.75 mmoles) were sealed together in a glass ampoule and set aside overnight at room

¹ C. W. Tullock (Du Pont de Nemours and Co.) U.S.P. 3,121,112/1964 (*Chem. Abs.*, 1964, **60**, 13143).

² H. J. Emeléus and G. L. Hurst, *J.*, 1964, 396.

³ H. J. Emeléus and B. W. Tattershall, *Z. anorg. Chem.*, 1964, **327**, 147.

⁴ R. G. Sowden and N. Davidson, *J. Amer. Chem. Soc.*, 1956, **78**, 1291.

⁵ T. M. Lowry and G. Jessop, *J.*, 1931, 323.

⁶ D. A. Barr and R. N. Haszeldine, *J.*, 1955, 2532.

⁷ J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1960, **82**, 396.

⁸ S. N. Nabi and N. Sheppard, *J.*, 1959, 3439.

⁹ J. A. A. Ketelaar and W. Vedder, *Rec. Trav. chim.*, 1955, **74**, 1482.

¹⁰ G. M. Barrow, *J. Phys. Chem.*, 1955, **59**, 987.

¹¹ R. N. Haszeldine and J. M. Kidd, *J.*, 1953, 3219.

temperature. The product, on fractionation, gave bistrifluoromethylaminosulphenyl chloride (2.322 g., 10.58 mmoles, 49%) (Found: Cl, 16.2; F, 53.5; S, 14.6%; *M*, 219. Calc. for C_2ClF_6NS : Cl, 16.15; F, 52.0; S, 14.59%; *M*, 219). The infrared spectrum, measured with Perkin-Elmer Infracord spectrophotometers, showed the following principal bands: 1358m, 1322s, 1255s, 1233s, 1170m, 975m, 777m, 712m, 658m, 582m, 559mw, 530mw, sh, 501s, 478s, 425m cm^{-1} .

Other products, identified spectroscopically, were present in other fractions in the following roughly estimated yields: $CF_3N:CF_2$, 12%; $(CF_3)_2NCl$, 19%; $(CF_3)_2NSCl$, 14%. These fractions were mixed with S_2Cl_2 (1.016 g., 7.53 mmoles), sealed in a silica irradiation ampoule, and irradiated for 4 days. Fractionation of the resulting mixture gave 1.584 g. (7.22 mmoles) of $(CF_3)_2NSCl$, bringing the total yield on mercurial taken to 82%.

Preparation of the sulphenyl chloride by irradiation. $(CF_3)_2NCl$ (1.12 g., 5.97 mmoles) and S_2Cl_2 (1.623 g., 12.03 mmoles) were sealed together in a silica ampoule (150-ml.) and irradiated with the unfiltered light from a Hanovia mercury-arc lamp for 4 days. $(CF_3)_2NSCl$ could not be completely purified, but a mixture (6.21 mmoles; *M*, 214) of this compound with SCl_2 was produced, corresponding to a yield of 99%. The infrared spectrum of this fraction was identical in the NaCl region with that of the material made from the mercurial.

Hydrolysis of $(CF_3)_2NSCl$. $(CF_3)_2NSCl$ (0.164 g., 0.746 mmole) was added to degassed water (1 ml.). In $\frac{1}{2}$ hr. at room temperature some sulphur had formed. Water was removed by fractionation, and the other volatile products were separated in a codistillation apparatus,¹² to yield CO_2 (0.0127 g., 0.287 mmole); $(CF_3)_2NH$ (0.043 g., 0.281 mmole); $[(CF_3)_2N]_2S$ (0.0048 g., 0.0144 mmole); unchanged $(CF_3)_2NSCl$ (0.0026 g., 0.0118 mmole). $(CF_3)_2NSCl$ was rapidly decomposed by 15% aqueous sodium hydroxide. After 1 hr. at 100° the solution was treated at room temperature with 30% aqueous hydrogen peroxide excess of which was removed by boiling for a short time. It was then found that F^- and SO_4^{2-} ions had been quantitatively produced.

One of the authors (B. W. T.) is indebted to the D.S.I.R. for a maintenance grant.

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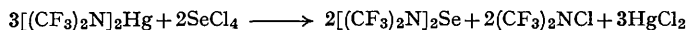
[Received, August 19th, 1964.]

¹² G. H. Cady and D. P. Siegwarth, *Analyt. Chem.*, 1959, **31**, 618.

1131. Preparation of Di(bistrifluoromethylamino) Selenide.

By R. C. DOBBIE and H. J. EMELÉUS.

BISTRIFLUOROMETHYLAMINO-SULPHUR compounds have been prepared by the reaction of mercuric bistrifluoromethylamide with sulphur¹ or sulphur halides,² and by heating *N*-chlorobistrifluoromethylamine with sulphur.³ Reaction of the mercurial with selenium at 250° did not yield di(bistrifluoromethylamino) selenide, although the corresponding reaction with sulphur gives a mixture of the monosulphide, $[(CF_3)_2N]_2S$, and the disulphide, $[(CF_3)_2N]_2S_2$, in roughly equal proportions. The main products from the reaction with selenium were perfluoro-2-azapropene, $CF_3N:CF_2$, and silicon tetrafluoride, arising from attack on the reaction tube. However, di(bistrifluoromethylamino) selenide was formed when mercuric bistrifluoromethylamide and selenium tetrachloride were heated in a sealed tube at 50°, the other products being mercuric chloride and *N*-chlorobistrifluoromethylamine. The quantities of the products established that the reaction could be represented as:



The monoselenide was identified from its infrared spectrum, molecular weight, and analysis. It was completely decomposed by water, but was stable when heated in glass up to 250°, showing that the failure to prepare it by heating the mercurial with selenium at 250° was not due primarily to decomposition of the desired product.

¹ J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1960, **82**, 396.

² H. J. Emeléus and B. W. Tattershall, preceding Note.

³ C. W. Tullock, U.S. P. 3,121,112/1964 (*Chem. Abs.*, 1964, **60**, 13143).

A vapour-pressure study of the compound in all-glass apparatus over the range 2—25 cm. gave the equation: $\log_{10} p$ (cm.) = $-1950/T + 7.16$. The extrapolated boiling point was 106°, the latent heat of vaporisation 8.91 kcal. mole⁻¹, and Trouton's constant 23.5.

The monoselenide was also prepared by the reaction of *N*-bromobistrifluoromethylamine with selenium at room temperature. The molecular weight of the product was intermediate between that for (CF₃)₂NSeBr and [(CF₃)₂N]₂Se. On the supposition that the former was present, the mixture was treated with mercury, with which the monoselenide reacts only slowly, and a pure sample of the latter was obtained. The selenyl bromide has not yet been separated. Diselenium dichloride reacted with mercuric bistrifluoromethylamide at room temperature. Here also the monoselenide was isolated as a major product. Another product was probably bistrifluoromethylaminoselenyl chloride.

Experimental.—Reaction of mercuric bistrifluoromethylamide with selenium. The mercurial (1.55 g., 3.07 mmoles) and selenium (0.271 g., 3.43 mmoles) were sealed in an evacuated tube and heated at 250° (2 hr.). The main volatile products were CF₃N:CF₂ (0.380 g., 2.86 mmoles) identified from its infrared spectrum, SiF₄ (0.095 g., 0.91 mmole) (*M*, 106), and unreacted mercurial (0.505 g., 1.00 mmole). Traces of CO₂, COF₂, CF₃NCO, (CF₃)₂NH, and (CF₃)₂N:CF:N:CF₃⁴ were identified spectroscopically.

Reaction of selenium tetrachloride with mercuric bistrifluoromethylamide. Selenium tetrachloride was prepared by the method of Nowak and Suttle⁵ (Found: Se, 36.2; Cl, 63.5. Calc. for SeCl₄: Se, 35.8; Cl, 64.2%). Mercurial (2.39 g., 4.74 mmoles) and selenium tetrachloride (0.877 g., 3.98 mmoles), sealed in a vacuum in an ampoule, reacted at 50—55° (12 hr.). Vacuum-fractionation of the products gave *di*(bistrifluoromethylamino) selenide (0.302 g., 0.790 mmole) (Found: Se, 20.1; F, 59.3%; *M*, 365. C₄F₁₂N₂Se requires Se, 20.6; F, 59.5%; *M*, 383), main infrared bands at 1330m, 1305s, 1272s, 1220s, 1208s, 1170m, sh, 970m, 768w, 700m, 650w, 556w cm⁻¹. The other products were SeF₄ (0.230 g., 1.64 mmoles) identified from its infrared spectrum,⁶ and (CF₃)₂NCl (0.256 g., 0.830 mmole) identified from its infrared spectrum¹ and molecular weight (*M*, 184). From the amounts of products recovered, 69.2% of the mercurial was consumed in the fluorination of SeCl₄ and 26.2% in the coupling reaction to give monoselenide.

Reaction of N-bromobistrifluoromethylamine with selenium. The bromo-compound was prepared and purified by the literature method.⁷ Selenium (0.389 g., 4.92 mmoles) and *N*-bromobistrifluoromethylamine (1.03 g., 4.43 mmoles) were sealed together in an evacuated tube. On warming to room temperature a vigorous reaction occurred and a red-brown liquid was formed. Fractionation gave (CF₃)₂NH (0.021 g., 0.14 mmole), CF₃N:CF₂ (0.024 g., 0.18 mmole), identified from their infrared spectra. The residual liquid (*M*, 340) had an infrared spectrum characteristic of (CF₃)₂N derivatives, and a maximum in the visible region at 406 mμ.

When the liquid (0.303 g.) was shaken with mercury the red colour disappeared. The volatile products were CF₃N:CF₂ (0.022 g., 0.17 mmole) and [(CF₃)₂N]₂Se (0.085 g., 0.222 mmole) (*M*, 390), the infrared spectrum of which was identical with that of the specimen previously prepared. An involatile oil left in the original reaction tube was Se₂Br₂ (0.213 g., 0.670 mmole).

Reaction of mercuric bistrifluoromethylamide with diselenium dichloride. The mercurial (2.90 g., 5.76 mmoles) and diselenium dichloride (1.25 g., 5.48 mmoles) reacted at room temperature in an evacuated sealed tube. The products were CF₃N:CF₂ (0.080 g., 0.60 mmole) (*M*, 132), also identified from its infrared spectrum, and a colourless liquid (0.740 g., 1.93 mmoles) identified as *di*(bistrifluoromethylamino) selenide (Found: F, 60.2%; *M*, 375. Calc. for C₄F₁₂N₂Se: F, 59.5%; *M*, 383). The infrared spectrum agreed with that of the specimen prepared earlier.

The remaining fractions were yellow liquids. One fraction (*M*, 288), with λ_{max}. 358 mμ and an infrared spectrum similar to that of the monoselenide, contained selenium and chlorine. This was evidence that the fraction was impure (CF₃)₂NSeCl (*M*, 267).

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⁴ G. L. Hurst, Thesis, Cambridge, 1963.

⁵ H. G. Nowak and J. F. Suttle, *Inorg. Synth.*, **5**, 125.

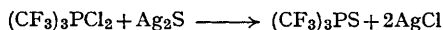
⁶ E. E. Aynsley, R. E. Dodd, and R. Little, *Spectrochim. Acta*, 1962, **18**, 1005.

⁷ H. J. Emeléus and B. W. Tattershall, *Z. anorg. Chem.*, 1964, **327**, 147.

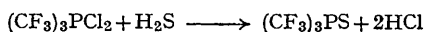
1132. Tris(trifluoromethyl)phosphine Sulphide, (CF₃)₃PS.

By R. G. CAVELL and H. J. EMELÉUS.

TRISTRIFLUOROMETHYLPHOSPHINE did not react with sulphur¹ even after three days at 180°, in contrast to the ease with which tertiary alkyl phosphines add sulphur² to yield the quinquevalent trialkylphosphine sulphides, R₃PS. Tris(trifluoromethyl)phosphine sulphide has now been prepared by first oxidising the tristrifluoromethylphosphine with chlorine, and treating the resultant tristrifluoromethyldichlorophosphorane with silver sulphide:



Heating to 60° for several days is required to consume all the dichlorophosphorane. The resulting phosphine sulphide was contaminated with small amounts of tristrifluoromethylphosphine, probably due to reduction of either the dichlorophosphorane or the phosphine sulphide by traces of elemental silver in the silver sulphide. This difficultly separable impurity was best removed by a fractional codistillation technique.³ Tris(trifluoromethyl)phosphine sulphide was also obtained from the room-temperature reaction of tristrifluoromethyldichlorophosphorane with hydrogen sulphide:



Tris(trifluoromethyl)phosphine sulphide is a volatile, white solid, which melts under autogeneous pressure at 6.5–7.2°. The vapour pressure of the solid, measured from –9 to 7°, obeys the linear equation: $\log_{10} p$ (mm.) = 8.478 – 1763/T, which gives a heat of sublimation of 8070 cal./mole. The vapour pressure of the liquid (9–35°) obeys the linear equation: $\log_{10} p$ (mm.) = 7.615 – 1518/T, which gives an extrapolated boiling point of 47.4°, a heat of vaporization of 6950 cal./mole, and a Trouton constant of 21.7.

Alkaline hydrolysis liberated two moles of fluoroform per mole of tris(trifluoromethyl)phosphine sulphide, and is thus analogous to the hydrolysis of the corresponding oxygen compound, (CF₃)₃PO, which also liberated two-thirds of its trifluoromethyl groups on hydrolysis,⁴ the third remaining attached to the phosphorus as the stable trifluoromethylphosphonic acid, CF₃•PO(OH)₂. The similarity in behaviour suggests that (CF₃)₃PS may yield the related sulphur-containing acid, CF₃•PS(OH)₂, on hydrolysis.

The fluorine-19 nuclear magnetic resonance spectrum of tris(trifluoromethyl)phosphine sulphide consists of a simple doublet, with an average chemical shift of 65.7 p.p.m. to high field of CCl₃F, arising from spin–spin coupling of the phosphorus with the equivalent fluorine nuclei. The coupling constant (J_{PCF_3}) was 108.7 c./sec., similar to the value of 113.4 observed⁵ for the related phosphine oxide, (CF₃)₃PO, and both values are distinctly larger than the observed range of P–CF₃ coupling constants for tervalent trifluoromethyl phosphorus compounds.⁵

The infrared spectrum has four strong bands in the carbon–fluorine stretch region (1100–1200 cm.⁻¹), and the pattern is similar to that for tristrifluoromethylphosphine which has the same molecular symmetry (C_{3v}). The medium intensity band at 750 cm.⁻¹ is probably the CF₃ deformation band. A strong band appears at 800 cm.⁻¹ for the phosphine sulphide which is not present for tristrifluoromethylphosphine, and is probably the P=S stretch. This absorption is found at 874 for thiophosphoryl fluoride,⁶ 753 for thiophosphoryl chloride,⁷ and at 718 cm.⁻¹ in thiophosphoryl bromide,⁸ so a value of 800 cm.⁻¹ for (CF₃)₃PS is not unexpected in view of the electronegativity of the CF₃ group.

¹ F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J.*, 1953, 1565.

² L. Maier, *Prog. Inorg. Chem.*, 1963, 5, 27.

³ G. H. Cady and D. P. Siegarth, *Analyt. Chem.*, 1959, 31, 618.

⁴ R. C. Paul, *J.*, 1955, 574.

⁵ K. J. Packer, *J.*, 1963, 960.

⁶ J. S. Ziomek, E. A. Piotrowski, and E. N. Walsh, *Phys. Rev.*, 1955, 98, 243.

⁷ H. Gerding and R. Westrik, *Rec. Trav. chim.*, 1942, 61, 842.

⁸ M. L. Delwaille and F. Francois, *Compt. rend.*, 1948, 226, 896.

Experimental.—Standard vacuum techniques were used throughout. Tristrifluoromethyl-dichlorophosphorane was prepared by the addition of one mole of chlorine to one mole of tristrifluoromethylphosphine.⁹ The product melted at 24° (lit.,¹⁰ 25°).

Reaction of tristrifluoromethyldichlorophosphorane with silver sulphide. Tristrifluoromethyl-dichlorophosphorane was treated in a sealed tube with silver sulphide for 1 week at room temperature. Fractionation of the volatile products indicated that unreacted dichlorophosphorane remained, so the reaction was continued for a further 3 days at 60°. Fractionation of the volatile products then yielded a material with *M*, 264 (Calc. for C₃F₉PS, 270), collected at -96°. Further vacuum-fractionation was without effect on the molecular weight, but fractional codistillation³ indicated the presence of two impurities, one of which was tristrifluoromethylphosphine. The majority of the material was identified as *tris(trifluoromethyl)phosphine sulphide* by molecular weight and analysis (Found: P, 11.1; S, 11.85%; *M*, 270.5. C₃F₉PS requires P, 11.5; S, 11.85%; *M*, 270). Alkaline hydrolysis of 1.23 mmoles (0.333 g.) of the compound yielded 2.38 mmoles of fluoroform, corresponding to 64.5% of the CF₃ groups in the molecule.

Reaction of hydrogen sulphide with tristrifluoromethyldichlorophosphorane. About 1 mmole of tristrifluoromethyldichlorophosphorane was treated with a small excess of hydrogen sulphide at room temperatures for 3 weeks. Vacuum-fractionation of the volatile products yielded slightly impure *tris(trifluoromethyl)phosphine sulphide*, identified from its infrared spectrum and molecular weight (Found: *M*, 265), and hydrogen chloride, also identified from infrared and molecular weight (Found: *M*, 37.2). The latter was contaminated with traces of silicon tetrafluoride, fluoroform, and (CF₃)₃PS. Titration of the chloride in the latter fraction indicated the presence of 2.1 mmoles of HCl. No hydrogen sulphide was recovered, even though taken in excess, as indicated by the formation of a white precipitate with silver nitrate in the titration.

Properties of tris(trifluoromethyl)phosphine sulphide. (a) *Vapour pressure.* The vapour pressure was measured from -9° to 35° in an all-glass spiral gauge microtensimeter. The results for the solid (-9° to 7°) are:

<i>t</i> (°C)	0.6	-9.1	-7.0	-4.8	-1.4	0.6	1.7	4.1	6.9	0.3
<i>p</i> (mm.)	110.5	63.77	72.54	80.62	99.34	110.55	115.90	132.43	153.54	110.0

and for the liquid (9 to 35°):

<i>t</i> (°C) . .	9.0	11.6	14.6	17.6	19.5	21.9	23.3	26.5	31.3	34.9	25.2	21.4
<i>p</i> (mm.)	170.33	190.64	219.30	248.79	269.99	296.64	314.54	357.23	428.58	490.69	340.45	290.41

(c) *Spectra.* The n.m.r. spectrum was measured on a sample contained in a 5-mm. tube with CCl₃F internal standard and solvent, at 40 Mc./sec. on a Varian instrument.⁵ The infrared spectrum, measured on a Perkin-Elmer Infracord, showed bands at 2295w, 1295m, 1280sh, 1220vs, 1205vs, 1175vs, 1150s, 1130sh, 1030vw, 800s (P-S), 732m, 580sh, 565m, 500sh, 483ms.

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[Received, August 25th, 1964.]

⁹ H. J. Emeléus, R. N. Haszeldine, and R. C. Paul, *J.*, 1955, 563.

¹⁰ H. J. Emeléus and G. S. Harris, *J.*, 1959, 1494.

1133. *Alkali-metal Nitrosyls.*

By N. GEE, D. NICHOLLS, and (Miss) V. VINCENT.

JOANNIS¹ was the first to observe the absorption of nitric oxide by solutions of alkali metals in ammonia. Subsequently, other workers^{2,3} established the empirical formula MNO

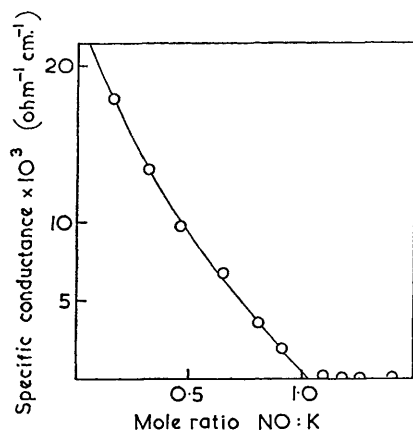
¹ J. A. Joannis, *Ann. Chim. Phys.*, 1906, 7, 84.

² E. Zintl and A. Harder, *Ber.*, 1933, 66, 760.

³ J. H. Frazer and N. O. Long, *J. Chem. Phys.*, 1938, 6, 462.

(M = Na or K) for the precipitates formed, and some evidence has been presented to support their formulation as nitrosyls, M^+NO^- . Despite the interesting implications of such a structure, the chemical and physical properties of these compounds have remained largely unexamined. We thus set out to study some of their reactions, and to examine their infrared spectra. During the course of our investigations, however, Goubeau and Laitenberger⁴ published the infrared spectrum of the sodium salt, and concluded that it contains the dimeric anion $N_2O_2^{2-}$, not being identical with the hyponitrite ion, but probably being the *cis*-form (C_{2v} symmetry).

A conductimetric titration of nitric oxide against a solution of potassium in ammonia at -63° (see the Figure) shows a sharp break in specific conductance at the 1:1 equivalence point. The curve for sodium is very similar. The conductance of the metal solution drops sharply as the white precipitate of $(KNO)_n$ separates, until, at the 1:1 point, the solution is decolorised and the conductance thereafter remains constant at a very low value. Isolation of the precipitates yielded amorphous diamagnetic solids which were indefinitely stable in



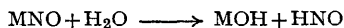
Conductimetric titration of nitric oxide against potassium in liquid ammonia.

dry air. Tensimetric studies, in liquid ammonia at -37° , on $(NaNO)_n$ and on sodium hyponitrite showed that neither compound formed any ammoniate at this temperature. Both the sodium and potassium nitrosyls showed surprising thermal stability. Slow decomposition of the sodium salt begins *in vacuo* at 155° ; after four hours at 300° , it had decomposed by some 60% according to:

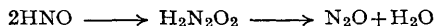


The potassium salt, however, showed only 7% decomposition in a comparable time at 300° . This thermal behaviour must be contrasted with that of sodium hyponitrite, which decomposes suddenly and explosively at $260\text{--}265^\circ$, yielding sodium nitrite, sodium oxide, and nitrogen.⁵

Both compounds react with protonic solvents, evolving nitrous oxide (Table 1). The initial reaction with water is probably (writing monomeric formulae for simplicity):



followed by



the relative amounts of nitrous oxide and hyponitrite ion produced depending upon the alkalinity of the solution.⁶ In the presence of acids, the hyponitrite will decompose so that,

⁴ J. Goubeau and K. Laitenberger, *Z. anorg. Chem.*, 1963, **320**, 78.

⁵ J. R. Partington and C. C. Shah, *J.*, 1931, 2071.

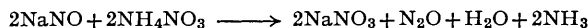
⁶ C. C. Addison and J. Lewis, *Quart. Rev.*, 1955, **9**, 130.

TABLE 1.

Compound	Temp. (time) (°) (hr.)	Reactant	Mol. wt. of evolved gas*	% Reaction, based on N ₂ O evolution
NaNO	-78(12), -37(2)	NH ₄ Cl in NH ₃	42	22
NaNO	-78(60), -37(2)	NH ₄ Cl in NH ₃		33
NaNO	-37(1)	NH ₄ NO ₃ in NH ₃	39	25
NaNO	-78(12), -37(2)	NH ₄ NO ₃ in NH ₃		32
NaNO	-78(72)	NH ₄ NO ₃ in NH ₃		98
NaNO	20(12)	H ₂ O	47	69
NaNO	20(12)	Dil. CH ₃ CO ₂ H	47	86
KNO	20(12)	Glac. CH ₃ CO ₂ H	43	95
KNO	100(1)	0·1N-H ₂ SO ₄		98

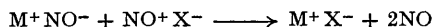
* In all of the reactions, the infrared spectrum of the gaseous product showed N₂O only.

with dilute sulphuric acid and glacial acetic acid, virtually all the nitrous oxide is recovered. The reaction of (NaNO)_n with ammono-acids appears to be slow at -78° and at -37°. Thus the reaction



proceeds to completion only after three days at -78°. This slow liberation of nitrous oxide is undoubtedly due to the low rate of decomposition of the hyponitrous acid at the low temperatures employed. Variation of the concentration of the ammono-acid had negligible effect upon the rate of evolution of nitrous oxide. From the reactions of these "nitrosyls" in protonic solvents, it is apparent that they do not possess the *trans*-hyponitrite anion. Sodium hyponitrite, for instance, is only partly decomposed by dilute hydrochloric and sulphuric acids, and yields a mixture of nitrous oxide, nitric oxide, and nitrogen.⁵

In an attempt to distinguish between a hyponitrite anion (with a structure other than *trans*) and the nitrosyl anion, we have studied the reactions of the "nitrosyls" with solutions containing the nitrosonium ion (NO⁺). The expected reaction of a nitrosyl would be:



i.e., the liberation of two moles of nitric oxide per mole of nitrosyl. In the reaction of (NaNO)_n or (KNO)_n with nitrosyl chloride alone, nitric oxide was indeed evolved, but, despite long reaction times at 0°, the yield of nitric oxide varied between 0·6 and 1·1 moles per mole of (MNO)_n in different experiments. The addition of iron(III) or aluminium(III) chloride to the nitrosyl chloride (with consequent formation of NO⁺MCl₄⁻ salts), prior to reaction with the "nitrosyls," did not significantly alter the yields of nitric oxide. In all the experiments in nitrosyl chloride, however, nitrous oxide was also evolved (in an approximate ratio N₂O:NO = 1/5), as well as traces of nitrogen. The weight of the residue, after the removal of all volatile materials *in vacuo*, was always larger than that expected for MCl, and qualitative tests established the presence of nitrate, but not nitrite, ions in the residues. Sodium hyponitrite behaved in a similar way towards nitrosyl chloride, liberating 0·93 mole of gas per 0·5 mole of Na₂N₂O₂, the gas once again being a mixture of nitric and nitrous oxides.

TABLE 2.

Infrared spectra, in the 5000—700 cm.⁻¹ region, of alkali-metal "nitrosyls."

NaNO	KNO	Assignment ⁴
1312m	1304m	ν(N=N)
1042s	1057s	ν _{asym} (N-O)
837s	857s	ν _{sym} (N-O)

The infrared spectra of the "nitrosyls" are recorded in Table 2. The data for (NaNO)_n agree well with those of Goubeau and Laitenberger.⁴ As well as the three broad absorptions listed in Table 2, some of the spectra showed absorptions due to nitrous oxide (at 2224, 1301, and 1287 cm.⁻¹) which would be formed by hydrolysis in the mull. Hieber and Jahn⁷

⁷ W. Hieber and A. Jahn, *Z. Naturforsch.*, 1958, **13b**, 195.

attributed the 2228 cm.^{-1} absorption in NaNO and $\text{Ba}(\text{NO})_2$ to the NO^- ion. The NO^- stretching frequency, however, is expected⁸ to be several-hundred wave-numbers lower than that of nitric oxide itself (1883 cm.^{-1}), so that the 2228 cm.^{-1} absorption is more likely to be due to the ν_3 mode in nitrous oxide.

Thus, while the reactions of the alkali-metal "nitrosyls" show that they are not *trans*-hyponitrites, their infrared spectra rule out their possible formulation as ionic nitrosyls, and we agree with other workers⁴ that they are best formulated as *cis*-hyponitrites. The NO^- ion has an even number of electrons, and may be either diamagnetic or paramagnetic (isoelectronic with O_2); thus, the diamagnetic properties of these compounds do not help in a consideration of their formulation as M^+NO^- .

Experimental.—Nitric oxide,⁹ nitrosyl chloride,¹⁰ and sodium hyponitrite¹¹ were prepared by standard methods. Ammonia was dried over sodium. All gaseous reagents and reaction products were purified by fractionation and/or chemically, and their volumes measured in a calibrated U-tube attached to a mercury manometer.

Reactions, tensimetric studies, and thermal decompositions were carried out in all-glass high-vacuum equipment. The infrared spectra of the "nitrosyls" were measured as mulls in Nujol (dried over sodium) and as KBr discs, on a Grubb Parsons double-beam instrument. The three broad peaks in the spectra of the "nitrosyls" disappeared upon exposing the compounds to moist air for a few minutes, confirming that they were due to the reactive anion.

Conductimetric titrations in liquid ammonia were carried out as follows. Nitrogen was passed through a solution of sodium in liquid ammonia at -63° , to remove reactive impurities. This gas was then used to sweep measured volumes of nitric oxide very slowly through the alkali-metal solution (*ca.* 0.2 g. of alkali metal in 50 ml. of liquid ammonia) *via* a fine glass sinter. The conductance was recorded when no further change occurred, and a further volume of nitric oxide was then passed. The reaction vessel was continually thermostated at -63° . The electrodes were of bright platinum; these caused no decomposition of the alkali-metal solution over a period of eight hr. at -63° . At the end of the titration, the white precipitate was filtered off, washed with several portions of liquid ammonia, and, finally, kept *in vacuo* for several hours at 20° prior to removal from the apparatus in a current of dry nitrogen. The potassium compound gave an analysis in accord with the formula KNO [Found: K (as the tetraphenylborate), 56.3; NH_3 , 0.20. Calc. for KNO : K, 56.5; NH_3 , 0.0%]. The diamagnetism of both compounds was confirmed qualitatively, by using electron spin resonance and Gouy magnetic methods. The "nitrosyls" were insoluble in all solvents with which they did not react, and reacted explosively with thionyl chloride and liquid sulphur dioxide.

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⁸ F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, 1962, p. 630.

⁹ J. D. Ray and R. A. Ogg, *J. Amer. Chem. Soc.*, 1956, **78**, 5993.

¹⁰ J. R. Morton and H. W. Wilcox, *Inorg. Synth.*, **4**, 48.

¹¹ L. W. Jones and A. W. Scott, *J. Amer. Chem. Soc.*, 1924, **46**, 2172.

1134. Spin-Spin Coupling with the Hydroxyl Protons of Alcohols.

By J. MALCOLM BRUCE and P. KNOWLES.

THE effects of spin-spin coupling between the hydroxyl and α -protons of simple alcohols have been detected for rigorously dried¹ samples, and for solutions in acetone² and dimethyl sulphoxide^{2,3} with which hydrogen bonding may occur. These effects are readily observed at 60 Mc./sec. for solutions in carbon tetrachloride, chloroform, and benzene if traces of acid are removed by distillation from solid sodium carbonate.⁴

¹ D. W. Moore, *Mellon Letters*, 1963, No. 52, p. 12; E. Krakower and L. W. Reeves, *Trans. Faraday Soc.*, 1963, **59**, 2528.

² D. E. McGreer and M. M. Mocek, *J. Chem. Educ.*, 1963, **40**, 358, and references therein.

³ O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, 1964, **86**, 1256.

⁴ J. M. Bruce and P. Knowles, *Proc. Chem. Soc.*, 1964, 294.

At 40° the spectrum of methanol so distilled consisted of two singlets, but a 26% w/v solution in carbon tetrachloride showed broad bands which became clearly resolved into a quartet and a doublet when the solution was diluted to 13%; with further dilution the quartet moved to higher field. The multiplets collapsed when a trace of hydrogen chloride was added. Well-resolved multiplets were observed even for 26% w/v solutions in chloroform or deuteriochloroform, and the position of the quartet was more sensitive to changes of concentration, suggesting solute-solvent interaction.⁵ The expected splitting patterns were readily obtained for solutions of ethanol and propan-2-ol in carbon tetrachloride.

For 13% w/v solutions of methanol in either carbon tetrachloride or benzene the hydroxyl resonances moved to higher field as the temperature was raised, and the multiplets persisted up to 80°, the highest temperature used.

Experimental.—Borosilicate glassware was used throughout, and was washed with distilled water, then with acetone, and dried in warm air. Solvents and solutes were fractionated through a short Dufton column and samples (5 c.c.) were then distilled from powdered anhydrous sodium carbonate (10 mg., "AnalaR"), the middle fraction (3 c.c.) being used. Precautions to exclude air or moisture were not taken. Spectra were measured with a Varian A-60 spectrometer for solutions contained in tubes closed by Polythene caps. Tetramethylsilane was used as an internal standard.

Methanol. The hydroxyl quartet and methyl doublet ($J = 5$ c./sec.) were observed at all the following concentrations (% w/v) except those for which their chemical shifts were similar. (a) At 40° in CCl_4 : 13, 6, 2%, τ_{OH} 5.6, 6.0, 7.0, τ_{Me} 6.63, 6.63, 6.60, respectively. (b) At 40° in CHCl_3 or CDCl_3 : 26, 12, 6, 3%, τ_{OH} 5.7, 6.5, 7.3, 8.1, τ_{Me} 6.58, 6.52, 6.55, 6.52, respectively. The multiplets collapsed after the solutions had been exposed to daylight for a few minutes. (c) At 40° in C_6H_6 : 12, 5, 2%, τ_{OH} 6.0, 6.8, 8.0, τ_{Me} 6.70, 6.80, 6.85, respectively. (d) For the temperatures 38, 44, 51, 60, 73, 80°: 13% in CCl_4 , $\Delta_{\text{Me}} - \Delta_{\text{OH}} = -64, -53, -44, -32, -15$, ca. -2 c./sec., respectively; 13% in C_6H_6 , $\Delta_{\text{Me}} - \Delta_{\text{OH}} = -41, -29, -17, 0, +21, +33$ c./sec., respectively.

Ethanol. At 40°, 37% in CCl_4 : τ_{OH} 5.1, triplet, $J = 5$ c./sec.; τ_{CH_2} 6.40, octet; τ_{Me} 8.83, triplet, $J = 7$ c./sec.

Propan-2-ol. At 40°, 48% in CCl_4 : τ_{OH} 5.3, doublet, $J = 4.5$ c./sec.; τ_{CH} 6.07, decet; τ_{Me} 8.85, doublet, $J = 6.5$ c./sec.

We thank Miss M. McIntyre and Mr. R. A. Dwek for the measurement of spectra, and the D.S.I.R. for the award of a research studentship (to P. K.).

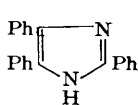
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER. [Received, September 3rd, 1964.]

⁵ Cf. W. G. Schneider, *J. Phys. Chem.*, 1962, **66**, 2653.

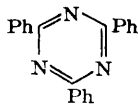
1135. The Thermal Decomposition of Benzyl Azide in Solution.

By B. COFFIN and R. F. ROBBINS.

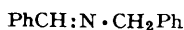
WE find that when benzyl azide is heated in boiling diphenyl ether until there is no more evolution of nitrogen, 2,4,5-triphenylimidazole (lophine) (I), 2,4,6-triphenyl-1,3,5-triazine (kyaphenine) (II), *N*-benzylidenebenzylamine (III), and a red (polymeric?) gum are formed. This result was sufficiently different from the reported¹ decomposition of benzyl azide



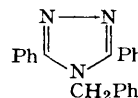
(I)



(II)



(III)



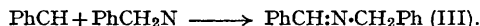
(IV)

¹ T. Curtius and G. Ehrhart, *Ber.*, 1922, **55**, 1559.

in *p*-xylene to cause us to re-investigate the latter work. Unlike Curtius and Ehrhart we found no 2,3,5,6-tetraphenylpyrazine (amaron) or tribenzylamine. Instead we isolated the anil (III) (obtained once by the German workers), kyaphenine (II), and polymer. Kyaphenine we believe was obtained by Curtius and Ehrhart but was incorrectly described by them as 4-benzyl-3,5-diphenyl-1,2,4-triazole (IV) (which has m. p. 219°² and not 229°). We also suggest that kyaphenine is the "unknown" of m. p. 229° isolated together with lophine when benzyl azide is heated in diethyl succinate.² We find no formation of lophine when *p*-xylene (at 183° for 10 hr.) is used as solvent, but at higher temperatures (~300° for 3 hr.) in this solvent lophine is formed in substantial amounts, together with kyaphenine (II), anil (III), and polymer. Curtius and Ehrhart describe no compound that could have been lophine. This is surprising, for their description of *NN'*-dibenzylbenzamidine corresponds to 4,5-dihydro-2,4,5-triphenylimidazole (amarine) (V), m. p. 106°, and ready oxidation³ of amarine to lophine is to be expected. Such oxidation would explain the absence of amarine in our own work. *NN'*-Dibenzylbenzamidine as described by Curtius and Ehrhart has m. p. 106° (picrate 234°), but later preparations of this amidine gave picrates of m. p. 146—147° and 145°.⁴

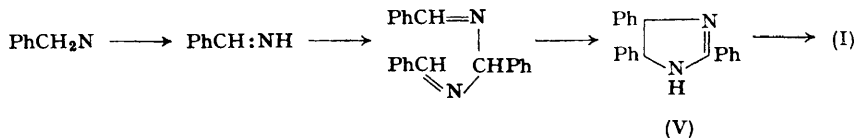
Amarine is the principal product (29%) of the vapour-phase pyrolysis² (360°/0.1 mm.; N₂ as diluent) of benzyl azide. Presumably reaction conditions inhibit complete dehydrogenation to lophine. However, some lophine (12%) is obtained together with *N*-benzylideneaniline (20%). It is of interest that Kreher and Kühling² postulate *N*-methylenaniline as an intermediate in the formation of *N*-benzylideneaniline. They suggest that the intermediate is formed by the rearrangement of an azene, PhCH₂N, produced by the elimination of nitrogen from the azide. Possibly a degree of phenyl participation in the loss of nitrogen should not be neglected. However, we were unable to detect any rearrangement product upon decomposing benzyl azide in either diphenyl ether or *p*-xylene, although such reaction might have been obscured by polymer formation. We have previously noted such rearrangements on thermally decomposing 2-azidomethyl- and 2,2'-diazidomethyl-biphenyl in diphenyl ether.⁵

This re-examination of the thermal decomposition of benzyl azide in *p*-xylene reveals a pattern different from that reported by Curtius and Ehrhart and yet related to its decomposition in diphenyl ether or in the vapour phase. These results, however, do not necessarily vitiate the suggestion of Curtius and Ehrhart that species such as PhCH₂N and PhCH play a part in product formation. PhCH could derive from PhCH₂N₃ by the elimination of hydrazoic acid. As evidence for this hydrazoic acid was detected, although not in stoichiometric amounts, in the exit gases from the pyrolysis of benzyl azide in diphenyl ether. The two species mentioned could provide one explanation of anil (III) formation; thus,



The absence of other coupling reactions might be due either to polymerisation or to the practical difficulties of isolating such products. An alternative route to (III) involves attack of PhCH upon the azide.

The species PhCH₂N may have an important role. Isomerisation to benzylideneamine and then further reaction through hydrobenzamide could give³ amarine (V) and hence lophine (I).



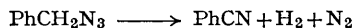
² R. Kreher and D. Kühling, *Angew. Chem., Internat. Edn.*, 1964, **3**, 309.

³ H. H. Strain, *J. Amer. Chem. Soc.*, 1927, **49**, 1558.

⁴ F. L. Pyman, *J.*, 1923, **123**, 3373; P. Oxley and W. F. Short, *J.*, 1947, 388.

⁵ B. Coffin and R. F. Robbins, *J.*, 1965, 1252.

Moreover, trimerisation of benzylideneamine and subsequent dehydrogenation to give kyaphenine (II) seems very likely. The possible formation of kyaphenine by trimerisation of benzonitrile seems not to take place. By analogy with CH_3N_3 (which gives HCN)⁶ benzonitrile could possibly arise by the decomposition



However, the gas obtained on decomposition of benzyl azide in diphenyl ether was shown by mass spectrometry to contain no hydrogen.

Kyaphenine on reduction gives lophine.⁷ This triazine may thus provide a source of the imidazole (with amarine as a possible reducing agent?).

Experimental.—Pyrolysis of the azides. (a) After heating (248–250°) benzyl azide¹ (3.0 g.) in diphenyl ether (10 ml.) until there was no further evolution of nitrogen the solvent was removed under a vacuum, to give a red gum. Trituration with light petroleum (b. p. 60–80°) (25 ml.) gave a beige product (1.2 g.). Crystallisation from glacial acetic acid (10 ml.) gave 2,4,6-triphenyl-1,3,5-triazine (0.13 g.) as shown by comparison with an authentic⁷ sample (infrared absorption, and m. p. and mixed m. p. 232°). Evaporation of the acetic acid filtrate and recrystallisation of the residue from ethanol gave 2,4,5-triphenylimidazole (0.94 g.), m. p. 284°, undepressed on admixture with an authentic⁸ sample (infrared spectra also identical).

On evaporation of the initial light-petroleum filtrate, a red gum was obtained. On distillation, this gave polymer (0.68 g.), b. p. 260–280°/2 mm., and *N*-benzylidenebenzylamine (0.11 g.), b. p. 130°/2 mm. (lit.,⁹ 143°/5 mm.). The anil was characterised by hydrolysis (5*N*- H_2SO_4) and identification of the fragments as benzaldehyde (2,4-dinitrophenylhydrazone, m. p. 237°) and benzylamine (benzoate, m. p. 106°, and toluene-*p*-sulphonate, m. p. 116°).

(b) Benzyl azide (4.0 g.) in *p*-xylene (15 ml.) after 10 hr. at 183° (sealed glass vessel) gave, after removal of the solvent, a gum. Trituration with warm methanol yielded 2,4,6-triphenyl-1,3,5-triazine (0.47 g.). The methanol extract on distillation then gave benzylidenebenzylamine (0.7 g.) and polymer (1.1 g.).

(c) In *p*-xylene (75 ml.) for 3 hr. at 190° (stainless steel autoclave), benzyl azide (15 g.) similarly gave the triazine (3.2 g.), anil (4.3 g.), and polymer (1.7 g.).

After 280° for 3 hr. a similar solution of azide in *p*-xylene gave, on cooling, 2,4,5-triphenylimidazole (2.7 g.). From the gum remaining on evaporation of the *p*-xylene was isolated the triazine (2.3 g.), anil (1.0 g.), and polymer (3.1 g.).

We are indebted for an award (to B. C.) from Hertfordshire County Education Authority.

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⁶ F. O. Rice and C. J. Grelecki, *J. Phys. Chem.*, 1957, **61**, 830.

⁷ A. H. Cook and D. G. Jones, *J.*, 1941, 278.

⁸ D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, 1937, **2**, 319.

⁹ G. H. Coleman and C. S. Nicholopoulos, *Proc. Iowa Acad. Sci.*, 1942, **49**, 286.

1136. *The Action of Hydrazine Hydrate on Rhodanines.*

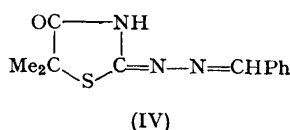
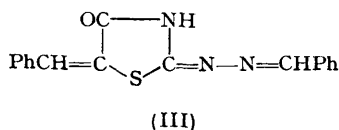
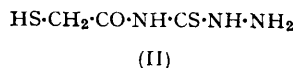
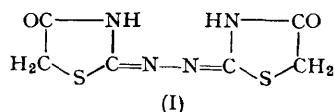
By J. S. DAVIDSON.

DIFFERING accounts^{1,2} have been given of the action of hot aqueous hydrazine hydrate on rhodanine (4-oxothiazole-2-thione). Whereas Taniyama and Yasui¹ obtained the azine (I), together with an unidentified product of m. p. 224–225°, in a recent patent² the reaction is claimed to yield 4-(mercaptoacetyl)thiosemicarbazide (II), although no m. p. or analysis is given.

¹ H. Taniyama and B. Yasui, *J. Pharm. Soc. Japan*, 1955, **75**, 200 (*Chem. Abs.*, 1956, **50**, 1777).

² A. Russ, G.P. 1,119,251/1961.

It has now been shown that, in cold ethanol, the reaction takes the latter course, affording the thiosemicarbazide (II), without evidence of the formation of the azine (I) or the substance of m. p. 224—225°. The benzylidene derivative of (II) decomposed above the m. p. with the formation of 5-benzylidenethiazolidine-2,4-dione 2-benzylidenehydrazone (III).



In 5-substituted rhodanines,³ the thiazolidine ring is more stable. Thus, 5,5-dimethylrhodanine, condensed with hydrazine hydrate and then reacted with benzaldehyde to afford 5,5-dimethylthiazolidine-2,4-dione 2-benzylidenehydrazone (IV). The same compound was obtained by condensing benzaldehyde thiosemicarbazone with ethyl α -bromoisobutyrate, using sodium ethoxide⁴ in absolute ethanol. The structure (IV) was confirmed by hydrolysis with boiling hydrochloric acid to give benzaldehyde, hydrazine hydrochloride, and 5,5-dimethylthiazolidine-2,4-dione.

Experimental.—4-(Mercaptoacetyl)thiosemicarbazide. Rhodanine (7 g.), suspended in cold ethanol (50 ml.), was treated with hydrazine hydrate (4 ml.). After 20 min., 4-(mercaptoacetyl)thiosemicarbazide (7.6 g., 92%) was filtered off. It was recrystallised from ethanol, and had m. p. 137—138° (decomp.) (Found: N, 25.45; S, 38.45. $\text{C}_3\text{H}_7\text{N}_3\text{OS}_2$ requires N, 25.45; S, 38.8%). The benzylidene derivative had m. p. 154° (decomp.) (Found: C, 47.4; H, 4.7; N, 16.4, S, 25.2. $\text{C}_{10}\text{H}_{11}\text{N}_3\text{OS}_2$ requires C, 47.5; H, 4.3; N, 16.6; S, 25.3%). On heating the benzylidene derivative in an oil-bath to 160—170° for 5 min., hydrogen sulphide was evolved and the melt resolidified. The solid was washed with hot ethanol, and then recrystallised from boiling pyridine, to give yellow felted needles, m. p. 289—293° (decomp.) (Found: C, 66.5; H, 4.4; N, 13.4; S, 10.4. Calc. for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{OS}$: C, 66.5; H, 4.25; N, 13.7; S, 10.4%). The infrared spectrum was identical with that of an authentic specimen of the azine (III), m. p. 291—295° (decomp.), prepared as previously described.⁵

5,5-Dimethylthiazolidine-2,4-dione 2-benzylidenehydrazone. 5,5-Dimethylrhodanine (2.12 g.) in ethanol (20 ml.) was treated with hydrazine hydrate (1.45 ml.). After 1 hr., the solvent was taken off at room temperature under a vacuum. The oily residue, dissolved in ethanol and then treated with benzaldehyde (4 g.) and a few drops of hydrochloric acid, yielded 5,5-dimethylthiazolidine-2,4-dione 2-benzylidenehydrazone (86%), m. p. 247° (from ethanol or pyridine) (Found: C, 58.7; H, 5.55; N, 16.8; S, 13.1. $\text{C}_{12}\text{H}_{13}\text{N}_3\text{OS}$ requires C, 58.3; H, 5.25; N, 17.0; S, 12.95%).

In the same way, 5-methylrhodanine afforded 5-methylthiazolidine-2,4-dione 2-benzylidenehydrazone (20%), m. p. 240—241°. The infrared spectrum was identical with that of an authentic specimen.⁴ The low yield is undoubtedly due to side-reactions. Thus, 5-methylrhodanine (4.46 g.) in ethanol (25 ml.) was treated with hydrazine hydrate (4 ml.), the mixture taken to dryness at room temperature, and the residue washed with a little ethanol, to yield thiosemicarbazide (0.66 g., 22%), m. p. 179—180°, identified by means of its benzylidene derivative, m. p. 162°, and its infrared spectrum.

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³ N. M. Turkevich and B. I. Shvydkii, *Ukrain. khim. Zhur.*, 1952, **18**, 513.

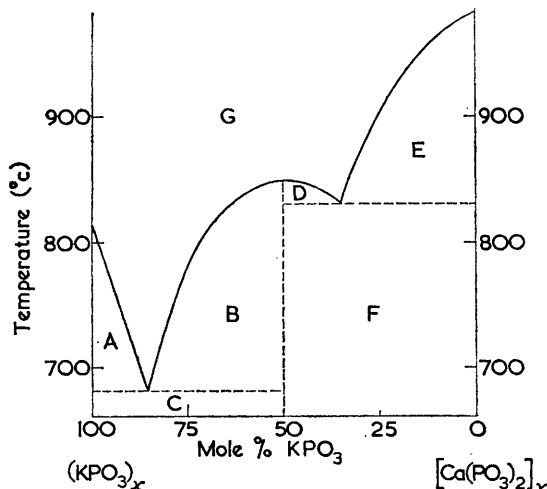
⁴ F. J. Wilson and R. Burns, *J.*, 1922, **121**, 870; 1923, **123**, 799.

⁵ N. M. Turkevich and E. V. Vladzimirskaya, *J. Gen. Chem. (U.S.S.R.)*, 1958, **28**, 1260.

1137. The System, Potassium Metaphosphate–Calcium Metaphosphate.

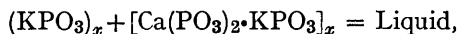
By J. B. GILL and R. M. TAYLOR.

THE system potassium metaphosphate $(\text{KPO}_3)_x$ –calcium metaphosphate $[\text{Ca}(\text{PO}_3)_2]_x$ (the term "metaphosphate" applies here to the long-chain form of polyphosphate) has been studied over the whole range of compositions, and the existence of a binary compound calcium potassium metaphosphate, $[\text{Ca}(\text{PO}_3)_2 \cdot \text{KPO}_3]_x$, has been established. The phase-relationship diagram, based on the heating-curve results of Table 1, is shown in the Figure.



Phase diagram for the system $(\text{KPO}_3)_x$ – $[\text{Ca}(\text{PO}_3)_2]_x$; A, liquid + $(\text{KPO}_3)_x$; B and D, liquid + $[\text{Ca}(\text{PO}_3)_2 \cdot \text{KPO}_3]_x$; C, solid $[\text{KPO}_3]_x$ + solid $[\text{Ca}(\text{PO}_3)_2 \cdot \text{KPO}_3]_x$; E, liquid + $[\text{Ca}(\text{PO}_3)_2]_x$; F, solid $[\text{Ca}(\text{PO}_3)_2 \cdot \text{KPO}_3]_x$ + solid $[\text{Ca}(\text{PO}_3)_2]_x$; G, liquid.

Potassium metaphosphate is the stable crystalline phase in contact with liquid from 100 to $86(\pm 1)$ mole % of $(\text{KPO}_3)_x$. The binary compound of composition $[\text{Ca}(\text{PO}_3)_2 \cdot \text{KPO}_3]_x$ melts congruently at $849.5(\pm 2)^\circ$, and this is the stable crystalline phase in contact with liquid from its eutectic with $(\text{KPO}_3)_x$ at $683(\pm 3)^\circ$ and $86(\pm 1)$ mole % of $(\text{KPO}_3)_x$, where the equilibrium is



to its eutectic with $[\text{Ca}(\text{PO}_3)_2]_x$ at $832(\pm 2)^\circ$ and $36(\pm 0.5)$ mole % of $(\text{KPO}_3)_x$, where the equilibrium is

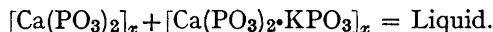


TABLE 1.

The melting points in the system $(\text{KPO}_3)_x$ – $[\text{Ca}(\text{PO}_3)_2]_x$.

Mole % KPO_3	100	95.0	90.0	85.0	80.0	66.7	55.5	53.8
M. p.	813°	760.5	718.5	695.5	713.5	819	846	848
Mole % KPO_3	50.0	46.1	44.4	40.0	36.0	33.3	16.7	0.0
M. p.	849.5°	846	843.5	838.5	833	848	938.4	977

X-Ray powder diffraction patterns of most of the samples indicated that only three stable crystalline phases, $(\text{KPO}_3)_x$, $[\text{Ca}(\text{PO}_3)_2]_x$, and $[\text{Ca}(\text{PO}_3)_2 \cdot \text{KPO}_3]_x$, exist in the system. Table 2 shows the d -spacings for the new binary compound $[\text{Ca}(\text{PO}_3)_2 \cdot \text{KPO}_3]_x$, together with

TABLE 2.

d -Spacings for $[\text{KPO}_3 \cdot \text{Ca}(\text{PO}_3)_2]_x$ on Cu $K\alpha$ -radiation.

d (Å)	5.9	5.2	3.90	3.23	2.95	2.85	2.59	2.23	2.18	2.06	1.96	1.95
Intensity	10	15	100	35	10	40	5	4	2	3	3	3

their relative intensities. The d -spacings and intensities for the end-members were in agreement with the values obtained by Morey^{1,2} for $(\text{KPO}_3)_x$ and α - $[\text{Ca}(\text{PO}_3)_2]_x$. No evidence for the existence of β - $[\text{Ca}(\text{PO}_3)_2]_x$ has been found in this work.^{3,4}

Experimental.—The compositions investigated were obtained by melting together weighed amounts of AnalaR potassium dihydrogen orthophosphate, recrystallised calcium dihydrogen orthophosphate monohydrate, and calcium carbonate. The calculated amounts of calcium carbonate were added in order to adjust the Ca:P ratio in the calcium dihydrogen orthophosphate to unity. All water and carbon dioxide was removed from the melts on heating, leaving only polyphosphates. The melts obtained were allowed to cool very slowly in order to induce crystallisation. In most cases they supercooled readily, and crystallisation of the samples was induced by heating the glassed material for a prolonged period (12—48 hr.) at a temperature about 30—50° below the melting point.

Crystalline samples were heated in platinum under standard heating conditions in an electric furnace, and the melting point of each sample, together with the corresponding eutectic temperatures, were deduced from the inflections in the heating curve obtained (cf. the thaw-melt method used by Rheinboldt).⁵ Temperatures were measured by a chromel–alumel thermocouple which was standardised frequently at the melting points of pure potassium bromide, sodium chloride, and potassium chromate.

The melting points, 813° for $(\text{KPO}_3)_x$ and 977° for $[\text{Ca}(\text{PO}_3)_2]_x$, agree with the values obtained by Morey.^{1,2}

The X-ray-diffraction data were obtained on a Phillips powder diffractometer incorporating a scintillation counter, with Cu $K\alpha$ -radiation and a nickel filter. The range of 2θ covered was 4—52°.

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¹ G. W. Morey, *J. Amer. Chem. Soc.*, 1954, **76**, 4724.

² G. W. Morey, *J. Amer. Chem. Soc.*, 1952, **74**, 5783.

³ A. O. McIntosh and W. L. Jablonski, *Analyt. Chem.*, 1956, **28**, 1424.

⁴ W. L. Hill, D. S. Reynolds, S. B. Hendricks, and K. D. Jacob, *J. Assoc. Offic. Agric. Chemists*, 1945, **28**, 105.

⁵ H. Rheinboldt, *J. prakt. Chem.*, 1925, **111**, 242.