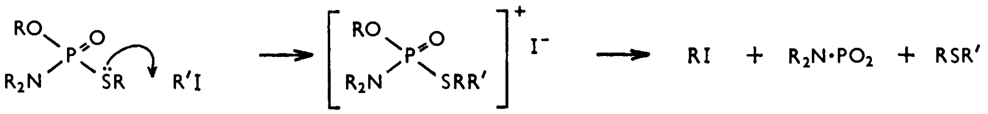
1083. *The Reactivity of Organophosphorus Compounds. Part X.*[1] *The Reaction of Phosphorothiolates with Alkyl Iodides.*

By A. J. Burn, J. I. G. Cadogan, and H. N. Moulden.

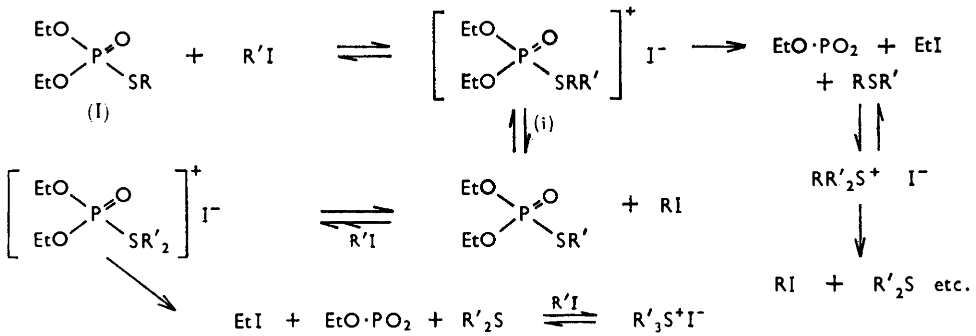
In Part IX of this series,[1] the reactivities of selected phosphoro- and phosphono-thionates toward alkyl iodides in the following reaction were reported:

The reaction was followed kinetically by measuring the rate of formation of the alkyl iodide (RI). In some cases there was evidence for the production of a small amount of alkyl iodide by an additional mechanism probably involving attack by the thiolate sulphur atom of the product on the alkyl halide (R'I):



Many years previously Emmett and Jones [2] reported the formation of trimethylsulphonium iodide in the reaction of methyl iodide with trimethyl phosphorothiolate (MeO)$_2$P(:O)·SMe, a reaction also suggestive of nucleophilic attack by the thiolate sulphur atom on methyl iodide.

These observations are of interest because they suggest localisation of electrons on the sulphur atom in phosphorothiolates despite the conjugative proximity of the $\geqslant$P=O group The possibility is also raised of the exchange of alkyl groups attached to the sulphur atom in phosphorothiolates by suitable choice of reagents. We therefore studied further the reactions of phosphorothiolates with alkyl iodides.



S-Benzyl diethyl phosphorothiolate (I; R = Ph·CH$_2$) and methyl iodide, after prolonged heating, gave in addition to starting material, ethyl iodide, benzyl iodide, and trimethylsulphonium iodide. The presence of diethyl *S*-methyl phosphorothiolate (I; R = Me) was inferred but could not be confirmed because its mixture with benzyl iodide could not be satisfactorily resolved by gas–liquid chromatography. However, a similar reaction with ethyl iodide instead of methyl iodide indicated that alkyl group exchange had occurred since the products included ethyl iodide, benzyl iodide, and triethyl phosphorothiolate (I; R = Et). Diethyl *S*-methyl phosphorothiolate (I; R = Me) reacted similarly with ethyl iodide to give triethyl phosphorothiolate and methyl iodide.

---

[1] Part IX, Burn and Cadogan, *J.*, 1961, preceding paper.

[2] Emmett and Jones, *J.*, 1911, **99**, 713.

The formation of these products can be explained on the basis of the annexed series of reactions. The extent to which each occurs depends on many factors, the most important being the electrophilicity of the α-carbon atom of the alkyl halide; for example, ethyl bromide did not react with thiolates under the standard conditions.

These observations show that the thiolate sulphur atom in phosphorothiolates is appreciably nucleophilic, suggesting that delocalisation of the sulphur lone pair of electrons with the phosphoryl group is not strongly developed. That delocalisation of the nitrogen lone pair of electrons of related phosphoramidates is also similarly reduced has been demonstrated previously.[3]

Experimental.—Gas–liquid chromatography was carried out with a Perkin-Elmer " Fraktometer," model 116, fitted with a high-sensitivity dual thermal-conductivity detector. The response was tested by analysis of mixtures of known composition and found to be satisfactory. The columns, 2 m. in length, consisted of a silicone oil (DC 200) on Celite (C) or di-n-decyl phthalate on Celite (A).

Preparation of compounds. Triethyl phosphorothiolate (b. p. 95°/12 mm., n_D^{25} 1·4553) and *S*-benzyl diethyl phosphorothiolate (b. p. 130°/0·2 mm., n_D^{25} 1·5234) were prepared as described by Cadogan and Moulden,[4] and diethyl *S*-methyl phosphorothiolate (b. p. 106°/8 mm., n_D^{25} 1·4547) as described in Part IX.[1]

Reaction of diethyl S-*methyl phosphorothiolate with ethyl iodide.* The thiolate (0·5 g.) and ethyl iodide (4·25 g., 10 mol.) were heated at 105° in a sealed tube for 47 hr. to give a clear liquid containing *ca.* 2% of an immiscible gum. The supernatant liquid was analysed by gas–liquid chromatography as follows:

(*a*) With a column temperature of 100°, packing C, and a flow of nitrogen of 12 ml./min., methyl iodide (1·2% of total iodide fraction) was detected in addition to ethyl iodide (relative retention times 1 : 1·2), indicating a 12% conversion of the *S*-methyl into *S*-ethyl thiolate on the assumption that reaction (i) is the only mode of formation of methyl iodide.

(*b*) With a column temperature of 170°, packing C, and a flow of nitrogen of 10 ml./min., triethyl phosphorothiolate (2% of total ester fraction) was detected in addition to diethyl *S*-methyl phosphorothiolate (relative retention times 1·33 : 1).

A similar experiment carried out at 105° for 130 hr. gave more of the unidentified gum (probably a sulphonium salt mixture). Analysis of the supernatant liquid indicated an increase in the amounts of methyl iodide (2·7% of total iodide, *i.e.*, 27% conversion based on reaction i) and of triethyl phosphorothiolate (3·4% of total ester).

Reactions of S-*benzyl diethyl phosphorothiolate.* (i) With methyl iodide. The thiolate (1·5 g.) and methyl iodide (4·1 g., 5 mol.) were heated at 105° for 6 hr. to give a dark red liquid containing crystals which were removed. The filtrate was analysed by gas–liquid chromatography under the conditions (*a*) and (*b*) described above, and shown to contain ethyl and methyl iodide (the former representing 0·25 mole/mole of thiolate) and a component having the same retention time as both benzyl iodide and diethyl *S*-methyl phosphorothiolate (*ca.* 0·1 mole/mole of *S*-benzyl thiolate). The presence of benzyl iodide was confirmed by conversion into benzyltriethylammonium iodide as described below.

A similar experiment was carried out at 100° (65 hr.) with thiolate (5·0 g.). The crystals were removed, and recrystallised from methanol, to give trimethylsulphonium iodide (1·01 g.), m. p. and mixed m. p. 209—210° (Found: C, 18·3; H, 4·6. Calc. for C_3H_9IS: C, 17·7; H, 4·4%). The mother liquors from the crystallisation gave an oil whose infrared spectrum showed the presence of more trimethylsulphonium iodide and inorganic phosphate. The filtrate from the original filtration was distilled to give the following fractions: (α) b. p. 40—58° (6·12 g.), (β) b. p. 68—70°/700 mm. (1·9 g.), and (γ) b. p. 112—114°/25 mm. (2·2 g.). Gas–liquid chromatography of each fraction was carried out as follows: Fraction (α) contained methyl iodide (4·58 g.) and ethyl iodide (1·52 g.) (2 m. column, C, at 50°). The analysis was repeated with an A column at 60°, the relative retention times being different but the result the same. Fraction (β) was similarly shown to contain methyl iodide (0·3 g.) and ethyl iodide (1·6 g.). Fraction (γ) was analysed by the use of a C column at 196°. There were seven components, three of which had low b. p. The main component (96%) had the same retention

---

[3] Cadogan, *J.*, 1957, 1079.

[4] Cadogan and Moulden, *J.*, 1961, 5524.

time as benzyl iodide and diethyl *S*-methyl phosphorothiolate. Slight resolution of these components was obtained by using an A column under the same conditions, but quantitative analysis was impossible.

(ii) *With ethyl iodide.* *S*-Benzyl diethyl phosphorothiolate (1·0 g.) and ethyl iodide (3·0 g., 5·0 mol.) were heated at 105° for 67 hr. No crystals were formed. A portion of the mixture was analysed by gas–liquid chromatography on a C column at 179°; the high-boiling components were thus identified as benzyl iodide (0·3 mole/mole of *S*-benzyl ester) and triethyl phosphorothiolate (12% of benzyl iodide present). The relative retention times were 1 : 1·2). The excess of ethyl iodide was removed by distillation and the residue was extracted with triethylamine, to give benzyltriethylammonium iodide (0·25 g., 0·2 mole/mole of *S*-benzyl ester), m. p. and mixed m. p. 163° (decomp.) on recrystallisation from ethanol–ether. Steinkopf and Bessaritsch [5] reported m. p. 168·5°.

King's College, Strand, London, W.C.2.

[*Received, June 29th,* 1961.]

---

[5] Steinkopf and Bessaritsch, *J. prakt. Chem.*, 1925, **109**, 230.

1084. *Characterisation of Sugars as* p-p'-*Nitrophenylazobenzoyl Derivatives.*

By El S. Amin.

p-p'-Nitrophenylazobenzoyl chloride has been used for identification and separation of alcohols,[1] amines,[2] thiols,[3] and amino-acids.[4] It has now been applied to sugars, giving polyacyl derivatives in fairly good yields from eight sugars in pyridine at 0°. The derivatives melt sharply and at much higher temperatures than do other derivatives.[6] They are insoluble in water and of varying solubility in organic solvents. The m. p.s differ sufficiently to be useful criteria, and the sugars can be quantitatively recovered from the esters by hydrolysis.

Experimental.—Evaporations were under reduced pressure at 50°.

Preparations. The sugar (0·5 mmole) was dissolved in dry pyridine (50 ml.) and cooled to 0°, and *p-p'*-nitrophenylazobenzoyl chloride [1] (4·00 mmoles for monosaccharides and 6·00 mmoles for disaccharides) was added in small portions with cooling. The mixture was kept for 2 weeks at 0°, then filtered through activated alumina (30 g.) that had been wetted with 30 ml. of pyridine. The main (lower) red band was eluted with a 5% solution (90 ml.) of pyridine in benzene; the solvent was removed and the ester purified by crystallisation from acetone. The *derivatives* shown in the Table were thus prepared. The derivatives obtained were predominantly in the α-form.

p-p'-Nitrophenylazobenzoates.

Ester of	M. p.	$[\alpha]_D^{25}$ *	Formula	Found: N (%)	Reqd.: N (%)
D-Arabinose	176°	−30°	$C_{57}H_{38}N_{12}O_{17}$	14·2	14·5
D-Xylose	174	+280	$C_{57}H_{38}N_{12}O_{17}$	14·4	14·5
α-D-Glucose	264	+285	$C_{71}H_{47}N_{15}O_{21}$	14·8	14·9
α-D-Fructose	150	−130	$C_{71}H_{47}N_{15}O_{21}$	14·9	14·9
α-D-Galactose	254	+510	$C_{71}H_{47}N_{15}O_{21}$	14·6	14·9
α-Lactose	238	+350	$C_{116}H_{78}N_{24}O_{35}$	14·0	14·2
α-Maltose	272	+35	$C_{116}H_{78}N_{24}O_{35}$	13·9	14·2
Sucrose	155	+40	$C_{116}H_{78}N_{24}O_{35}$	14·4	14·2

* 5% w/v in $CHCl_3$.

Recovery. The ester (260 mg.) was dissolved in dioxan (20 ml.), and methanol (15 ml.) containing sodium methoxide (~12 mg.) was added. The mixture was refluxed for 30 min.,

---

[1] Hecker, *Chem. Ber.*, 1955, **88**, 1666; Amin and Hecker, *ibid.*, 1956, **89**, 695.

[2] Amin, *J.*, 1957, 3764; 1959, 1619.

[3] Amin, *J.*, 1958, 4769.

[4] Amin, *J.*, 1960, 1953.

[6] Coleman, Farnham, and Miller, *J. Amer. Chem. Soc.*, 1942, **64**, 1501.

then 6N-sodium hydroxide (3 ml.) and water (30 ml.) were added. Refluxing was continued for another 30 min., the solution was diluted to about 200 ml. with water, and 125—150 ml. of solvent were evaporated. The residual solution was filtered, cooled, and made slightly acid with dilute hydrochloric acid. After cooling to allow complete precipitation of *p-p'*-nitrophenylazobenzoic acid, the mixture was filtered to give the sugar quantitatively in the filtrate.

Chromatography. A mixture (4 mg.) of pairs of sugar esters in 1 : 4 acetone–chloroform was passed down columns of silica (50 g.) prepared by suspension in 1 : 1 : 1 chloroform–benzene–light petroleum (b. p. 60—80°). The chromatogram was developed with acetone–chloroform and from appropriate zones extraction gave pure esters. Pairs separated were esters of galactose with lactose, of glucose with fructose, maltose, or sucrose, and of lactose with sucrose.

ALEXANDRIA UNIVERSITY, EGYPT.

[*Received, June 2nd,* 1961.]

1085. *Interaction of Boron Trichloride with Dioxan and 1,3-Dioxolan.*

By S. COOPER, M. J. FRAZER, and W. GERRARD.

WHEN the 1 : 1 complex[1,2] of dioxan and boron trichloride was heated just above the m. p., exothermic ether fission (1) occurred, the known [3] propensity of 2-chloroethoxyboron

$$C_4H_8O_2,BCl_3 \longrightarrow (Cl{\cdot}CH_2{\cdot}CH_2{\cdot}O)_2BCl + (Cl{\cdot}CH_2{\cdot}CH_2{\cdot}O)_3B + BCl_3 \quad . \quad . \quad . \quad . \quad (1)$$

chlorides to undergo mutual replacement (metathesis) accounting for production of the borate. At 180° under reflux, 1,2-dichloroethane, boric oxide, and boron trichloride were obtained. The 2 : 3 dioxan–boron trichloride complex [2] gave the same compounds. The dioxan–boron tribromide 1 : 1 complex [2] at 30° gave 1,2-dibromoethane and 2-bromoethyl metaborate (2).

$$C_4H_8O_2,BBr_3 \longrightarrow Br{\cdot}CH_2{\cdot}CH_2Br + \tfrac{1}{3}(Br{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BO)_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In early work,[4] determination of the electric moment of boron trichloride in dioxan indicated co-ordination; but it was stated that the boron chloride caused no decomposition of dioxan, and that boron tribromide reacted violently and formed decomposition products. Later [1] only the 1 : 1 chloro-complex was isolated, and pyrolysis in a vacuum gave unspecified amounts of hydrogen chloride and " 2-vinyloxyethyl dichloroborate," although in another experiment, an unstated amount of a non-volatile tarry residue containing boron and chlorine was obtained.

1,3-Dioxolan did not form an isolable complex with boron trichloride, but immediately underwent ether fission to give chloromethoxyethyl esters (3). The esters have similar spectra, quite different from that of dioxolan. There is absorption in the region 1320—1470 cm.$^{-1}$ which is typical of the ROB structure, there are also bands between 1120 and 1135 cm.$^{-1}$ and at 845 cm.$^{-1}$; further, when $n = 1$ or 2, there is absorption at 940 and 910 cm.$^{-1}$ which we attribute to $-BCl_2$ and $-BCl$, respectively. The products of reactions 5 and 6 give similar spectra, except that the chloro-ethers did not absorb in the region 1320—1470 cm.$^{-1}$. One other feature common to the spectra of all those compounds that contain the chloromethoxy-group is a sharp band at 1724 cm.$^{-1}$ (1613 cm.$^{-1}$ in the case of the dichloroborinate). This could be attributed to coupling between the C–Cl and the C–O–C vibration, but this band is absent from the spectrum of bischloromethyl ether. On

---

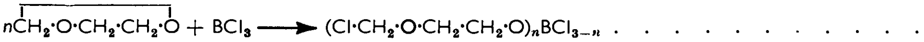
[1] Holliday and Sowler, *J.*, 1952, 11.

[2] Frazer, Gerrard, and Mistry, *Chem. and Ind.*, 1958, 1263.

[3] Edwards, Gerrard, and Lappert, *J.*, 1955, 1470.

[4] Lane, McCusker, and Curran, *J. Amer. Chem. Soc.*, 1942, **64**, 2076.

being heated the dichloroborinate ($n = 1$) underwent a mutual replacement reaction (4), and the chloroboronate ($n = 2$) afforded 2-chloroethyl chloromethyl ether as one



$$n\overline{CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O} + BCl_3 \longrightarrow (Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O)_nBCl_{3-n} \quad (3)$$

$$2Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}BCl_2 \longrightarrow (Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O)_2BCl + BCl_3 \quad (4)$$

$$(Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O)_2BCl \xrightarrow{\text{heat}} Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl + \text{Other products} \quad (5)$$

$$(Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O)_3B \xrightarrow{\text{heat}} Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2Cl + (CH_2{\cdot}O)_2B{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2Cl \quad (6)$$

decomposition product (5), whereas the borate ($n = 3$) gave 1,2-bischloromethoxyethane and 2-chloromethoxyethyl ethylene borate (6).

Experimental.—Where not stated herein, satisfactory analytical data were obtained for all reactants and products. Easily hydrolysed (e.h.) chlorine is that responding to cold water.

Thermal decomposition of dioxan–boron trihalide complexes. The tendency of 2-chloroethyl dichloroborinate, and bis-2-chloroethyl chloroboronate to undergo mutual replacement to afford boron trichloride and tris-2-chloroethyl borate hindered the isolation of analytically pure chloroboron compounds. The 1 : 1 boron trichloride complex [1,2] (16·22 g., 3 mol.) was heated to about 95°, whereupon exothermic decomposition occurred, and a temperature of 170° was quickly attained. 0·5 Hr. later the system was at 50°, and distillation at 18 mm. then afforded impure bis-2-chloroethyl chloroboronate (8·77 g.), b. p. 76—83°/18 mm., tris-2-chloroethyl borate (0·37 mol.), b. p. 64°/0·06 mm., n_D^{20} 1·4558, and boron trichloride (0·65 g.) (trap at −80°). The chloroboronate (7·48 g., 1·38 mol.), n_D^{20} 1·4550 (Found: B, 5·5; e.h. Cl, 17·4; Cl, 51·1. Calc. for $C_4H_8BCl_3O_2$: B, 5·3; e.h. Cl, 17·3; Cl, 51·9%), remained after the distilled material had been held at 20°/18 mm. for several hours to attain constancy in e.h. chlorine.

Similarly the 2 : 3 complex,[2] $2C_4H_8O_2,3BCl_3$ (14·03 g., 1 mol.) gave bis-2-chloroethyl chloroboronate (6·5 g., 1·2 mol.) (Found: B, 5·5; e.h. Cl, 17·4; Cl, 51·2%), analysed after being at 20°/0·02 mm. for 12 hr. when the e.h. chlorine content was constant, and tris-2-chloroethyl borate (0·23 mol.), b. p. 68°/0·1 mm., n_D^{20} 1·4558. The trap (−80°) contained boron trichloride (0·93 mol.), and a further trap containing pyridine held boron trichloride (0·32 mol.) as the complex. The 2 : 3 complex lost 6% of its weight at 22°/0·04 mm. in 35 hr.; but the rate of loss was extremely slow by that time. When the 1 : 1 complex (19·0 g.) system was heated at 180° (reflux, 3 hr.) it gave 1,2-dichloroethane (6·62 g.), b. p. 81—82°, n_D^{20} 1·4455. Continued heating gave more of the dichloride (0·95 g.) and a black solid (10·55 g.) (Found: B, 11·2; Cl, 30·0%).

The 1 : 1 tribromide complex [2] (6·02 g., 1 mol.) was heated at 130° for 0·5 hr., to afford 1,2-dibromoethane (0·98 mol.), b. p. 130—131°, n_D^{20} 1·5381, a residue (0·9 g.) (Found: B, 16·1%), and a trap (−80°) condensate (1·07 g.) (Found: B, 1·0; e.h. Br, 6·0%). When the complex (14·45 g.) was heated to 30°, decomposition occurred, and the resultant brown liquid afforded colourless crystals (3·8 g.), m. p. 64—68° (Found: B, 6·9; e.h. Br, 0·0; Br, 53·5. $C_2H_4BBrO_2$ requires B, 7·2; Br, 53·0%) of *2-bromoethyl metaborate*. The infrared spectrum showed absorption bands in the region 1050—1100 cm.$^{-1}$ and also in the region 720—735 cm.$^{-1}$ which are characteristic of metaborates.[5] The filtrate gave 1,2-dibromoethane (8·10 g., 96%), b. p. 129—131°, and a black solid (1·70 g.) (Found: B, 10·6; e.h. Br, 0·0%).

Interaction of 1,3-*dioxolan and boron trichloride.* The dioxolan (1, 2, or 3 mol.) was added dropwise to boron trichloride (14·1 g., 1 mol.) in n-pentane (25 c.c.) at −80°. The 2-chloromethoxyethyl boron ester was held at 20°/20 mm. and then analysed (see Table).

Formation of $(Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O)_nBCl_{3-n}$ from 1,3-dioxolan (n mol.).

	Yield	Found (%)		Required (%)			
n	(%)	B	e.h.Cl	B	e.h.Cl	n_D^{20}	d_{20}^{20}
1	98·8	5·5	55·0	5·6	55·7	1·4587	1·369
2	97·0 *	4·0	39·9	4·1	40·2	1·4611	1·301
3	94·0	3·25	31·5	3·2	31·4	1·4632	1·297

* B. p. 46°/0·15 mm.

The dichloroborinate ($n = 1$) (30·96 g.), heated at 45—50°/4·0 mm. for 4 hr., gave the chloroboronate ($n = 2$) (16·1 g., 75%), b. p. 46°/0·15 mm., n_D^{24} 1·4612, and boron trichloride (9·2 g.,

---

[5] Lappert, *J.*, 1958, 2790.

97·0%). The chloroboronate ($n = 2$) (10·70 g., 96·5%), b. p. 44°/0·15 mm., was also obtained by addition of 1,3-dioxolan (1 mol.) to the dichloroborinate ($n = 1$) (8·00 g., 1 mol.).

Analogously, from the chloroboronate ($n = 2$) (2·75 g., 1 mol.) and 1,3-dioxolan (1 mol.), mixed at −80°, the product then being held at 20°/15 mm. for 7 hr., the borate ($n = 3$) (3·52 g., 100%), n_D^{20} 1·4633, d_{20}^{20} 1·297, was obtained.

The chloroboronate ($n = 2$) (64·37 g.) was held at 50°/20 mm. for 5 hr. Distillation then afforded 2-chloroethyl chloromethyl ether (22·7 g., 73%), b. p. 65°/18 mm., n_D^{20} 1·4568 (Found: e.h. Cl, 27·7; Cl, 55·1. Calc. for $C_3H_6Cl_2O$: e.h. Cl, 27·5; Cl, 55·0%), a liquid (4·52 g.), b. p. 78—82°/18 mm. (Found: B, 0; e.h. Cl, 36·4; Cl, 46·8%), a liquid (3·0 g.), b. p. 102—110°/18 mm. (Found: B, 0; e.h. Cl, 37·4%), a trap (−80°) condensate (4·81 g.), and a non-volatile residue (21·0 g.) (Found: B, 12·5%).

The borate ($n = 3$) (27·6 g.) was heated at 56°/0·3 mm. and distillation afforded a trap (−80°) condensate (2·61 g.), 1,2-bischloromethoxyethane (8·66 g.), b. p. 48—54°/0·3 mm. [redistilled (7·1 g.), b. p. 87°/3·0 mm.] (Found: e.h. Cl, 44·1. Calc. for $C_4H_8Cl_2O_2$: e.h. Cl, 44·6%), and *chloromethoxyethyl ethylene borate* (14·45 g.), b. p. 98—105°/0·3 mm. [redistilled (7·9 g.), b. p. 96—98°/0·3 mm.] (Found: B, 6·1; e.h. Cl, 19·8. $C_5H_{10}BClO_4$ requires B, 6·0; e.h. Cl, 19·7%).

NORTHERN POLYTECHNIC,
HOLLOWAY ROAD, LONDON, N.7.

[*Received, June 6th,* 1961.]

1086. *Thiosuccinimides.*

By R. J. CREMLYN.

SEVERAL succinimides and thioamides are fungitoxic;[1] it was, therefore, decided to prepare a range of thiosuccinimides as potential fungicides. The only known member of this group is *N*-phenylthiosuccinimide which has been prepared by boiling methyl *N*-phenylsuccinamate with phosphorus pentasulphide in toluene,[2] but attempts to repeat this gave very poor yields. However, similar treatment of *N*-phenylsuccinimide with phosphorus pentasulphide afforded a reasonable yield of the monothio-derivative; this method has been extended to the synthesis of *N*-alkyl- and *N*-aryl-thiosuccinimides. In a few cases the dithio-derivatives were also isolated, but their preparation generally required more drastic conditions, under which extensive decomposition occurred, so that in the majority of experiments only the monothiosuccinimides have been obtained. The best procedure for synthesising the monoalkylthiosuccinimides was the interaction of equimolar quantities of succinimide and phosphorus pentasulphide in toluene or xylene at 100° for 1 hour for the lower ($<C_5$) or at the boiling point of the solvent for 3—4 hours for the higher ($>C_5$) homologues.

Reissert and Moré's [2] method for preparing thiosuccinamic acids was not satisfactory, because during neutralisation with hydrochloric acid some loss of sulphur as hydrogen sulphide always occurred, and often was sufficient to prevent isolation of a reasonably pure thiosuccinamic acid.

The thiosuccinimides were characterised by a colour test and by their ultraviolet absorption spectra in absolute alcohol. The *N*-alkyl- and *N*-aryl-thiosuccinimides show two characteristic maxima at 270 and 320 mμ, but the dithio-compounds exhibit only the latter peak, which is known to represent the thiocarbonyl group.[3] The band at 270 mμ is probably a function of the ·CO·CH$_2$·CH$_2$·CS· grouping, because the corresponding *N*-substituted succinimides have no absorption bands in the 200—410 mμ region.[4] When alcoholic solutions of the lower *N*-alkyl ($<C_6$) thiosuccinimides are evaporated at

---

[1] Searle and Arnold, U.S.P. 2,462,835/1949; Wolf, Closson, and Ligett, U.S.P. 2,726,981/1955; Ludwig and Ross, *Canad. J. Bot.*, 1957, **35**, 65.

[2] Reissert and Moré, *Ber.*, 1906, **39**, 3298.

[3] Braude, *Ann. Reports*, 1945, **42**, 105.

[4] Turner, *J.*, 1957, 4555.

room temperature, the ultraviolet spectra of the residues showed no absorption peak in this region, indicating that complete exchange of sulphur for oxygen had occurred. A similar reaction has been reported at 60—100° for aqueous solutions of thiosuccinic anhydride.[5] In contrast, *N*-hexylthiosuccinimide showed weak absorption peaks at 270 and 320 mμ after evaporation of the solution, and the higher alkyl- ($>C_6$) and aryl-thiosuccinimides were apparently quite stable.

Experimental.—*N*-Alkylsuccinimides were prepared by treating[6] succinic anhydride with the corresponding amine. *N*-Arylsuccinimides were obtained from the intermediate arylsuccinamic acid by dehydration with acetyl chloride.[7]

Thiosuccinimides. The *N*-substituted succinimide (1 mole) was dissolved in boiling toluene or xylene, and finely powdered phosphorus pentasulphide (1 mole) gradually added. The mixture was gently boiled under reflux, with stirring, until the solution darkened and the phosphorus pentasulphide disappeared (1—4 hr.), leaving an oily mass adhering to the sides of the flask. The mixture was filtered hot, allowed to cool, and evaporated under reduced pressure. The residue was dissolved in ethanol (charcoal) and filtered. The product was then obtained by standard methods of crystallisation or fractionation under reduced pressure. Details are given in the Tables.

N-Alkylthiosuccinimides.

				Found (%)				Required (%)			
N-Subst.	M. p./b. p.	Yield (%)	Formula	C	H	N	S	C	H	N	S
H	100—104°	25	C_4H_5NOS	41·9	4·2	11·9	27·6	41·7	4·4	12·2	27·8
Me	52—54	28	C_5H_7NOS	46·2	5·3	10·7	25·3	46·5	5·4	10·8	24·9
Bu^n	95—100/0·2[a]	40	$C_8H_{13}NOS$	56·1	7·7	8·0	19·3	56·1	7·6	8·2	18·7
Bu^i	70—75/0·2	51	$C_8H_{13}NOS$	56·3	7·4	8·0	19·4	56·1	7·6	8·2	18·7
n-C_5H_{11}	65—70/0·15[b]	58	$C_9H_{15}NOS$	57·8	7·9	7·3	17·2	58·4	8·1	7·6	17·3
n-C_6H_{13}	100—105/0·2[c]	35	$C_{10}H_{17}NOS$	59·8	8·3	6·9	16·6	60·3	8·5	7·0	16·1
Cyclohexyl	54—56	29	$C_{10}H_{15}NOS$	60·4	7·6	6·5	16·9	60·1	7·6	7·1	16·2
n-C_8H_{17}	150—155/0·35[d]	65	$C_{12}H_{21}NOS$	63·1	10·1	6·0	13·8	63·4	10·2	5·8	13·2
n-$C_{12}H_{25}$	145—149/0·2[e]	52	$C_{16}H_{29}NOS$	67·3	10·1	5·1	11·0	67·8	10·2	4·9	11·3

[a] n_D^{20} 1·5589. [b] n_D^{18} 1·5490. [c] n_D^{20} 1·5669. [d] n_D^{21} 1·5420. [e] n_D^{16} 1·5383.

N-Arylthiosuccinimides.

				Found (%)				Required (%)			
N-Subst.	M. p.	Yield (%)	Formula	C	H	N	S	C	H	N	S
Ph	116° *	40	$C_{10}H_9NOS$	—	—	—	17·0	—	—	—	16·8
$PhCH_2$	60—62	44	$C_{11}H_{11}NOS$	63·8	5·5	6·8	16·4	64·4	5·4	6·8	15·9
2-MeC_6H_4	52—55	29	$C_{11}H_{11}NOS$	64·3	5·4	6·6	16·4	64·4	5·4	6·8	15·9
4-MeC_6H_4	98—100	60	$C_{11}H_{11}NOS$	64·5	5·6	7·0	15·3	64·4	5·4	6·8	15·9
2-ClC_6H_4	92—93	57	$C_{10}H_8ClNOS$	53·4	3·8	6·4	13·7	53·2	3·5	6·2	14·2
4-ClC_6H_4	94—96	35	$C_{10}H_8ClNOS$	53·5	3·7	6·3	13·6	53·2	3·5	6·2	14·2
4-$MeOC_6H_4$	110—111	59	$C_{11}H_{11}NO_2S$	60·2	5·1	6·1	14·2	59·8	5·4	6·3	14·5
2,4-$Me_2C_6H_3$	85—88	55	$C_{12}H_{13}NOS$	65·5	5·8	6·3	14·7	65·8	5·9	6·4	14·6
2,5-$Me_2C_6H_3$	69—72	46	$C_{12}H_{13}NOS$	65·6	6·0	6·7	14·5	65·8	5·9	6·4	14·6
2,4-$Cl_2C_6H_3$	99—101	52	$C_{10}H_7Cl_2NOS$	46·7	2·7	6·0	11·7	46·2	2·7	5·4	12·3
1-$C_{10}H_7$	144—145	25	$C_{14}H_{11}NOS$	69·6	4·6	5·8	13·9	69·7	4·6	5·8	13·3

* Lit., m. p. 116—117°.

N-Alkyldithiosuccinimides.

				Found (%)				Required (%)			
N-Subst.	M. p./b. p.	Yield (%)	Formula	C	H	N	S	C	H	N	S
H	84—87°	10	$C_4H_5NS_2$	36·9	3·4	10·4	48·4	36·6	3·8	10·7	48·8
Et	76—79/0·05	62	$C_6H_9NS_2$	44·8	5·8	8·6	39·9	45·3	5·7	8·8	40·2
Bu^n	110/0·4	15	$C_8H_{13}NS_2$	51·6	7·1	7·1	33·8	51·3	7·0	7·5	34·2
n-$C_{10}H_{21}$	135—138/0·2[g]	32	$C_{14}H_{25}NS_2$	61·3	9·5	5·8	23·4	61·8	9·2	5·2	23·6
1-$C_{10}H_7$	168—170	20	$C_{14}H_{11}NS_2$	65·5	4·5	5·5	24·4	65·4	4·3	5·4	24·9

[f] n_D^{20} 1·6112. [g] n_D^{20} 1·5080.

---

[5] Auger, *Ann. Chim.*, 1891, **22**, 333.

[6] Rice, Reid, and Grogan, *J. Org. Chem.*, 1954, **19**, 884.

[7] Tingle and Cram, *Amer. Chem., J.*, 1907, **37**, 597.

N-*Benzylthiosuccinamic acid.* The following *N*-substituted thiosuccinamic acids were obtained by Reissert and Moré's method:[2] N-*benzyl*, white shining platelets (43%), m. p. 100—102° (from benzene) (Found: C, 59·8; H, 6·4; N, 5·9; S, 14·4. $C_{11}H_{13}NO_2S$ requires C, 59·2; H, 5·8; N, 6·3; S, 14·3%); *N*-phenyl (33%), m. p. 106—108° (lit.,[2] m. p. 106—107°); N-p-*tolyl* (44%), m. p. 122° (Found: C, 60·3; H, 6·0; N, 5·8; S, 13·6. $C_{11}H_{13}NO_2S$ requires C, 59·2; H, 5·8; N, 6·3; S, 14·3%); and N-p-*methoxyphenyl* (70%), m. p. 118—119° (Found: C, 55·9; H, 5·2; N, 6·4; S, 12·6. $C_{11}H_{13}NO_3S$ requires C, 55·2; H, 5·4; N, 5·9; S, 13·4%).

Colour test. When a dilute alcoholic solution (2 mg., 5 c.c.) of a thiosuccinimide was treated with one or two drops of a 10% aqueous sodium hydroxide solution, characteristic transient colours developed. The generally observed sequence was the following: Cherry Red $\longrightarrow$ Dark Blue $\longrightarrow$ Purple $\longrightarrow$ Dark Green or Brown.

The author thanks Dr. W. R. Boon of Plant Protection Ltd. for permission to publish this work.

Brunel College of Technology,
Acton, London, W.3.

[*Received, June* 13*th*, 1961.]

1087. *Evidence for a Single-stage Two-electron Exchange in the Thallous–Thallic Reaction.*

By A. G. Sykes.

The kinetics of the reaction $2V^{IV} + Tl^{III} \longrightarrow 2V^{V} + Tl^{I}$ at 80° have been studied with the addition of excess of Tl^{I} and found to be independent of the latter ion.[1] It is concluded that the Tl^{I}–Tl^{III} exchange, which is appreciable under the conditions of these experiments, is a single-stage two-electron transfer.

There has recently been much discussion as to whether the simultaneous, or near-simultaneous, transfer of two electrons (possibly by group transfer) is possible for reactions in solution,[2] in particular for oxidation–reduction reactions between metal ions. Of interest in this respect are $Tl^{III} + U^{IV} \longrightarrow Tl^{I} + U^{VI}$ (ref. 3), $Tl^{III} + 2Cr^{II} \longrightarrow Tl^{I} + (Cr^{III})_2$ (ref. 4), and $Tl^{III} + (Hg^{I})_2 \longrightarrow Tl^{I} + 2Hg^{II}$ (ref. 5), which have been discussed earlier,[6] and the Tl^{I}–Tl^{III} exchange.[7,8] While single-stage two-electron processes entail greater environmental changes than corresponding one-electron changes do, it may happen that the former are favoured energetically if consecutive one-electron changes require the production of one, or possibly two, unstable intermediates. The kinetics of the Tl^{I}–Tl^{III} exchange, with Tl^{III} labelled, give no information concerning the intermediate formation of unstable Tl^{II} ions.

As was reported previously,[6] the kinetics of the V^{IV}–Tl^{III} system indicate a mechanism:

$$Tl^{III} + V^{IV} \rightleftharpoons Tl^{II} + V^{V}$$
$$Tl^{II} + V^{IV} \longrightarrow Tl^{I} + V^{V}$$

which is similar to that of the Fe^{II}–Tl^{III} reaction.[9] Three experiments were performed at 80°, with initial concentrations of reagents $[V^{IV}] = 0{\cdot}00954$M, $[Tl^{III}] = 0{\cdot}01414$M, $[V^{V}] = 0$, $[H^+] = 1{\cdot}8$M, and initial concentrations of $[Tl^{I}] = 0$, 0·04431M, and 0·1317M, respectively. All the reagents used were perchlorates and the ionic strength I was made 3·0M by use of sodium perchlorate. Plots of $[V^{IV}]$ against time were all identical, showing that the

---

[1] Sykes, Thesis, Manchester University, 1958.

[2] See, *e.g.*, Westheimer, *Chem. Rev.*, 1949, **45**, 419; Higginson and Marshall, *J.*, 1957, 447.

[3] Harkness and Halpern, *J. Amer. Chem. Soc.*, 1959, **81**, 3526.

[4] Ardon and Plane, *J. Amer. Chem. Soc.*, 1959, **81**, 3197.

[5] Armstrong and Halpern, *Canad. J. Chem.*, 1957, **35**, 1020.

[6] Higginson, Rosseinsky, Stead, and Sykes, *Faraday Soc. Discuss.*, 1960, **29**, 49.

[7] Harbottle and Dodson, *J. Amer. Chem. Soc.*, 1951, **73**, 2442.

[8] Prestwood and Wahl, *J. Amer. Chem. Soc.*, 1949, **71**, 3137.

[9] Ashurst and Higginson, *J.*, 1953, 3044.

initial presence of Tl^{I} in the concentrations stated has a negligible effect; the initial rate of disappearance of Tl^{III} was $0{\cdot}904 \times 10^{-4}$ mole l.$^{-1}$ min.$^{-1}$.

From data by Prestwood and Wahl[8] at 25—50·1°, $[H^+] = 1{\cdot}8$M, and $I = 3{\cdot}68$M, the rate constant for the Tl^{I}–Tl^{III} reaction at 80° $\{k = k' + (k''/[H^+])\}$ can be obtained by extrapolating activation-energy plots of k' and k'', and is $k = 0{\cdot}272$ mole^{-1} min.$^{-1}$.

More recent work by Gilks and Waind[10] suggests that k will vary for ionic strengths $I = 3{\cdot}0$—3·68M, but a variation greater than a factor of 2 seems unlikely. The rate of exchange of Tl^{III}, $d[Tl^{III}]/dt = -k[Tl^{III}][Tl^{I}]$, is therefore $1{\cdot}70 \times 10^{-4}$ mole l.$^{-1}$ min.$^{-1}$ for the second run and $5{\cdot}06 \times 10^{-4}$ mole l.$^{-1}$ min.$^{-1}$ for the third, *i.e.*, both rates are of the same order as that of the V^{IV}–Tl^{III} reaction. Were Tl^{II} an intermediate in the exchange reaction the rate of the V^{IV}–Tl^{III} reaction would be expected to increase appreciably on addition of Tl^{I}. It is therefore concluded that the Tl^{I}–Tl^{III} exchange is by a single two-electron change.

Similar conclusions have recently been reported by Gryder and Dorfman[11] after observations on the Ce^{IV}–Tl^{I} system in the presence of Tl^{III}.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,
MANCHESTER 13.

[*Received, June 9th*, 1961.]

---

[10] Gilks and Waind, *Faraday Soc. Discuss.*, 1960, **29**, 102.

[11] Gryder and Dorfman, *J. Amer. Chem. Soc.*, 1961, **83**, 1254.

1088. *The Thermal Isomerization of Spirobicyclopropane.*

By M. C. FLOWERS and H. M. FREY.

SPIROBICYCLOPROPANE (spiropentane) undergoes a first-order thermal isomerization to give methylenecyclobutane in the temperature range 360—410° C. The isomerization

was carried out in an " aged " Pyrex-glass vessel, and plots that were accurately of first order were obtained for decompositions varying from 20 to 70%. The rate constants for this transformation are:

10^4k (sec.$^{-1}$)	25·4	10·4	4·13	1·53
t (° C)	408·4	394·5	380·5	366·2

The standard deviation of the rate constant at 408·4° is 0·58%.

These data fit the Arrhenius equation $k = 10^{15{\cdot}86} \exp(-57{,}570/\boldsymbol{R}T)$ sec.$^{-1}$ with a standard deviation of less than 10 cal. The very small deviation shows the high reproducibility of the results but is no indication of the true error in the determination of the energy of activation which is probably of the order of ±600 calories resulting largely from temperature uncertainties. The first-order rate constant is independent of pressure from 25 to 350 mm., but fall off has started at 13·5 mm. All the evidence at present strongly suggests this to be a true unimolecular transformation.

In the temperature range where the isomerization occurs the spirobicyclopropane molecule also decomposes to yield one molecule of allene and one of ethylene. This reaction is slower than the isomerization and has a higher energy of activation. At 408° C, some 9% of the reaction proceeds by this path, whereas at 366° C it accounts for about 7% of the products. The reactions of the methylenecyclobutane are scarcely significant under the experimental conditions employed. Its decomposition to allene (and ethylene) accounts for only about 4% of the allene formed. Its isomerization to 1-methylcyclobut-1-ene which appears to be heterogeneous is likewise insignificant.

The observed activation energy of 57,570 cal. is considerably smaller than that for the isomerization of cyclopropane to propene [1] or 1,1-dimethylcyclopropane to 2-methylbut-2-ene and 3-methylbut-1-ene.[2] This is not unexpected since this isomerization, in contrast to those of the cyclopropanes, does not require the breaking of any carbon–hydrogen bonds. The very large pre-exponential factor (even allowing for the degeneracy of 8 in the reaction path) implies a transition state which is very " loose " in comparison with the highly strained spirobicyclopropane structure.

Experimental.—Spirobicyclopropane (spiropentane) was prepared from pentaerythritol tetrabromide by the method of Applequist *et al.*[3] Unsaturated impurities were removed by treating the crude product with bromine at −78°. After being washed with sodium carbonate solution and water the spiro-compound was dried and fractionally distilled at −24°. The distillate consisted of spirobicyclopropane (97%) and 1,1-dimethylcyclopropane (3%). This mixture was separated on a preparative gas-chromatographic column (liquid phase, dinonyl phthalate) followed once again by fractionation at −24° and yielded spirobicyclopropane (99·95% pure).

Methylenecyclobutane was prepared from pentaerythritol tetrabromide by the method of Roberts and Sauer.[4] The crude product was fractionally distilled at −24°. The final product contained 2·3% of the spiro-compound and 0·1% of other impurities.

1-Methylcyclobutene was prepared by isomerisation of methylenecyclobutane on a sodium–alumina catalyst.

Allene was prepared from 2,3-dichloropropene and purified by low-temperature fractionation; its purity was 99·8%.

The purity of all compounds was determined by gas chromatography. The absence of impurities of high molecular weight was proved by mass spectrometry.

The Pyrex-glass vessel (1·4 l.) was in a furnace whose temperature could be maintained indefinitely to better than 0·1° C. The temperature gradient over the entire length of the vessel was less than 0·5° C. Diaphragm valves were employed throughout to avoid troubles associated with the absorption of hydrocarbons in stopcock grease. Analysis was by gas chromatography, a 30 ft. × 0·17 in. (i.d.) coiled copper column containing bis-2-cyanoethyl ether on Chromosorb being maintained at 0°. Hydrogen was the flow gas and a Gow-Mac katharometer was the detector. The signals from the katharometer were fed, *via* a variable attenuator, to a 0—1 mv Sunvic recorder fitted with a retransmitting slide-wire. Signals from this slide-wire were used to drive an integrating motor. The analytical precision was better than ±0·5%.

Calibration mixtures were prepared in a specially designed vacuum system which employed only greaseless valves to avoid absorption errors.

We thank the Chemical Society and the Department of Scientific and Industrial Research for grants for equipment. M. C. F. thanks the Esso Petroleum Company for the award of a studentship.

CHEMISTRY DEPARTMENT, SOUTHAMPTON UNIVERSITY. [*Received, May 24th,* 1961.]

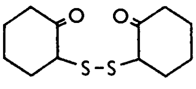
---

[1] Falconer, Hunter, and Trotman-Dickenson, *J.*, 1961, 609.
[2] Flowers and Frey, *J.*, 1959, 3953.
[3] Applequist, Fanta, and Henrikson, *J. Org. Chem.*, 1958, **23**, 1715.
[4] Roberts and Sauer, *J. Amer. Chem. Soc.*, 1949, **71**, 3925.

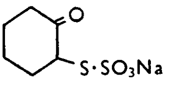
1089. *Reactions of Sodium 2-Oxocyclohexyl Thiolsulphate.*

By BRIAN MILLIGAN and J. M. SWAN.

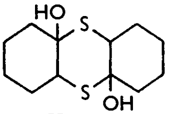
BY reaction of 2-chlorocyclohexanone with sodium sulphide, Backer *et al.*[1] prepared a compound, allegedly $C_{12}H_{18}O_2S_2$, m. p. 150°, which they formulated as di-(2-oxocyclohexyl) disulphide (I). We have prepared sodium *S*-2-oxocyclohexyl thiolsulphate (II) by reaction of 2-chlorocyclohexanone with sodium thiosulphate, and have converted it both by the action of sodium sulphide * and by oxidation into a disulphide, m. p. 80°, shown to be the authentic disulphide (I) by elemental analysis, molecular-weight determination, infrared spectral analysis, and by preparation of a bis-2,4-dinitrophenylhydrazone. The preparation of Backer *et al.* was repeated and the substance, m. p. 150°, designated " A," was shown to have the composition $C_{12}H_{20}O_2S_2$ rather than $C_{12}H_{18}O_2S_2$, and by infrared analysis to contain hydroxyl but no carbonyl group. When 2-chlorocyclohexanone was allowed to react with sodium hydrogen sulphide rather than disodium sulphide, another product, " B," was obtained, isomeric with " A," and for which the m. p. varied from 143—144° to 168—170° depending on the solvent used for crystallization and the nature of the glass of the m. p. tube. The melting points of these samples of " B " were depressed on admixture with " A." The infrared spectra of " A " and " B " were virtually identical, except that the samples of " B " showed a very weak band at 1720 cm.$^{-1}$, indicating the presence of traces of a carbonyl compound. After 3 months the melting point of " A " had fallen to 133° and the infrared spectrum showed weak carbonyl absorption.



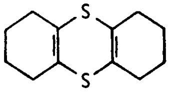
(I)



(II)



(III)



(IV)

α-Mercapto-ketones are known to dimerize readily with formation of 2,5-dihydroxy-1,4-dithians;[2,3,4] we therefore suggest that compounds " A " and " B " are isomers or mixtures of isomers of perhydro-4a,8a-dihydroxythianthren (III), for which six geometrical isomers are possible. Hesse and Jörder[3] have shown that 2,5-dihydroxy-1,4-dithian exists as two geometric isomers, although they were unable to obtain these pure owing to their ready interconversion by way of 2-mercaptoacetaldehyde during crystallization. Hesse and Jörder also believed that the low values obtained for molecular weights (Rast method) were due to partial decomposition to 2-mercaptoacetaldehyde. The low and variable values obtained for the molecular weights of compound (III) (m. p. 150°, *M* 158, 217; m. p. 168—170°, *M* 162) may be explained similarly, as may also the variable melting points of compound " B " and the presence of a weak carbonyl band in the infrared spectra.

Baker and Barkenbus[4] have prepared 1,4-dithiens by reaction of sodium *S*-phenacyl thiolsulphate and several derivatives thereof with ethanolic hydrogen chloride, but the reaction failed with sodium *S*-acetonyl thiolsulphate. However, from a similar reaction with compound (II) we obtained the octahydrothianthren (IV). This compound was also prepared by treatment of perhydro-4a,8a-dihydroxythianthren, m. p. 168—170° with hydrogen chloride, so providing further proof of structure.

---

* Reactions of thiolsulphates with sodium sulphide often lead to trisulphides, but in this case (as in some others) the corresponding disulphide was obtained (Milligan, Saville, and Swan, *J.*, 1961, 4850.

[1] Backer, Strating, and Huisman, *Rec. Trav. chim.*, 1941, **60**, 381.

[2] Groth, *Arkiv Kemi, Min., Geol.*, 1924, **9**, 63; Hromatka and Engel, *Monatsh.*, 1948, **78**, 29, 38; Haberl, Grass, Hromatka, Brauner, and Preisinger, *ibid.*, 1955, **86**, 551; Haberl and Grass, *ibid.*, p. 599; Geiseler and Stache, *Chem. Ber.*, 1961, **94**, 337.

[3] Hesse and Jörder, *Chem. Ber.*, 1952, **85**, 924.

[4] Baker and Barkenbus, *J. Amer. Chem. Soc.*, 1936, **58**, 262.

Experimental.—Light petroleum had b. p. 55—70°. "Woelm" alumina (activity 1) was used for chromatography. M. p.s were determined in soda-glass capillary tubes. Microanalyses and molecular-weight determinations were carried out by the C.S.I.R.O. Microanalytical Laboratory.

Sodium S-2-*oxocyclohexyl thiolsulphate* (II). A mixture of 2-chlorocyclohexanone [5] (13·2 g.) and sodium thiosulphate pentahydrate (24·8 g.) in 50% aqueous ethanol (200 ml.) was heated under reflux for 1 hr. and then evaporated to dryness. The residue was extracted with boiling ethanol (100 ml.), and an equal volume of ether added to the extract. The *product* (15·0 g., 65%) separated as flocculent white needles, m. p. 169° (decomp.) (Found: C, 30·8; H, 4·3; S, 27·3. $C_6H_9NaO_4S_2$ requires C, 31·0; H, 3·9; S, 27·6%).

Di-(2-*oxocyclohexyl*) *disulphide* (I). (*a*) Bromine water was slowly added with shaking to an aqueous solution of sodium *S*-2-oxocyclohexyl thiolsulphate (II) until a faint yellow colour persisted. This was discharged by addition of a little sodium thiosulphate, and the precipitate was crystallized from aqueous methanol. The *product* separated as colourless needles, m. p. 80° [Found: C, 55·8; H, 7·1; S, 24·6%; *M* (Rast), 242. $C_{12}H_{18}O_2S_2$ requires C, 55·8; H, 7·0; S, 24·8%; *M*, 258], $\nu_{max.}$ 1693s cm.$^{-1}$ (KBr disc). The compound gave a *bis*-2,4-*dinitrophenylhydrazone*, yellow needles, m. p. 221° (from methyl cyanide) (Found: C, 47·1; H, 4·2; N, 18·0; S, 10·2. $C_{24}H_{26}N_8O_8S_2$ requires C, 46·6; H, 4·2; N, 18·1; S, 10·4%).

(*b*) 0·1M-Sodium sulphide (100 ml.) was added dropwise with stirring to a solution of the thiolsulphate (II) (4·6 g.) in phosphate buffer (100 ml.; pH 8) and kept overnight, then filtered. The precipitate was dried and crystallized from light petroleum, giving di-(2-oxocyclohexyl) disulphide (1·1 g.), m. p. 76—79°.

Perhydro-4a,8a-*dihydroxythianthren* (III). (*a*) (cf. Backer *et al.*[1]). Hydrogen sulphide was passed into an ice-cold solution of sodium (11·5 g.) in ethanol (250 ml.) until a weight increase of 8·5 g. was recorded. One-fifth of this solution was added dropwise with stirring to a solution of 2-chlorocyclohexanone (13·4 g.) in ethanol (50 ml.) at 0°. After 1 hr. the resulting precipitate was filtered off, dried, and extracted with several portions of boiling benzene. The *product* (0·97 g., 7·5%) crystallized from these extracts; further crystallization from light petroleum or ethanol raised the m. p. to 150° (Found: C, 55·4; H, 7·6; S, 24·6%; *M*, 158, 217. $C_{12}H_{20}O_2S_2$ requires C, 55·3; H, 7·7; S, 24·6%; *M*, 260), $\nu_{max.}$ (OH) 3455 cm.$^{-1}$ (in CCl_4), 3322 cm.$^{-1}$ (KBr disc), no absorption in the region 1600—2000 cm.$^{-1}$. After 3 months the m. p. had fallen to 133° and the infrared spectrum showed additional weak absorption at 1720 cm.$^{-1}$ (in CCl_4).

(*b*) A solution from sodium (11·5 g.) in ethanol (250 ml.), containing hydrogen sulphide (15·0 g.), was added with stirring to a solution of 2-chlorocyclohexanone (67 g.) in ethanol (250 ml.) at 0°. The precipitate was filtered off, dried, and extracted with boiling benzene, from which separated the product (22·1 g.), m. p. 154—157°. Several crystallizations from butan-1-ol raised the m. p. to 168—170°, but subsequent crystallization from ethanol caused the m. p. to fall to 153°, and, from chloroform, to 143—144°. The m. p. of each sample was depressed on admixture with a sample, m. p. 150°, prepared by method (*a*). A sample, m. p. 168—170°, was dried at 100° for 2 hr. for analysis [Found: C, 55·8; H, 7·8; S, 24·6%; *M*, (Rast), 162. $C_{12}H_{20}O_2S_2$ requires C, 55·3; H, 7·7; S, 24·6%; *M*, 260]. The infrared spectra of $CHCl_3$ solutions of samples, m. p. 168—170°, 153°, and 143—144° were the same as that of the product, m. p. 150°, obtained in (*a*) except for the presence of a very weak carbonyl absorption band at 1720 cm.$^{-1}$. All samples after three successive meltings and resolidifications had m. p.s in the range 125—135°.

1,2,3,4,5,6,7,8-*Octahydrothianthren* (IV). Anhydrous hydrogen chloride was passed through a suspension of sodium *S*-2-oxocyclohexyl thiolsulphate (10 g.) in boiling ethanol (200 ml.). The mixture was evaporated under reduced pressure and the residue partitioned between ethyl acetate and water. The ethyl acetate extract gave an oil (3·0 g.) which was chromatographed in light petroleum on alumina. The *product* (2·3 g.) crystallized from ethanol as prisms, m. p. 97° (Found: C, 63·9; H, 7·3; S, 28·5. $C_{12}H_{16}S_2$ requires C, 64·2; H, 7·2; S, 28·6%), $\nu_{max.}$ (in CCl_4) 1611 cm.$^{-1}$ (C:C).

Dehydration of perhydro-4a,8a-*dihydroxythianthren.* Anhydrous hydrogen chloride was passed through a boiling solution of perhydro-4a,8a-dihydroxythianthren (2·0 g.; m. p. 168—170°) in dioxan (50 ml.) under reflux for 3 hr. The solution was evaporated and the residue

---

[5] Newman, Farbman, and Hipsher, *Org. Synth.*, 1945, **25**, 22.

dissolved in light petroleum and chromatographed on alumina. The first fractions eluted (0·40 g.) were crystallized from ethanol, giving the octahydrothianthren (0·21 g.); m. p. 97°.

The authors thank Drs. W. F. Forbes and E. Spinner for the infrared spectral determinations. Technical assistance by Mr. B. Caldwell is gratefully acknowledged.

Division of Protein Chemistry, C.S.I.R.O. Wool Research Laboratories,
Parkville N.2 (Melbourne), Victoria, Australia. [*Received, July 7th,* 1961.]

1090 *Some Reactions of Sulphur Chloride Pentafluoride.*

By A. G. Massey and K. J. Packer.

Sulphur chloride pentafluoride is known to break up in the presence of ultraviolet radiation to give $SF_5\cdot$ and Cl· radicals;[1] similarly iron pentacarbonyl loses carbon monoxide to form lower iron carbonyls. It was therefore hoped that reaction of these two compounds would give rise to iron carbonyl derivatives containing sulphur pentafluoride groups. However, the initial experiments showed that sulphur chloride pentafluoride was too vigorous an oxidising agent for iron pentacarbonyl.

There was little reaction at −78°; more than 80% of the sulphur chloride pentafluoride was recovered after 24 hours. When the mixture was warmed to −23° a steady evolution of carbon monoxide commenced but it was impossible to isolate any product since on attempted manipulation, necessarily at room temperature, a vigorous reaction took place in which almost all the carbonyl groups of the iron pentacarbonyl were evolved as carbon monoxide; the remaining volatile material contained carbonyl fluoride, chloride, chloride fluoride, and sulphide. The final residue was a mixture of ferric chloride and fluoride.

Treatment of the iron pentacarbonyl with deficiency of sulphur chloride pentafluoride gave a brown product which contained terminal carbonyl groups but no S–F bonds. If the reaction (with excess of either reagent) was stopped after 5 minutes at room temperature an infrared spectrum of the solid product showed small peaks at 1800 and 1730 $cm.^{-1}$, the region normally associated with bridging carbonyl groups. It is possible that interaction of these bridging carbonyl groups with either sulphur chloride pentafluoride or sulphur tetrafluoride (formed in the initial stages of the reaction) gives rise to the carbonyl halides noted among the products. In support of this is the fact that these peaks disappear when the reaction is allowed to continue; also nickel carbonyl, which does not easily form bridging carbonyl groups, produces no carbonyl halides on reaction with sulphur chloride pentafluoride.

The $Ni(CO)_4$–SF_5Cl reaction is slow at room temperature, about 95% of the carbonyl groups being evolved as carbon monoxide over a period of several hours: $Ni(CO)_4 + SF_5Cl \longrightarrow NiClF_2 + 4CO + SF_4$. Carbon monoxide can be recovered unchanged when mixed with sulphur chloride pentafluoride in Pyrex vessels. However, if the vessel is provided with a quartz side-arm and irradiated with ultraviolet light, interaction takes place, carbonyl fluoride chloride, COFCl, being the predominant product. Small amounts of carbonyl fluoride and carbonyl sulphide are also formed, apparently arising from a side reaction between sulphur tetrafluoride and the carbon monoxide.

Experimental.—The volatile materials were handled in a conventional vacuum system; carbon monoxide was measured by means of a Töpler pump. The gaseous reaction products were fractionated and each fraction was weighed before being subjected to infrared analysis; one such fraction often showed infrared peaks corresponding to seven or more compounds.

Reaction of carbon monoxide with sulphur chloride pentafluoride. Sulphur chloride pentafluoride (0·82 mmole) and carbon monoxide (4·05 mmoles) were sealed into a vessel provided

---

[1] Roberts, *Quart. Rev.*, 1961, **15**, 30.

with a quartz side-arm; the quartz was irradiated, at a distance of 5 cm., by a 500-w medium-pressure mercury discharge for 5 hr. 3·66 mmoles of carbon monoxide were removed unchanged; the fraction volatile at −140° (57·6 mg.) contained carbonyl fluoride and chloride fluoride, traces of carbonyl sulphide and sulphur hexa- and tetra-fluoride, and some unchanged sulphur chloride pentafluoride ($COF_2 : COClF$ = *ca.* 1 : 15); the fraction volatile at −95° (87·4 mg.) contained carbonyl chloride a little carbonyl chloride fluoride, disulphur decafluoride, sulphur chloride pentafluoride, and small amounts of sulphuryl fluoride and silicon tetrafluoride arising from adventitious hydrolysis of sulphur tetrafluoride and subsequent attack of the glass vessel by the hydrogen fluoride so produced; no products were retained by the −95° trap.

Reaction of nickel carbonyl with the sulphur chloride pentafluoride. Nickel carbonyl (0·64 mmole) reacted slowly with sulphur chloride pentafluoride (0·77 mmole) to produce carbon monoxide (2·43 mmoles) in 17 hr. After another 21 hr. a further 0·05 mmole of carbon monoxide was recovered. The fraction volatile at −126° (62·0 mg.) contained mostly sulphur tetrafluoride, but small quantitites of carbonyl sulphide and sulphur chloride pentafluoride were also present; the fraction volatile at −78° (31·2 mg.) contained sulphur chloride pentafluoride and hydrolysis products of sulphur tetrafluoride. Nothing was retained by the −78° trap. The residue, by titration, contained 0·60 mequiv. of chloride ion.

Reaction of iron pentacarbonyl with sulphur chloride pentafluoride. Sulphur chloride pentafluoride (0·80 mmole) and iron pentacarbonyl (1·54 mmoles) were allowed to react at −23° for 30 min.; 0·44 mmole of carbon monoxide was removed. The fraction volatile at −78° (16·5 mg.) contained mostly sulphur tetrafluoride together with a little unchanged sulphur chloride pentafluoride. The solid product evolved a further 0·35 mmole of carbon monoxide in another 2 hr. at −23°. After 48 hr. at room temperature, 2·54 mmoles of carbon monoxide and 0·56 mmole of unchanged iron pentacarbonyl were recovered. The residue, on treatment with concentrated nitric acid, produced 0·76 mmole of carbon monoxide; the amount of chloride ion, by titration, was 0·63 mequiv.

Reaction of an excess of iron carbonyl with sulphur chloride pentafluoride. Sulphur chloride pentafluoride (0·88 mmole) and iron pentacarbonyl (1·38 mmoles) were allowed to react at room temperature for 96 hr.; 5·32 mmoles of carbon monoxide were evolved. The fraction volatile at −78° (82·0 mg.) contained carbonyl fluoride, sulphide, and chloride fluoride, but no sulphur tetrafluoride or hydrolysis products thereof; nothing was retained by the −78° trap. On treatment with concentrated nitric acid the residues evolved 0·12 mmole of carbon monoxide; the content of chloride ion (by titration) was 0·82 mequiv.

Reaction of iron carbonyl with an excess of sulphur chloride pentafluoride. Sulphur chloride pentafluoride (0·85 mmole) and iron pentacarbonyl (0·76 mmole) were allowed to react at room temperature for 144 hr.; 3·49 mmoles of carbon monoxide were evolved. The fraction volatile at −140° (19·5 mg.) contained carbonyl fluoride and sulphide, sulphur tetra- and hexa-fluoride, and a slight remainder of the chloride pentafluoride. The fraction volatile at −95° (118·2 mg.) contained sulphur chloride pentafluoride, sulphuryl fluoride, and silicon tetrafluoride, with traces of carbonyl chloride, fluoride, and sulphide. The fraction involatile at −95° (23·3 mg.) was pure disulphur dichloride (0·17 mmole).

The tube was resealed under a vacuum and heated at 120° for 23 hr.; no carbon monoxide was evolved. The fraction volatile at −140° (17·8 mg.) contained carbonyl sulphide, chloride fluoride, and fluoride, and sulphur tetrafluoride. The remaining fraction (1·6 mg.) was sulphur dioxide. Chloride ion in the residue after hydrolysis amounted to 0·30 mequiv.

Reaction of carbon monoxide with sulphur tetrafluoride. Qualitative experiments showed that no carbonyl fluoride was formed when carbon monoxide and sulphur tetrafluoride were left in Pyrex vessels for up to 17 hr. However, when the mixture was irradiated with ultraviolet light through a quartz side-arm, slow reaction was observed in which considerable amounts of carbonyl fluoride and sulphur hexafluoride and traces of carbonyl sulphide were produced.

We are indebted to Imperial Chemical Industries Limited, Alkali Division, for a gift of sulphur chloride pentafluoride, to the Mond Nickel Co. for gifts of nickel and iron carbonyl, and to D.S.I.R. for a maintenance grant (to K. J. P.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, July 10th*, 1961.]

1091. *Studies of the Coal-tar Bases. Part IX.*[1] *A New Method of Isolation of 2,3-Dimethyl- and 2,4,6-Trimethyl-pyridine.*

By R. F. Evans and W. Kynaston.

In this laboratory, the three major components of the commercial β-picoline fraction of coal-tar, 2,6-dimethyl- and 3- and 4-methyl-pyridine, have been separated by fractional distillation in the presence of an azeotrope-forming substance such as acetic or propionic acid.[2] Albert,[3] improving an earlier method,[4] has shown that, if the mixture of bases is first converted into the *N*-oxides, fractional distillation separates the three *N*-oxides from which the parent pyridine bases can be recovered by treatment with phosphorus trichloride.

Accordingly a lutidine fraction containing 2,3-, 2,4-, and 2,5-dimethylpyridine was converted into the *N*-oxides; at −12°, 2,3-dimethylpyridine *N*-oxide separated preferentially. Similarly, the *N*-oxides produced from a mixture of 2,3,6- and 2,4,6-trimethylpyridines deposited 2,3,6-trimethylpyridine *N*-oxide at −12°. Nitration[1] of the mixed *N*-oxides at 100° was accompanied by widespread oxidation and only 26% of the 2,4,6-trimethylpyridine *N*-oxide could be recovered; at 60—80°, oxidation was less and 2,4,6-trimethylpyridine *N*-oxide of 90% purity was recovered. Recycling this *N*-oxide through the nitration procedure did not improve the purity. Hence the *N*-oxide was reduced with iron and acetic acid to the parent 2,4,6-trimethylpyridine which was purified through its hydrochloride.[5]

Lutidine and collidine *N*-oxides can be nitrated if there is a vacant 4-position in the pyridine nucleus. The infrared spectra possess intense bands at 1240~1275 cm.$^{-1}$, characteristic of the *N*-oxide linkage.[6]

Experimental.—Microanalyses were carried out by Miss M. Corner and staff of this laboratory. M. p.s are corrected.

Oxidation of lutidines. For reference, specimens (5 g.) of 2,3-,[7] 2,4-,[8] and 2,5-dimethylpyridine[8] were separately converted into their *N*-oxides with glacial acetic acid (50 ml.) and 30% hydrogen peroxide (12 ml.) according to Ochiai's procedure.[9] 2,3-Dimethylpyridine *N*-oxide, b. p. 118°/4 mm., and 2,5-dimethylpyridine *N*-oxide, b. p. 86°/0·3 mm., were converted into their 4-nitro-derivatives. 2,4-Dimethylpyridine *N*-oxide, b. p. 91°/0·3 mm., was recovered unchanged from the nitration medium.[10] The oxides are hygroscopic.

2,3-Dimethylpyridine *N*-oxide (1·6 g.) was heated under reflux on the steam-bath for 3½ hr. with concentrated sulphuric acid (3·7 ml.; *d* 1·98) and concentrated nitric acid (1·3 ml.; *d* 1·42). The mixture was poured into ice-water, made alkaline with aqueous sodium hydroxide, and extracted with chloroform. The dried (Na_2SO_4) extract, on evaporation, furnished a residue (2·4 g.) which, recrystallised from 96% alcohol, gave *2,3-dimethyl-4-nitropyridine* N-*oxide*, m. p. 91·5—93° (Found: C, 49·9; H, 5·2; N, 16·4. $C_7H_8N_2O_3$ requires C, 50·0; H, 4·8; N, 16·7%).

2,5-Dimethylpyridine *N*-oxide (1·1 g.) was similarly treated with concentrated sulphuric acid (5 ml.) and concentrated nitric acid (1 ml.) for 1 hr., affording *2,5-dimethyl-4-nitropyridine* N-*oxide*, m. p. 151—152° (from 96% alcohol) (Found: C, 49·9; H, 4·9; N, 16·5%).

The lutidine mixture investigated was a fraction, b. p. 148—158°, enriched in the 2,3-isomer by removal[8] of 2,4- and 2,5-dimethylpyridine as the hydrochloride and the phenol

---

[1] Part VIII, Evans, *J.*, 1959, 1312.
[2] Coulson and Jones, *J. Soc. Chem. Ind.*, 1946, **65**, 169.
[3] Albert, *Chem. and Ind.*, 1958, 582.
[4] Ochiai, Ikehara, Kato, and Irekawa, *J. Pharm. Soc. Japan*, 1951, **71**, 1385.
[5] Brown, Johnson, and Podall, *J. Amer. Chem. Soc.*, 1954, **76**, 5556.
[6] Katritzky, *Quart. Rev.*, 1959, **13**, 372.
[7] Wibaut and Kooyman, *Rec. Trav. chim.*, 1944, **63**, 231.
[8] Coulson, Cox, Herington, and Martin, *J.*, 1959, 1934.
[9] Ochiai, *J. Org. Chem.*, 1953, **18**, 534.
[10] Ishikawa, *J. Pharm. Soc. Japan*, 1945, **65**, 6.

complex, respectively. Infrared analysis revealed that the 2,3- and 2,5-isomers together amounted to 40% of this fraction.

This fraction (108 g.) was converted into the *N*-oxides with glacial acetic acid (500 ml.) and 30% hydrogen peroxide (98 ml.) according to Ochiai's procedure.[9] The oxides were distilled and a fraction (102 g.) of b. p. 108—120°/0·3 mm. was cooled to −12° overnight and then filtered. The solid (11·2 g.), on crystallisation from acetone at −12°, afforded 2,3-dimethylpyridine *N*-oxide (5·1 g.), identified by its infrared spectrum.

Oxidation of collidines. 2,3,6-Trimethylpyridine [1] (1·9 g.) was oxidised to the *N*-oxide in glacial acetic acid (20 ml.) by 30% hydrogen peroxide (3·7 ml.). 2,3,6-*Trimethylpyridine* N-*oxide,* b. p. 84°/0·2 mm., crystallised from ether–acetone at −12° as a dihydrate, m. p. 63° (Found: C, 56·4; H, 9·3; N, 8·0. $C_8H_{15}NO_3$ requires C, 55·5; H, 8·8; N, 8·1%), $\nu_{max.}$ (in $CHCl_3$) 3380, 1630 cm.$^{-1}$ (OH stretching and OH deformation, respectively), and 1268 cm.$^{-1}$ (N–O).

The *picrate* crystallised from ethanol as yellow needles, m. p. 97—98·5° (Found: C, 45·6; H, 3·8; N, 15·1. $C_{14}H_{14}N_4O_8$ requires C, 45·9; H, 3·9; N, 15·3%).

The collidine fraction, b. p. 106—107°/100 mm., obtained by the refractionation through a 50-plate column of a crude collidine, was shown by infrared analysis to contain 2,3,6-trimethylpyridine (45%) and its 2,4,6-isomer together with a trace of 3-ethylpyridine. This mixture (121 g.) was converted into the *N*-oxides with glacial acetic acid (600 ml.) and 30% hydrogen peroxide (198 ml.) as usual.[9]

The mixed *N*-oxides (76·2 g.; b. p. 98—101°/0·4 mm.) were kept at −12° overnight and the solid (11·7 g.) was collected on a cooled filter. Infrared analysis revealed that the solid was substantially 2,3,6-trimethylpyridine *N*-oxide. The filtrate (62·1 g.), concentrated sulphuric acid (200 ml.; *d* 1·98), and concentrated nitric acid (30 ml.; *d* 1·42) were heated on the steam bath for $\frac{3}{4}$ hr. at 60° ± 5° and 1 hr. at 75° ± 5°, then poured into ice-cold water (500 ml.), made slightly alkaline with ice-cold concentrated aqueous sodium hydroxide, and filtered. The solid, crystallised from alcohol, furnished 2,3,6-trimethyl-4-nitropyridine *N*-oxide [1] (17·8 g.). Three chloroform extractions of the filtrate, and distillation of the dried (Na_2SO_4) chloroform extract, gave 2,4,6-trimethylpyridine *N*-oxide (28 g., 70%), b. p. 80—88°/0·1 mm., of 90—95% purity. Crystallisation of the distillation residue from alcohol at −12° led to the recovery of additional 2,3,6-trimethyl-4-nitropyridine *N*-oxide (1·7 g.; total 67% based on 2,3,6-trimethylpyridine).

A binary mixture (48·2 g.) of collidine *N*-oxides containing 65% of the 2,3,6-isomer afforded 2,3,6-trimethylpyridine *N*-oxide (7·9 g.) on cooling to −15° for 24 hr. The filtrate (33·8 g.), on nitration with concentrated sulphuric acid (104 ml.) and concentrated nitric acid (27 ml.) on the steam bath for 7 hr., afforded a 60% yield of 2,3,6-trimethyl-4-nitropyridine *N*-oxide but only 26% of the 2,4,6-trimethylpyridine *N*-oxide was recovered.

2,4,6-*Trimethylpyridine.* 2,4,6-Trimethylpyridine *N*-oxide (14·9 g.), iron powder (7·5 g.), and glacial acetic acid (150 ml.) were heated on the steam-bath for 2 hr., then made alkaline with aqueous sodium hydroxide and steam distilled. Ether-extraction of the distillate and distillation of the dried (Na_2SO_4) extract afforded 2,4,6-trimethylpyridine (9·5 g., 72%), b. p. 170—172°. The infrared spectrum of this material revealed the presence of 5—10% of the 2,3,6-isomer. No improvement could be effected in the purity of the 2,4,6-trimethylpyridine if the *N*-oxide, before reduction, was re-treated with a nitrating mixture. The 2,4,6-trimethylpyridine was finally freed from its 2,3,6-isomer by conversion into the mixed hydrochlorides,[9] followed by one crystallisation from alcohol and decomposition with alkali. Infrared examination confirmed the absence of 2,3,6-trimethylpyridine in the specimen.

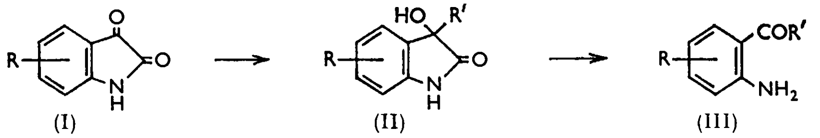
NATIONAL CHEMICAL LABORATORY, D.S.I.R.,
TEDDINGTON, MIDDLESEX.
[Present address (R. F. E.):
DEPARTMENT OF MEDICAL CHEMISTRY, AUSTRALIAN NATIONAL UNIVERSITY,
CANBERRA, AUSTRALIA.]

[*Received, July* 18*th,* 1961.]

1092. *Indoles. Part VI.*[1] *Some Dioxindoles and their Conversion into o-Aminoaryl Ketones.*

By B. Mills and K. Schofield.

Earlier papers in this series described the synthesis of *o*-aminoaryl ketones by the oxidative fission of the 2,3-bond of indole derivatives. The availability of a good range of isatins (I), the possibility of converting these into dioxindoles (II) by reaction with Grignard reagents,[2] and the feasibility of oxidising the dioxindoles to *o*-aminoaryl ketones (III),[3] promised access to compounds not easily obtainable *via* indoles.



Kohn[2] carried out a number of the reactions (I ⟶ II) by adding powdered isatin to an excess of Grignard reagent in ether. More recently[4] a lithium reagent was used instead of the Grignard reagent, and also an attempt was made[5] to overcome some of the disadvantages of Kohn's method by extracting isatin from a Soxhlet thimble into a boiling solution of a Grignard reagent in benzene. Our own experiments, carried out in 1955,[6] were very similar to those of Baumgarten and Creger,[5] but in a number of cases we found it preferable to add the Grignard reagent, in benzene, to a stirred suspension of the isatin in the same solvent rather than to use a Soxhlet apparatus. In the reaction between 4-chloroisatin and phenylmagnesium bromide the immediate product of the reaction was the 1 : 1 complex of 4-chloroisatin and 4-chloro-3-phenyldioxindole. The latter was liberated by passage of the complex, in benzene, over alumina.

Inagaki[3] used alkaline hydrogen peroxide solution to oxidise 3-phenyldioxindole to 2-aminobenzophenone. With some variations in detail this method was successful in all but one of the cases (that of 3-benzyldioxindole) which we examined. However, we found it better to carry out the oxidations by treating solutions of the dioxindoles in alkali with potassium ferricyanide. Whilst hydrogen peroxide gave a cleaner initial product, potassium ferricyanide gave better yields, but it also failed with 3-benzyldioxindole.

The present syntheses of 2-amino-4- and -6-chlorobenzophenone prove the constitution of 4-chloro-2,3-diphenylindole described earlier,[1] for this indole could be converted into 2-amino-6-chlorobenzophenone.

Experimental.—*3-Substituted dioxindoles.* The Grignard solution was prepared in ether in the usual way, and the ether was then replaced by benzene. The resulting solution was added dropwise to a suspension of the isatin stirred in benzene, and the mixture was then refluxed, decomposed with dilute sulphuric acid, and steam-distilled. The solid residue was collected and digested with 20% aqueous potassium hydroxide. Filtration and acidification gave the product. The following are notes on the preparations listed in Table 1.

(1) Yellow needles, m. p. 208—209°, from ethanol.

(2) Yellow plates, m. p. 208—210°, from ethanol.

(3) The reaction solution was decomposed with ice and acetic acid. The ether layer was separated, and the aqueous layer was extracted continuously with ether. Evaporation of the combined ether solutions, after being washed and dried, gave the product as yellow needles, m. p. 163—165° (from ethanol).

(4) Yellow needles, m. p. 166—168°, from benzene.

---

[1] Part V, Ockenden and Schofield, *J.*, 1957, 3175.

[2] Kohn, *Monatsh.*, 1910, **31**, 747; Kohn and Ostersetzer, *ibid.*, 1913, **34**, 789.

[3] Inagaki, *J. Pharm. Soc. Japan*, 1939, **59**, 5.

[4] Bruce, *J.*, 1959, 2366.

[5] Baumgarten and Creger, *J. Amer. Chem. Soc.*, 1960, **82**, 4634.

[6] Mills, Ph.D. Thesis, London, 1955.

(5) The *complex* formed red needles, m. p. 225—228° (Found: C, 59·3; H, 3·3. $C_{14}H_{10}ClNO_2,C_8H_4ClNO_2$ requires C, 59·7; H, 3·2%). Passage of the complex in benzene over alumina gave an almost quantitative yield of 4-*chloro*-3-*phenyldioxindole*, which formed yellow needles, m. p. 259—261° (Found: C, 65·3; H, 3·8. $C_{14}H_{10}ClNO_2$ requires C, 64·7; H, 3·9%), from ethanol.

(6) Yellow needles, m. p. 243—244° (Found: C, 64·0; H, 3·9%), from ethanol.

(7) The reaction mixture was decomposed with ice and dilute hydrochloric acid, and the solid was collected. Fractional crystallisation from ethanol gave golden needles (1·62 g.) of 4-*chloro*-3-*methyldioxindole*, m. p. 240—241° (Found: C, 54·5; H, 3·8. $C_9H_8ClNO_2$ requires C, 54·6; H, 4·0%), and a mixture (0·6 g.) which was not separated further.

TABLE 1.

Dioxindole	Isatin[a] (g.)	in benzene (c.c.)	Grignard reagent from organic halide (g.)	in benzene (c.c.)	Time of reflux (hr.)	Yield (%)
(1) 3-Phenyl	1·5	50	9·6	50	0·5	50
(2) 3-*o*-Tolyl	5·0	250	32·0	100	1	60
(3) 3-Methyl[b]	15·0	750	72·0	300	0·25	63
(4) 3-Benzyl	10·0	200	47·5	,,	3	37
(5) 4-Chloro-3-phenyl	2·0	75	9·4	50	24	35[c]
(6) 6-Chloro-3-phenyl	15·0	350	70·0	250	3	54
(7) 4-Chloro-3-methyl[b]	5·0	200	19·5	75	1	30

[a] 4- and 6-Chloroisatin were made by the method of Senear *et al.*[7] These experiments were carried out in ether. [c] Of 1 : 1 complex (see below).

Oxidations with hydrogen peroxide. The dioxindole in aqueous sodium hydroxide was treated with an excess of hydrogen peroxide. The yellow solution was heated on the steam-bath until oxygen evolution ceased, and the amine was extracted with ether. The details are in Table 2.

TABLE 2.

Dioxindole	Wt. (g.)	25% NaOH (c.c.)	H_2O_2 (30-vol.) (c.c.)	Yield of amine (%)
3-Phenyl	0·2	3·2	2·0	52
3-*o*-Tolyl	1·0	20	20	76[a]
3-Methyl	0·4	8	12	21[b]
6-Chloro-3-phenyl	1·5	25	15	45[c]
4-Chloro-3-methyl	0·4	8	12	12[d]

[a] 2-Amino-2′-methylbenzophenone formed yellow needles, m. p. 79—80° (Found: C, 79·4; H, 6·1. Calc. for $C_{14}H_{13}NO$: C, 79·6; H, 6·2%), from aqueous ethanol. [b] The yield of *o*-acetamidoacetophenone (m. p. and mixed m. p. 73—75°) obtained by acetylating the crude reaction product. [c] In small-scale experiments yields up to 95% were obtained. 2-*Amino*-4-*chlorobenzophenone* formed yellow needles, m. p. 83—85° (Found: C, 67·0; H, 3·9. $C_{13}H_{10}ClNO$ requires C, 67·4; H, 4·3%) (from aqueous ethanol). [d] From aqueous ethanol 2-amino-6-chloroacetophenone gave yellow plates, m. p. 88—90° (Found: C, 56·2; H, 4·4. Calc. for C_8H_8ClNO: C, 56·6; H, 4·7%).

TABLE 3.

Dioxindole	Wt. (g.)	KOH in water (g.)	KOH in water (c.c.)	Ferricyanide in water (g.)	Ferricyanide in water (c.c.)	Crude product (g.)	Crude product m. p.
3-*o*-Tolyl	4·8	16·8	50	13·2	30	3·8	72—76°
3-Methyl	0·4	1·0	3·0	1·62	10	0·15[a]	—
4-Chloro-3-phenyl	0·1	0·35	1·1	0·25	2	0·04[b]	91—95
6-Chloro-3-phenyl	1·5	4·9	14·7	3·6	30	0·87	78—81
4-Chloro-3-methyl	0·4	1·0	3·0	1·34	10	0·05	84—87

[a] Of *o*-acetamidoacetophenone, formed by acetylating the crude product. [b] 2-Amino-6-chlorobenzophenone separated from aqueous ethanol as yellow prisms, identical with the compound described in the text.

Oxidations with potassium ferricyanide. The dioxindole in 30% potassium hydroxide solution was treated with aqueous potassium ferricyanide, and the mixture was heated for 0·5 hr. on the steam-bath. On cooling, the crude amines were collected. For details see Table 3.

---

[7] Senear, Sargent, Mead, and Koepfli, *J. Amer. Chem. Soc.*, 1946, **68**, 2695.

Ozonisation of 4-*chloro*-2,3-*diphenylindole* [by D. W. OCKENDEN]. 4-Chloro-2,3-diphenylindole (0·5 g.) in ethyl acetate (25 c.c.) was ozonised at 0° by the method described earlier.[8] The *ozonide* (0·34 g.) formed prisms, m. p. 172—174° (decomp.) (Found: C, 68·8; H, 4·2. $C_{20}H_{14}ClNO_3$ requires C, 68·3; H, 4·0%). The ozonide (0·25 g.), ethyl acetate (25 c.c.), and 5% palladised charcoal (0·2 g.) were shaken with hydrogen. When the reaction was complete (15 min.) the mixture was filtered and the solvent was removed. 2-*Benzamido*-6-*chlorobenzophenone* formed needles, m. p. 140—141° (Found: C, 72·7; H, 4·4. $C_{20}H_{14}ClNO_2$ requires C, 71·5; H, 4·2%). The amide (0·3 g.), concentrated hydrochloric acid (10 c.c.), and acetic acid (10 c.c.) were boiled for 3 hr. Concentration, basification, and recrystallisation of the product from benzene–ligroin gave 2-*amino*-6-*chlorobenzophenone* (80%), as yellow prisms, m. p. 101—103° (Found: C, 67·7; H, 4·8. $C_{13}H_{10}ClNO$ requires C, 67·4; H, 4·4%), identical with the compound described in Table 2.

WASHINGTON SINGER LABORATORIES,
PRINCE OF WALES ROAD, EXETER.

[*Received, July 25th,* 1961.]

---

[8] Ockenden and Schofield, *J.*, 1953, 612.

1093. *Geometrical Isomerism in an Azine.*

By IAN FLEMING and JOHN HARLEY-MASON.

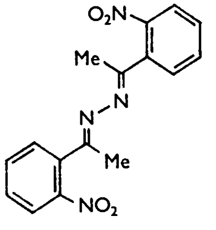
DURING a synthetic study we have made *o*-nitroacetophenone azine from hydrazine and *o*-nitroacetophenone. The azine was a mixture of two separable crystalline forms, yellow prisms, m. p. 135°, and paler yellow needles, m. p. 128°, designated A and B respectively.

The mixture of A and B, after being kept for 4 months in daylight (or after treatment with liquid hydrogen cyanide for one week at room temperature), gave a mixture of A and a third crystalline form, C, very pale yellow prisms, m. p. 166—167°.

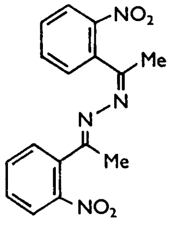
The evidence that A, B, and C are the three theoretically possible geometrical isomers of *o*-nitroacetophenone azine, (I), (II), and (III), is as follows:

(*a*) After separation, forms A, B, and C did not revert to the mixtures on recrystallisation from a variety of solvents.

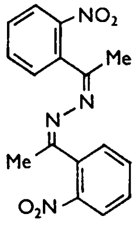
(*b*) Irradiation of each of the separated isomers in dioxan solution with ultraviolet light for 4 hr. caused some interconversions: A gave A and a little C. C gave C and a little A. B, however, gave a roughly equal mixture of A, B, and C.



(I)



(II)



(III)

(*c*) The similar but not identical infrared spectra were consistent with the structure.

(*d*) The ultraviolet spectra, taken in ethanol, were similar but not identical. A and B gave strong end-absorption with no maximum above 210 mμ, the curve of form A being displaced relative to that of B by about 10 mμ to longer wavelengths. The curve of form C was similar in position to that of B, but a maximum at 217 mμ (ε 24,300) was just resolved. All three spectra were similar to that of *o*-nitrobenzaldehyde azine.[1]

(*e*) The nuclear magnetic resonance spectra of forms A and C showed a sharp singlet at τ 7·7 and 7·9, respectively, due to the methyl protons. The spectrum of B, however, showed a symmetrical doublet centred at τ 7·55. This indicates that form B is the unsymmetrical isomer (II), since in this case it is possible for the two methyl groups to be exposed to different shielding effects from the benzene rings.

---

[1] Ferguson and Branch, *J. Amer. Chem. Soc.*, 1944, **66**, 1467.

The fact that form A is the most abundant and has the strongest ultraviolet and visible absorption indicates that it has the structure (I), which shows the least strain in approaching planarity. Form C, therefore, is assigned structure (III).

To the best of our knowledge this is the first example of the isolation and characterisation of all three possible geometrical isomers of an azine. Dale and Zechmeister [2] were able to separate two forms each of cinnamaldehyde azine and phenylpentadienal azine geometrically isomeric in the azine system. The all-*trans*-forms were crystalline but they obtained the " *cis* I " forms only as oils and no analyses were reported.

Experimental.—Nuclear magnetic resonance spectra were obtained for pyridine solutions at 40 Mc./sec. by using a Varian Associates V4300B spectrometer and 12" electromagnet with flux stabilisation and sample spinning. Positions of reference are quoted on the τ scale [τ ($SiMe_4$) = 10·00] and have been measured against tetramethylsilane as an internal reference, with the aid of the side-bands generated by a Muirhead-Wigan D695A decade oscillator. The infrared spectra were recorded on a Perkin-Elmer model 21 with a sodium chloride prism, for Nujol and hexachlorobutadiene mulls.

Light petroleum refers to the fraction boiling between 40° and 60°.

o-*Nitroacetophenone azine.* *o*-Nitroacetophenone (13·2 g.) was refluxed with 100% hydrazine hydrate (2 g.) in ethanol (8 ml.) containing concentrated hydrochloric acid (4 drops) for 7 hr. The mixture was left to cool overnight, to give pale yellow crystals (11·9 g., 92%), m. p. 117—129°.

Separation of isomers A and B. The crude azine (1 g.) was dissolved in benzene (20 ml.); to the filtered solution light petroleum (20 ml.) was added, and the mixture kept at room temperature without disturbance for 1 hr. The deep yellow prisms of *form A* were collected (0·2 g.), m. p. 135° (Found: C, 58·7; H, 4·3; N, 17·5. $C_{16}H_{14}N_4O_4$ requires C, 58·9; H, 4·3; N, 17·2%), $\nu_{max.}$ 1621 (C=N), 1576 (Ar), 1536 and 1371 (NO_2) cm.$^{-1}$.

The mother liquor was evaporated, the residue dissolved in benzene (7 ml.), to the filtered solution light petroleum (15 ml.) was added, and the mixture kept at room temperature for 24 hr. The precipitated crystals were separated by hand to give *isomer B* as clusters of pale yellow needles (0·1 g.), m. p. 128° (Found: C, 58·5; H, 4·6; N, 17·5%), $\nu_{max.}$ 1626, 1575, 1523, and 1353 cm.$^{-1}$.

Preparation of isomer C. *o*-Nitroacetophenone azine (the mixture of A and B) was kept in a glass bottle in diffused daylight for 4 months. On repeating the separation above, forms A and C crystallised together and were separated by hand. Form C, when recrystallised from acetone, had m. p. 166—167° [Found: C, 58·8; H, 4·7; N, 17·5%; *M* (in CH_2Cl_2; cf. Iyengar [3]), 311 ± 20. $C_{16}H_{14}N_4O_4$ requires *M*, 326), $\nu_{max.}$ 1628, 1575, 1523 and 1353 cm.$^{-1}$.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August* 1*st*, 1961.

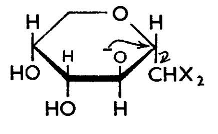
---

[2] Dale and Zechmeister, *J. Amer. Chem. Soc.*, 1953, **75**, 2384.
[3] Iyengar, *Rec. Trav. chim.*, 1954, **73**, 789.

1094. *Diethylsulphonyl-(2-O-methyl-α-D-arabopyranosyl)methane and its Behaviour with Base.*

By L. HOUGH and A. C. RICHARDSON.

THE degradation of diethylsulphonylpyranosylmethane derivatives (*e.g.*, II; R = H) with base proceeds by a nucleophilic mechanism involving the cleavage of the 1,α-bond by participation with a lone pair of electrons on the ring-oxygen atom.[1] In the alkaline hydrolysis of phenyl glycosides the 2-hydroxyl group participates in the elimination of the phenoxide ion.[2] Since an analogous mechanism (cf. A) may be operative in the degradation of the cyclic disulphones, a suitably protected derivative, namely, diethylsulphonyl-(2-*O*-methyl-α-D-arabopyranosyl)methane (II; R = Me), was prepared and its behaviour with base examined.



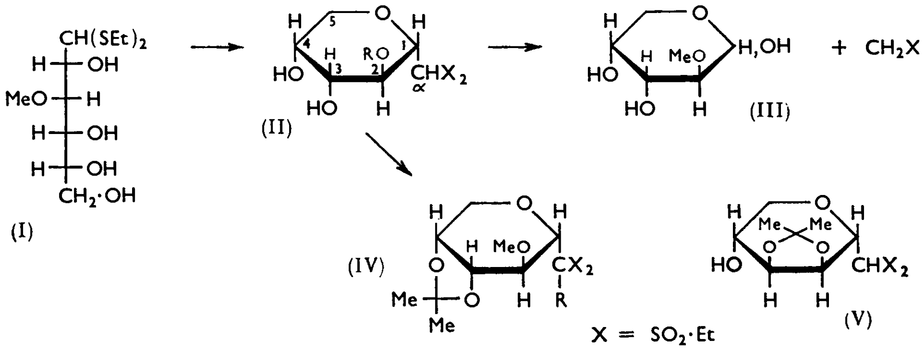
(A)

---

[1] Hough and Richardson, *Proc. Chem. Soc.*, 1959, 193.
[2] Ballou, *Adv. Carbohydrate Chem.*, 1954, **9**, 59.

3-*O*-Methyl-D-glucose was readily converted into the corresponding diethyl dithioacetal (I) which was oxidised by aqueous peroxypropionic acid to a syrupy disulphone. Periodate oxidation of this sulphone was consistent with the cyclic structure (II; R = Me), since it was rapidly oxidised by one mol. of periodate, after which a slower over-oxidation took place. The molecular rotation ($[M]_D$ +3040° in methanol) was similar to that of α-D-arabopyranosyldiethylsulphonylmethane (II; R = H) ($[M]_D$ +3800°), thus indicating the α-configuration for the diethylsulphonylmethyl group. The structure of the disulphone (II; R = Me) was confirmed by conversion into a syrupy mono-*O*-isopropylidene derivative (IV; R = H) and subsequent *C*-methylation with silver oxide and methyl iodide to the known 1,1-diethylsulphonyl-1-(3,4-*O*-isopropylidene-2-*O*-methyl-α-D-arabopyranosyl)ethane (IV; R = Me).

Diethylsulphonyl-(2-*O*-methyl-α-D-arabopyranosyl)methane (II; R = Me) was readily cleaved by dilute aqueous ammonia into diethylsulphonylmethane and 2-*O*-methyl-D-arabinose (III; R = Me),[3,4] which was characterised by conversion into the crystalline 3,4-*O*-isopropylidene derivative.[4] The degradation was complete after 5 days. Consequently the reaction of diethylsulphonylpyranosylmethane derivatives with base is not analogous to that of the alkali-sensitive glycosides, in as much as the 2-hydroxyl does not participate in the elimination of the diethylsulphonylmethyl group. It is noteworthy that diethylsulphonyl-(2,3-*O*-isopropylidene-α-D-lyxopyranosyl)methane (V) was stable towards base, but this inhibition has been attributed to steric factors resulting from the superimposition of the five-membered ring on to the six-membered ring.[1]



Experimental.—M. p.s were determined on the Kofler micro-heating stage. Evaporations were under reduced pressure. Paper chromatography was carried out by the descending method at room temperature on Whatman No. 1 filter paper with the following mobile phases: (i) butan-1-ol–pyridine–water (10 : 3 : 3 v/v); (ii) butan-1-ol–ethanol–water (40 : 11 : 19 v/v). The compounds were detected with 4% w/v ammoniacal silver nitrate and rates of movement are quoted relative to that of rhamnose (R_{Rh}) and the solvent front (R_F).

3-O-*Methyl*-D-*glucose diethyl dithioacetal* (I). A mixture of 3-*O*-methyl-D-glucose (2·54 g.), ethanethiol (5 ml.), and concentrated hydrochloric acid (2·5 ml.) was shaken for 2½ hr. The resulting solution was diluted with ethanol and neutralised with lead carbonate. The solution, after filtration, was concentrated to a syrup, which crystallised on addition of ether. The crystals were collected and recrystallised from ether (750 ml.) giving, as three crops (2·66 g., 68%), 3-O-*methyl*-D-*glucose diethyl dithioacetal*, m. p. 72—76°, $[\alpha]_D$ −16·7° (*c* 1·23 in MeOH), R_{Rh} 2·0 (solvent i) and 2·24 (solvent ii) (Found: C, 44·2; H, 8·1; S, 20·6. $C_{11}H_{24}O_5S_2$ requires C, 44·0; H, 8·0; S, 21·3%).

Oxidation of 3-O-*methyl*-D-*glucose diethyl dithioacetal with aqueous peroxypropionic acid.* A solution of the dithioacetal (1·18 g.) in 50% aqueous dioxan (20 ml.) was cooled to −10°, an

[3] D. C. C. Smith and Barker, *Chem. and Ind.*, 1952, **30**, 1035.

[4] Huffman, Lewis, F. Smith, and Spriesterbach, *J. Amer. Chem. Soc.*, 1955, **77**, 4346.

excess of aqueous peroxypropionic acid added dropwise with stirring, and the solution then kept at $-10°$ for ½ hr. After a further ½ hr. at room temperature concentration yielded a syrup which was dried under a high vacuum to *diethylsulphonyl-*(2-O-*methyl*-α-D-*arabopyranosyl*)-*methane* (1·35 g.), a glass, $[\alpha]_D$ $-8·6°$ (*c* 6·75 in MeOH), R_{Rh} 1·85 (solvent i) and 2·04 (solvent ii) (Found: C, 37·8; H, 6·5; OMe, 8·8. $C_{11}H_{22}O_8S_2$ requires C, 38·2; H, 6·4; OMe, 9·0%).

Reaction of the 2-*O*-methyl derivative with acetic anhydride containing an equal volume of pyridine or a trace of sulphuric acid yielded a syrupy di-*O*-acetate.

The disulphone (0·054 g.) was treated with 0·01M-sodium metaperiodate (100 ml.) and the uptake of oxidant and the release of formic acid were determined.[5] The following results were obtained:

Time (hr.)	½	1	2½	4	5½	24	48
Periodate uptake (mol.)	0·77	0·85	1·0	1·06	1·07	1·36	1·58
Formic acid (mol.)	0·08	0·13	0·13	0·11	0·26	0·45	0·72

Treatment of diethylsulphonyl-(2-O-*methyl*-α-D-*arabopyranosyl*)*methane with dilute aqueous ammonia.* The disulphone (0·23 g.) was dissolved in *ca.* 0·5N-ammonia (10 ml.), and the reaction followed by paper chromatography; one reducing sugar was produced which was indistinguishable from 2-*O*-methylarabinose. Reaction was complete after 5 days, then the reaction mixture was extracted continuously with chloroform to remove diethylsulphonylmethane. The aqueous layer was then concentrated to a pale yellow syrup (0·082 g., 74%) of 2-*O*-methyl-D-arabinose,[3,4] $[\alpha]_D$ $-105°$ (*c* 0·82 in H_2O), R_F 0·43 (solvent ii).

A solution of the syrup (0·041 g.) in acetone (10 ml.) containing concentrated sulphuric acid (1 drop) was shaken for 18 hr. with anhydrous copper sulphate (0·5 g.). After neutralisation with ammonia (*d* 0·88; 2 drops) the solution was filtered and the filtrate concentrated to a crystalline residue. Sublimation gave 3,4-*O*-isopropylidene-2-*O*-methyl-D-arabinose [4] (0·016 g.), m. p. 115—117°, R_{Rh} 2·0 (solvent i) (Found: C, 52·5; H, 7·9; OMe, 15·9. Calc. for $C_9H_{16}O_5$: C, 52·9; H, 7·8; OMe, 15·2%).

Protection and C-*methylation of the disulphone.* A mixture of the disulphone (0·64 g.), dry acetone (20 ml.), anhydrous copper sulphate (2 g.), and concentrated sulphuric acid (1 drop) was shaken for 24 hr., neutralised with ammonia (*d* 0·88; 2 drops), filtered, and concentrated to a syrup, which was extracted with ether (2 × 25 ml.). Concentration of the combined extracts afforded the isopropylidene derivative as a colourless syrup (0·48 g.).

This derivative was heated with finely powdered anhydrous calcium sulphate in methyl iodide (15 ml.) for 24 hr. Freshly prepared silver oxide (2 g.) was added in small portions during the first 3 hr. The insoluble material was then removed and the filtrate evaporated to a crystalline residue. Recrystallisation from methanol yielded plates (0·17 g.) of 1,1-diethylsulphonyl-1-(3,4-*O*-isopropylidene-2-*O*-methyl-α-D-arabopyranosyl)ethane, m. p. 175—185° (unchanged on recrystallisation), $[\alpha]_D$ $-8·8°$ (*c* 0·57 in MeOH). The infrared spectrum was identical with that of an authentic sample prepared from α-D-arabopyranosyldiethylsulphonylmethane (II; R = H) by conversion into its 3,4-*O*-isopropylidene derivative and subsequent methylation with silver oxide and methyl iodide.

One of us (A. C. R.) thanks the Department of Scientific and Industrial Research for a Maintenance Award.

THE UNIVERSITY, BRISTOL. [*Received, August 4th,* 1961.]

---

[5] Hough and Coxon, *J.*, 1961, 1463.