NOTES.

The Liquid Dinitrogen Tetroxide Solvent System. Part XVII. The Equilibrium between Alkylammonium and Nitrosonium Tetranitratozincates.*

By C. C. ADDISON, N. HODGE, and R. THOMPSON.

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THE liquid obtained on dissolving zinc in a solution of alkylammonium nitrate in liquid dinitrogen tetroxide contains the anion $[Zn(NO_3)_4]^{2-}$; the corresponding cations are NR_4^+ and NO^+. The salt which separates on crystallisation from these solutions varies with the nature of the group NR_4^+. The results may be interpreted in terms of an equilibrium

$$(NR_4)_2[Zn(NO_3)_4] + 2N_2O_4 \rightleftharpoons (NO)_2[Zn(NO_3)_4] + 2NR_4NO_3 \quad . \quad . \quad . \quad . \quad (1)$$

When NR_4^+ is the ethylammonium ion, the equilibrium is displaced towards the left-hand side (Part XVI, *loc. cit.*). As the number of ethyl groups in the NR_4^+ ion is increased, the equilibrium is displaced progressively towards the right-hand side.

Reaction with Diethylammonium Nitrate Solutions.—Reaction commenced immediately on addition of zinc to the homogeneous solution. Nitric oxide was evolved, and a green, viscous liquid rose from the zinc block in globules to form an upper phase. As reaction proceeded, the volume of the upper layer increased, and the diethylammonium nitrate concentrated in this

* Part XVI, *J.*, 1954, 1138.

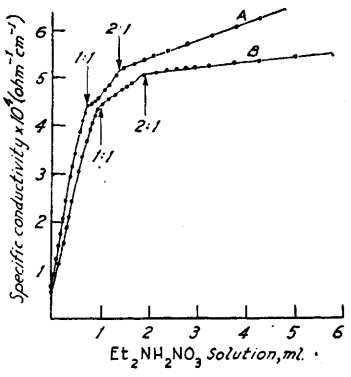
layer, leaving a lower layer consisting of almost pure dinitrogen tetroxide. When sufficient zinc dissolved the layers became inverted and crystallisation occurred from the lower layer. With a 9% solution the layers were inverted after 10 hr., and crystallisation commenced after a further 8 hr. The product formed fine, needle-shaped crystals which contained diethylamine, zinc, nitrate, and combined dinitrogen tetroxide, but the diethylamine : zinc ratio falls considerably below that required by the formula $(Et_2NH_2)_2[Zn(NO_3)_4]$. The analysis varies with the concentration of the diethylammonium nitrate solution from which the product was crystallised. The analyses in Table 1 are calculated on the basis of 1 g.-atom of zinc. The

TABLE 1.

NO_3^- (g.-ions)	$Et_2NH_2^+$ (g.-ions)	N_2O_4 (mols.)	NO_3^- (g.-ions)	$Et_2NH_2^+$ (g.-ions)	N_2O_4 (mols.)	NO_3^- (g.-ions)	$Et_2NH_2^+$ (g.-ions)	N_2O_4 (mols.)
2·41 (4·25)	0·205	1·84	2·50 (4·25)	0·41	1·75	2·66 (4·08)	0·62	1·42
2·24 (4·12)	0·235	1·88	—	0·44	1·68	2·39 (3·69)	0·62	1·30
2·32 (4·10)	0·265	1·78	2·37 (3·78)	0·56	1·41	2·50 (3·93)	0·65	1·43
2·32 (3·99)	0·375	1·67						

results are consistent if it is assumed that all the N_2O_4 molecules exist in the compound in the form of NO^+ and NO_3^- ions, and that the latter are combined in the $[Zn(NO_3)_4]^{2-}$ ion. The numerals in parentheses in col. 1 then give the total number of NO_3^- ions associated with each g.-atom of zinc, and the mean Zn : NO_3 ratio is 1 : 4·02.

If isomorphous replacement of NO^+ by $Et_2NH_2^+$ in the crystals is excluded because of difference in ionic size, the products may be regarded as mixtures of the compound $(NO)_2[Zn(NO_3)_4]$ with either $(Et_2NH_2)_2[Zn(NO_3)_4]$ or an "acid" salt $(Et_2NH_2)_x(NO)_y[Zn(NO_3)_4]$ of definite composition. In spite of the wide variations in $Et_2NH_2^+$ and NO^+ content, their sum is constant within experimental error (mean total 2·05 g.-ions, limits 1·92—2·16 g.-ions) which excludes the presence of the separate components N_2O_4, $Zn(NO_3)_2$, and $Et_2NH_2NO_3$. Attempts to obtain crystals containing an amine content above the range shown in Table 1 (by use of solutions containing up to 60% of diethylammonium nitrate) resulted in formation of a viscous liquid from which no crystalline product could be separated. Therefore, although the compound $(Et_2NH_2)_2[Zn(NO_3)_4]$ may be capable of preparation by other methods, a compound in which the $Et_2NH_2^+$: NO^+ ratio is 0·65 : 1·35 represents the limit in the presence of liquid dinitrogen tetroxide. Thus when up to about 0·65 mole of solid diethylammonium nitrate was added to 1 mole of the compound $(NO)_2[Zn(NO_3)_4]$ an equivalent quantity of liquid dinitrogen tetroxide could be decanted from the crystalline product. The addition of greater quantities of diethylammonium nitrate did not appreciably increase the yield of dinitrogen tetroxide. The product liquefied immediately on heating, and all dinitrogen tetroxide could be removed at 100°. At 160° the clear liquid decomposed vigorously, evolving fumes containing nitrogen dioxide, diethylnitrosamine, and nitric acid, and leaving a solid residue of zinc oxide, zinc nitrate, and charred organic matter. At 210° (the temperature at which zinc nitrate begins to decompose) a second vigorous reaction occurred, in which organic matter was oxidised and pure zinc oxide remained. Electrolysis of solutions of the product in both nitromethane and nitrobenzene confirmed the presence of the NO^+ ion in these solutions. Analyses of the contents of the anode and cathode compartments indicated migration of zinc to the anode.



The Figure shows conductometric titration curves obtained on the addition of a 1·8% solution of diethylammonium nitrate (in nitromethane) to 10 ml. of a 0·164% zinc nitrate solution at 0° (curve *A*) or of a 0·247% solution at −15° (curve *B*). The arrows indicate the points on the curves at which the ratio $Et_2NH_2NO_3$: $Zn(NO_3)_2$ is 1 : 1 and 2 : 1. As with the monoethyl compound, there is a pronounced break at the 2 : 1 ratio in each curve, although no such break is obtained in the presence of dinitrogen tetroxide. In this system, however, the break in the curves at the 1 : 1 ratio is much more pronounced. This may be compared with observations by Nayar and Pande (*J. Indian Chem. Soc.*, 1951, **28**, 107; *Proc. Indian Acad. Sci.*, 1949, **30**, *A*, 251) on the formation of complex compounds between lead nitrate and the alkali-metal nitrates in aqueous solution.

Reaction with Triethylammonium Nitrate Solutions.—Fresh solutions form a single liquid

phase over the full concentration range, and only separate into two phases very slowly (*e.g.*, after 10 hr. with a 5% solution). Reaction with zinc follows the same course as with the diethyl compound, but is more rapid. The product quickly crystallised in fine needles (after 30 min. when a 7% solution was used) which were readily filtered off. Table 2 gives analytical results on separate preparations (calculated on the basis of 1 g.-atom of zinc).

TABLE 2.

NO_3^- (g.-ions)	Et_3NH^+ (g.-ions)	N_2O_4 (mols.)	NO_3^- (g.-ions)	Et_3NH^+ (g.-ions)	N_2O_4 (mols.)
2·38 (4·16)	0·273	1·78	2·18 (4·08)	0·220	1·90
2·28 (4·01)	0·225	1·73	2·25 (4·15)	0·290 (g.-ions Me_3NH^+)	1·90

The amine content is less, and the dinitrogen tetroxide content greater, than with the diethylammonium compounds, and the analysis of the reaction product is not altered significantly when trimethyl- is used in place of triethyl-ammonium nitrate. The total number of nitrate groups present (given in parentheses) indicate that the products are again based on the $[Zn(NO_3)_4]^{2-}$ ion, but the equilibrium (equation 1) is further displaced towards the right-hand side on substitution of the tertiary for the secondary amine.

Reaction with Tetraethylammonium Nitrate Solutions.—This reaction proceeded in a similar manner to those described above, and the product was again obtained as fine needles. The amine content of this product was very small (0·03 g.-ion/g.-atom of Zn). When heated, the product decomposed vigorously at 200°, emitting jets of blue flame.

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Crystalline 2 : 4-*Di*-O-*methyl*-D-*glucose.*

By D. J. BELL and D. J. MANNERS

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ALTHOUGH both methyl 2 : 4-di-*O*-methyl-α- and -β-D-glucopyranosides have been described (Robertson and Waters, *J.*, 1931, 1709; Reeves, Adams, and Goebel, *J. Amer. Chem. Soc.*, 1940, **62**, 2881; Dewar and Fort, *J.*, 1944, 492), the present authors are unaware of any report on the free sugar. This has now been obtained in crystalline form, together with certain crystalline derivatives, by a simple preparation starting from laminarin (essentially a β1 : 3-linked glucosan), as follows: Laminarin ⟶ *O*-trityl-laminarin ⟶ di-*O*-methyl-*O*-trityl-laminarin ⟶ crude di-*O*-methyl-D-glucose ⟶ methyl 2 : 4-di-*O*-methyl-β-D-glucoside ⟶ 2 : 4-di-*O*-methyl-D-glucose.

The new sugar is conveniently characterised through its crystalline triacetate or its aniline derivative. The constitution assigned depends on the following observations: (*a*) heated with phenylhydrazine at pH 4·5, the sugar yielded 4-*O*-methyl-D-glucosazone, (*b*) a solution of the sugar in dry methanol containing 2% of dry hydrogen chloride showed a constant $[\alpha]_D$ of +61·4°, after 72 hours, indicating failure to form a furanoside; (*c*) periodate oxidation of the sugar yielded 0·98 mole of formaldehyde; (*d*) the methyl β-pyranoside did not react with sodium metaperiodate within 260 hours; and (*e*) a mixed melting point of the sugar with 3 : 4-di-*O*-methyl-D-glucose was markedly depressed.

2 : 4-Di-*O*-methyl-D-glucose has been found in the hydrolysis products of the trimethyl ether of the dextran synthesised by *Betacoccus arabinosaceous* (Barker, Bourne, Bruce, and Stacey, *Chem. and Ind.*, 1952, 1156); it should be a useful reference compound in structural studies of glucosans containing 1 : 3- and 1 : 6-linkages.

Experimental.—Rotations were measured in 2-dm. tubes.

O-*Trityl-laminarin.* Dried laminarin (10·0 g.) was treated, in dry pyridine, with chlorotriphenylmethane under the conditions prescribed for cellulose by Honeyman (*J.*, 1947, 168). Use of less than 2·5 mols. of etherifying agent per expected primary alcoholic group gave poor yields. The mixture was poured into a large volume of methanol; the precipitated triphenylmethyl ether was collected and washed with methanol, dissolved in pyridine, filtered, and reprecipitated by methanol (yield, 23·6 g., 94%) (Found: CPh_3, 56·1. $C_{25}H_{24}O_5$ requires CPh_3, 60·1%).

Di-O-methyl-O-trityl-laminarin. Trityl-laminarin (25·0 g.), dissolved in dioxan (150 ml.), was stirred rapidly with methyl sulphate (60 ml.) and sodium hydroxide flakes (50 g.) at 50—60° for 6 hr. (Glen, Myers, and Grant, *J.*, 1951, 2568). Pouring the mixture into well-stirred ammonia solution (~ 1%) precipitated a pale yellow granular powder. A dioxan solution of the dried material was filtered through a well-packed layer of anhydrous sodium sulphate on a sintered-glass filter (porosity 3). The pale yellow filtrate was poured into water containing some sodium chloride (to assist flocculation), and the resulting precipitate of the ether dried under reduced pressure (over P_2O_5) (yield, 24·0 g., 90·0%) (Found: OMe, 14·6; CPh_3, 53·5. $C_{27}H_{28}O_5$ requires OMe, 14·3; CPh_3, 56·0%).

Methyl 2 : 4-*di*-O-*methyl*-β-D-*glucoside.* Dimethyltrityl-laminarin (24·0 g.) was stirred on the boiling-water bath with acetic acid (180 ml.), dioxan (100 ml.), and 2N-sulphuric acid (20 ml.), a clear yellow solution quickly resulting. A further 230 ml. of 2N-sulphuric acid was added in small portions to prevent formation of a precipitate. After 2 hr. the dioxan and acetic acid were removed by distillation under reduced pressure. The crystals of triphenylmethanol were filtered off and the filtrate was neutralised with barium carbonate. After filtration, and removal of traces of ions by Wadman's method (*J.*, 1952, 3051) the neutral fluid was evaporated under reduced pressure. The resulting syrup (4·0 g.) could not be crystallised (from it the 1 : 3 : 6-tri-*O*-acetate may be prepared, see below). The crude sugar (2·8 g.) was converted into the crystalline methyl β-glucoside (1·0 g.) by Oldham's procedure (*J. Amer. Chem. Soc.*, 1934, **56**, 1360); none of the intermediary products could be crystallised. Recrystallised twice from ether, the substance had m. p. 120—121° (Reeves *et al.*, *loc. cit.*, record m. p. 122—123°), $[\alpha]_D^{20}$ −26·8° (*c*, 3·4 in H_2O), −18·4° (*c*, 2·1 in acetone) {Dewar and Fort, *loc. cit.*, record $[\alpha]_D$ −16·3°, (*c*, 3·1 in acetone)}.

Periodate oxidation of methyl 2 : 4-*di*-O-*methyl*-β-D-*glucoside.* The substance (10·0 millimole) was treated (cf. Greville and Northcote, *J.*, 1952, 1945) with sodium metaperiodate (2·43 mols.). Periodate was not reduced in 260 hr.

2 : 4-*Di*-O-*methyl*-D-*glucose.* The glucoside (700 mg.) was hydrolysed with N-hydrochloric acid at *ca.* 100° to constant optical rotation (2 hr.). After neutralisation with silver carbonate, the filtered solution yielded a colourless syrup (600 mg.) which crystallised on drying in a high vacuum. Recrystallised from ethyl acetate or propyl acetate the *sugar* (fine needles) had m. p. varying from 125° to 129°, $[\alpha]_D^{20}$ +43·3° (4 min.) ⟶ +73·7° (const., 1000 min.) (*c*, 2·8 in H_2O) (Found: C, 46·2; H, 7·7; OMe, 29·6. $C_8H_{16}O_6$ requires C, 46·2; H, 7·7; OMe, 29·8%).

A 3·3% solution in dry methanol containing 2% (w/v) of hydrogen chloride had: $[\alpha]_D^{18}$ initial +76·7°; +72·5° (24 hr.); +65·5° (46 hr.); +61·4° (72 hr., const.) (cf. Irvine and Hirst, *J.*, 1922, **121**, 1213).

The sugar (46·0 mg.) was kept in a mixture of phosphate buffer (pH 7·5) and 6 ml. of 0·3M-sodium periodate for 36 hr. (cf. Bell and Greville, *J.*, 1950, 388), giving finally 63·4 mg. of formaldehyde–dimedone derivative, m. p. 191—193 (corr.) (0·98 mol.).

The sugar (69 mg.), heated at 100° for 6 hr. with 4·5 mols. of phenylhydrazine in 0·2M-sodium acetate buffer in the presence of bisulphite ion (Hamilton, *J. Amer. Chem. Soc.*, 1934, **56**, 487), yielded yellow needles of a monomethyl-phenylosazone. Recrystallised from 50% aqueous ethanol the substance (needles) melted at 158—160°, undepressed when mixed with the original sample of 4-*O*-methyl-phenyl-D-glucosazone of Munro and Percival (*J.*, 1935, 873) kindly provided by Dr. E. E. Percival (Found: N, 15·1; OMe, 9·6. Calc. for $C_{19}H_{24}O_4N_4$: N, 15·0; OMe, 8·4%).

2 : 4-*Di*-O-*methyl*-N-*phenylglucosylamine.* Treated with aniline (7 parts) in ethanol (10 parts) at 20° for 48 hr. (Dr. E. J. Bourne, personal communication), the sugar yielded an *aniline* derivative (fine needles from ethanol). Three preparations had m. p. 196° (Found: C, 59·2; H, 7·6; N, 5·6; OMe, 21·7. $C_{14}H_{21}O_5N$ requires C, 59·1; H, 7·4; N, 4·9; OMe, 21·9).

1 : 3 : 6-*Tri*-O-*acetyl*-2 : 4-*di*-O-*methyl*-β-D-*glucose.* With acetic anhydride and sodium acetate at 100° for 30 min., the sugar yielded the crystalline 1 : 3 : 6-*tri*-O-*acetyl*-2 : 4-*di*-O-*methyl*-β-D-*glucose*, which crystallised from chloroform–light petroleum (b. p. 40—60°) as thick needles, m. p. 105—106°, $[\alpha]_D^{20}$ +11·5° (in $CHCl_3$; *c*, 7·3) (Found: C, 49·8; H, 6·6; OMe, 18·6. $C_{14}H_{22}O_9$ requires C, 50·3; H, 6·6; OMe, 18·6%).

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Crystalline 1-O-*Methyl*-D-*fructose.*

By S. Bayne and Jennifer Wildy.

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Of the five possible monomethyl ethers of fructose only 3-*O*-methyl-D-fructose has been crystallised (Irvine and Hynd, *J.*, 1909, **95**, 1220). 1-*O*-Methyl-D-fructose was first obtained by Ohle (*Ber.*, 1925, **58**, 2577) by methylation of " β "-di-*O*-*iso*propylidene-D-fructose; the methods for its preparation and the evidence for the structure of the parent di-*O*-*iso*propylidenefructose have been reviewed recently by Barry and Honeyman (*Adv. Carbohydrate Chem.*, 1952, **7**, 81, 71).

1-*O*-Methyl-D-fructose has now been crystallised and obtained chromatographically pure. The crystalline sugar melts slowly at 76—78° when examined on the Kofler hot-stage microscope, and in methanol solution it exhibits well-marked mutarotation. Its constitution is confirmed by reconversion into 1-*O*-methyldi-*O*-*iso*propylidene-D-fructose on treatment with acid acetone, and by its reduction to crystalline 1-*O*-methyl-D-mannitol.

1-*O*-Methyl-D-fructose forms crystalline phenylhydrazones with phenylhydrazine and 2 : 5-dichlorophenylhydrazine. With an excess of phenylhydrazine, D-glucose phenylosazone is formed (cf. Ohle, *loc. cit.*). The displacement in this way of the methoxyl adjacent to the reducing group is now well established. Brigl and Schinle (*Ber.*, 1929, **62**, 1716) prepared glucosazone from 2-*O*-methyl-D-glucose and 6-*O*-methylglucosazone has been obtained from 2 : 6-di-*O*-methyl-D-glucose (Freudenberg and Hüll, *Ber.*, 1941, **74**, 237). Although Hibbert, Tipson, and Brauns (*Canad. J. Res.*, 1931, **4**, 235) were unable to prepare an osazone from 1 : 3 : 4-tri-*O*-methyl-D-fructose, Hirst, Mitchell, Percival, and Percival (*J.*, 1953, 3170) have recently obtained crystalline 4 : 5-di-*O*-methylglucosazone from 1 : 4 : 5-tri-*O*-methyl-D-fructose.

From its normal reducing properties and from its optical behaviour the crystalline sugar is probably β-1-*O*-methyl-D-fructopyranose.

Experimental.—M. p.s marked (*K*) were determined on a Kofler micro-melting-point block and these alone are corrected.

1-O-*Methyl*-2 : 3-4 : 5-*di*-O-iso*propylidene*-D-*fructose*. 2 : 3-4 : 5-Di-*O*-*iso*propylidene-D-fructose was methylated by the method of Glen, Myers, and Grant (*J.*, 1951, 2568). The syrupy product, after crystallisation from aqueous methanol and from light petroleum, had m. p. 48—49°, $[\alpha]_D^{20}$ −36·5° (*c*, 1·00 in EtOH).

1-O-*Methyl*-D-*fructose*. 1-*O*-Methyl-2 : 3-4 : 5-di-*O*-*iso*propylidene-D-fructose (9·0 g.) was heated at 100° for 6 hr. with 0·1N-sulphuric acid (200 c.c.), decolorised with charcoal, and neutralised with lead carbonate. After treatment with a mixture of ion-exchange resins (cf. Bell, *J.*, 1953, 1231) the solution was evaporated to a pale yellow syrup (6·3 g.) which crystallised. Recrystallisation from ethyl acetate–ethanol gave 1-O-*methyl*-D-*fructose*, m. p. 76—78° (*K*), $[\alpha]_D^{21}$ −110·9° ⟶ −52·7° (24 hr.; const.) (*c*, 1·822 in MeOH), −88·5° ⟶ −82·3° (20 min.; const.) (*c*, 2·26 in H_2O) (Found : C, 43·7; H, 7·3; OMe, 16·9. $C_7H_{14}O_6$ requires C, 43·3; H, 7·2; OMe, 16·0%).

On a paper chromatogram developed with *n*-butanol–acetic acid–water (4 : 1 : 5) and treated with triphenyltetrazole spray, 1-*O*-methyl-D-fructose had R_F 0·34 (3-*O*-methyl-D-fructose, R_F 0·36) and was free from fructose (R_F 0·21); it is less sweet than fructose and is very hygroscopic.

1-*O*-Methyl-D-fructose (1·0 g.) was dissolved in acetone containing 4% (w/v) sulphuric acid. After 12 hr. the di-*O*-*iso*propylidene derivative (0·6 g.), m. p. and mixed m. p. 48—49°, was isolated.

Phenylhydrazones and phenylosazones from 1-O-*methyl*-D-*fructose*. With phenylhydrazine, D-glucosephenylosazone, m. p. 207° (identified by conversion into 2-phenyl-4-D-*arabo*tetrahydroxybutyl-2 : 1 : 3-triazole, m. p. 194°), was obtained (cf. Brauns and Frush, *Bur. Stand. J. Res.*, 1931, **6**, 449). With 2 : 4-dinitrophenylhydrazine under the conditions described by Neuberg (*Arch. Biochem.*, 1946, **2**, 457) 1-*O*-methyl-D-fructose (116 mg.) gave D-glucose 2 : 4-dinitrophenylosazone (286 mg.). 1-O-*Methyl*-D-*fructose phenylhydrazone*, m. p. 133° (Found : C, 55·3; H, 7·3; N, 10·8. $C_{13}H_{20}O_5N_2$ requires C, 54·9; H, 7·0; N, 9·9%), and 1-O-*methyl*-D-*fructose*

2 : 5-*dichlorophenylhydrazone*, m. p. 139° (Found : C, 43·4; H, 5·0; N, 7·7. $C_{13}H_{18}O_5N_2Cl_2$ requires C, 44·2; H, 5·1; N, 7·9%), were prepared in the usual way.

Reduction of 1-O-*methyl*-D-*fructose*. 1-*O*-Methyl-D-fructose (1·47 g.) was refluxed for 2 hr. with freshly prepared Raney nickel (15 g.) in 70% ethanol (150 c.c.) (Karabinos and Ballum, *J. Amer. Chem. Soc.*, 1953, **75**, 4501). The filtrate was evaporated and the residue crystallised from methanol, giving 1-O-*methyl*-D-*mannitol* (0·4 g.), m. p. 119°, $[\alpha]_D^{20}$ +6·81° (*c*, 4·40 in H_2O) (Found : C, 42·9; H, 7·9; OMe, 18·0. $C_7H_{16}O_6$ requires C, 42·9; H, 8·2; OMe, 15·8%), identified by comparison with an authentic sample (Bayne, Fewster, and Hawksley, to be published) prepared from 5 : 6-anhydro-1 : 2-3 : 4-di-*O*-*iso*propylidene-D-mannitol (Wiggins, *J.*, 1946, 388).

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Some Phosphorus-containing Derivatives of 2 : 2 : 2-*Trichloroethanol.*

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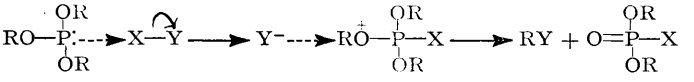
ALCOHOLS readily react with phosphorus trichloride to form ultimately the trialkyl phosphite; from this, hydrogen chloride rapidly removes one alkyl group, and the second and the third such group if the alcoholic carbon atom is sufficiently reactive (Gerrard, *J.*, 1940, 1464; 1944, 85; Gerrard and Whitbread, *J.*, 1952, 914; Gerrard, Isaacs, Machell, Smith, and Wyvill, *J.*, 1953, 1920; Gerrard and Shepherd, *J.*, 1953, 2069). It has been suggested by Gerrard *et al.* (*J.*, 1952, 914) that interaction of an alkyl phosphite with hydrogen halide, halogen (Gerrard and Philip, *Research*, 1948, **1**, 477), or ethyl iodide (Arbusov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 687; Kosolopoff, " Organophosphorus Compounds," Wiley, New York, 1950; Gerrard and Green, *J.*, 1951, 2550) involves a mechanism depicted thus :



where X = H, R, or Hal; Y = Hal. Chloretone and 2 : 2 : 2-trichloroethanol are the only alcohols yet shown not to conform with this scheme. The latter alcohol reacted comparatively slowly with phosphorus trichloride and gave the dichloridite, $PCl_2{\cdot}OR$, and chloridite, $PCl(OR)_2$, and also the trialkyl phosphite which is unique in that it can be isolated from the mixture, because it resists dealkylation by hydrogen chloride. With trichloro-*tert.*-butanol (chloretone) (Gerrard and Wyvill, *Research*, 1949, **2**, 536) reaction is even slower and goes no further than the chloridite, $PCl(OR)_2$, even in the presence of pyridine, a restriction attributed to steric hindrance to the properly oriented approach of the chloridite and the third molecule of alcohol.

Tris-2 : 2 : 2-trichloroethyl phosphite did not react with ethyl iodide; but it did readily with chlorine, and afforded the trialkyl phosphate by a mechanism still obscure. The usual reaction gives the phosphorochloridate : $P(OR)_3 + Cl_2 = RCl + P(O)Cl(OR)_2$. A plausible explanation for this departure from the above reaction scheme is that the nucleophilic reactivity of the lone pair of electrons on the phosphorus atom is reduced by the cumulative inductive effect of the 9 chlorine atoms, and in addition or alternatively, the function of the lone pair is hindered by the disposition of chlorine atoms in its vicinity. It could be suggested that the first step does occur, but that it is the " end-on " bimolecular replacement on carbon which is hindered by a disposition of groups similar to that prevailing in the *neo*pentyl structure (Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173; Gerrard, Nechvatal, and Wilson, *J.*, 1950, 2088). In this case one would expect some evidence that the first step does occur, whereas in fact none was found.

The lone pair of electrons on the phosphorus atom in triphenyl phosphite can undergo reaction, although the second step is held up because the phenyl group is not usually amenable to nucleophilic substitution. However, there is no doubt that the first step in the overall reaction scheme has occurred; *e.g.*, the phosphite and methyl iodide afford triphenyl methyliodophosphoranetrioate, $(PhO)_3PMeI$, as a crystalline compound (Michaelis and Kähne, *Ber.*, 1898, **31**, 1048; Landauer and Rydon, *J.*, 1953, 2224).

2 : 2 : 2-Trichloroethanol reacted negligibly with phosphorus oxychloride alone; but in the presence of pyridine the dichloridate, $RO{\cdot}P(O)Cl_2$, was quickly formed, the chloridate was formed more slowly, and 5 days were required for nearly quantitative formation of the phosphate. The phosphite, however, was quickly formed when phosphorus trichloride was used in conjunction with pyridine.

Experimental.—Easily hydrolysable chlorine is denoted by Cl (e.h.). 2 : 2 : 2-Trichloroethanol was prepared by reduction of chloral (*Org. Synth.*, **15**, 80).

Interaction with phosphorus trichloride. By a general procedure (cf. Gerrard, *loc. cit.*) addition of the alcohol (4·5 g., 1 mol.) to phosphorus trichloride (6·2 g., 1·5 mols.) afforded 2 : 2 : 2-*trichloroethyl phosphorodichloridite* (2·2 g.), b. p. 42°/0·1 mm., n_D^{22} 1·5140 [Found: Cl (e.h.), 28·2. $C_2H_2OCl_5P$ requires Cl (e.h.), 28·3%], *bis*-(2 : 2 : 2-*trichloroethyl*) *phosphorochloridite* (1·22 g.), b. p. 95—96°/0·1 mm., n_D^{22} 1·5167 [Found: Cl (e.h.), 9·7. $C_4H_4O_2Cl_7P$ requires Cl (e.h.), 9·7%], tris-2 : 2 : 2-trichloroethyl phosphite (1·83 g.), b. p. 125—127°/0·1 mm., n_D^{22} 1·5178 (Found: Cl, 66·5. Calc. for $C_6H_6O_3Cl_9P$: Cl, 67·0%), and a residue (0·52 g.). The relative amounts of these compounds depend on the proportions of alcohol and trichloride, and on subsequent treatment. Even with 2 mols. of trichloride to 1 mol. of alcohol (8·1 g.), the reaction mixture, after being heated at 60—65° for 1 hr., gave the triester (4·0 g.), b. p. 133—135°/0·2 mm., n_D^{21} 1·5172 (Found: Cl, 66·8%), as well as the chloridite (2·9 g.), b. p. 95—96°/0·1 mm., n_D^{18} 1·5170 [Found: Cl (e.h.), 9·7%], and dichloridite (1·6 g.) [Found: Cl (e.h.), 28·3%]. The alcohol (8·14 g., 3 mols.) and trichloride (1 mol.), shaken mechanically for 6 hr. at 15°, afforded hydrogen chloride (which was absorbed by potassium hydroxide), unchanged alcohol (0·5 g.), and the triester, b. p. 129—130°/0·1 mm., n_D^{22} 1·5177 (Found: Cl, 67·0%); the yield of the ester (88%) corresponded closely with the amount of hydrogen chloride. The triester (84% yield), b. p. 122°/0·05 mm. (Found: Cl, 66·9%), was also obtained by addition of phosphorus trichloride (1 mol.) to the alcohol (3 mols.) and pyridine (3 mols.) in pentane at −10°, base hydrochloride (99·5%) (Found: Cl, 30·3; C_5H_5N, 67·7. Calc. for C_5H_5N,HCl: Cl, 30·7; C_5H_5N, 68·5%) being quickly obtained.

Treated with hydrogen chloride for 10 hr. at 95—100°, the triester, b. p. 128°/0·1 mm., n_D^{18} 1·5172 (Found: Cl, 66·5%), was recovered. The result was the same when hydrogen bromide was used.

The phosphite and ethyl iodide. After being heated with ethyl iodide at 95—105° for 18 hr., the phosphite (94%), b. p. 128°/0·1 mm., n_D^{22} 1·5175 (Found: Cl, 67·0%), was recovered.

The phosphite and chlorine. Passage (1 hr. at −15°) of dry chlorine into the phosphite (5·58 g.) dissolved in pentane caused immediate precipitation of white *tris*-2 : 2 : 2-*trichloroethyl phosphate* (4·32 g.), b. p. 160°/0·2 mm., m. p. 71—72° (Found: Cl, 64·8. $C_6H_6O_4Cl_9P$ requires Cl, 64·9%). The other products have not yet been identified.

The alcohol and phosphorus oxychloride. The phosphate (recryst. from pentane), m. p. 72° (Found: C, 14·4; H, 1·5; Cl, 64·8. Calc. for $C_6H_6O_4Cl_9P$: C, 14·6; H, 1·5; Cl, 64·9%), was obtained by addition of phosphorus oxychloride (1 mol.) to the alcohol (3 mols.) and pyridine (3 mols.) in ether at −10°. Complete precipitation of the base hydrochloride (97·6%) (Found: Cl, 29·4; C_5H_5N, 66·2%) required 5 days at 15°. In the absence of base, interaction of the alcohol (7·6 g.) and oxychloride (7·7 g.) was very slow. After being for 30 min. at 130°, the mixture showed no sign of reaction, and even after 160 hr. at 25°, a mere trace of hydrogen chloride was evolved, and evaporation at 25°/0·1 mm. left only 0·2 g. of residue.

Addition of pyridine (3·8 g., 1 mol.) to a mixture of alcohol (1 mol.) and oxychloride (1 mol.) in ether at −10° immediately precipitated the base hydrochloride, and the filtered solution afforded a residue (9·6 g., 20°/0·1 mm.) from which the *alkyl phosphorodichloridate* (5·7 g.), b. p. 57·5°/0·1 mm. [Found: Cl (e.h.), 26·5; Cl (total), 65·3. $C_2H_2O_2Cl_5P$ requires Cl (e.h.), 26·6; Cl (total), 66·6%], higher-boiling fractions (1·65 g.) containing decreasing amounts of easily hydrolysed chlorine, and a residue (1·6 g.) were obtained.

Action of heat on the phosphite. Kabachnik and Rossüskaya (*Bull. Acad. Sci. U.R.S.S.*,

Classe Sci. Chim., 1946, 403) have shown that tri-2-chloroethyl phosphite isomerises (40%) (cf. Arbusov, *loc. cit.*) when heated for 5 hr. at 150—160° :

$$(Cl{\cdot}CH_2{\cdot}CH_2{\cdot}O)_3P \longrightarrow Cl{\cdot}CH_2{\cdot}CH_2{\cdot}P(:O)(O{\cdot}CH_2{\cdot}CH_2Cl)_2$$

However, we found that when the 2 : 2 : 2-trichloroethyl ester (6·90 g.) was heated at 160—165° for 5 hr., it was recovered (6·15 g.), b. p. 134—135°/0·2 mm., n_D^{20} 1·5173 (Found : Cl, 67·0%).

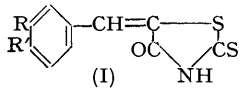
THE NORTHERN POLYTECHNIC, HOLLOWAY ROAD, N.7. [*Received, October 29th,* 1953.]

The Preparation of β-p-Hydroxyphenyl-α-mercaptopropionic Acid and Some Related Acids, and the Action of Tyrosinase on the Former.

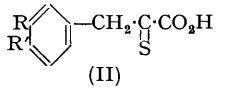
By D. G. BEW and G. R. CLEMO.

[Reprint Order No. 4829]

β-*p*-HYDROXYPHENYL-α-THIOPROPIONIC (II*a*) and some related acids have been prepared by the condensation of the corresponding aldehyde with rhodanine, followed by hydrolysis. Reduction in aqueous solution with sodium amalgam then gave the required mercapto-acids (III).



(I)



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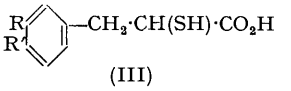

(III)

(*a* : R = H, R′ = OH.) (*b* : R = R′ = OH.) (*c* : R = H, R′ = OMe.) (*d* : R = R′ = OMe.)

The action of tyrosinase on β-*p*-hydroxyphenyl-α-mercaptopropionic acid (III*a*) was examined to see if hydroxylation to β-(3 : 4-dihydroxyphenyl)-α-mercaptopropionic acid (III*b*) and subsequent cyclisation to 5 : 6-dihydroxythionaphthen-2-carboxylic acid or 5 : 6-dihydroxythionaphthen would occur. It is possible that the action of the enzyme might cease with the production of (III*b*) since the functional group involved in the cyclisation has properties so widely different from those of the amino-group in tyrosine. The oxidation was carried out by drawing air through a buffered solution of the mercapto-acid (III*a*) in the presence of a solution of mushroom tyrosinase. A control experiment with tyrosine was carried out simultaneously to check the activity of the enzyme. Working up as described by Raper and Oxford (*Biochem. J.*, 1927, **21**, 89), which involved treatment with methyl sulphate, gave only β-*p*-methoxyphenyl-α-methylthiopropionic acid, identical with the product obtained by the action of methyl sulphate on an alkaline solution of (III*a*).

Unsuccessful attempts were also made to cyclise β-(3 : 4-dimethoxyphenyl)-α-mercapto-propionic acid to 5 : 6-dimethoxythionaphthen-2-carboxylic acid by the use of alkaline ferricyanide or bromine in chloroform.

Experimental.—Tyrosinase was prepared by the method of Mallette, Lewis, Ames, Nelson, and Dawson (*Arch. Bioch.*, 1948, **16**, 283).

β-*p*-Hydroxyphenyl-α-thiopropionic acid (II*a*) was prepared as described by Andreasch (*Monatsh.*, 1908, **39**, 435) and β-(3 : 4-dimethoxyphenyl)-α-thiopropionic acid (II*d*) by the procedure of Julian and Sturgis (*J. Amer. Chem. Soc.*, 1935, **57**, 1126).

β-p-*Hydroxyphenyl-α-mercaptopropionic acid* (III*a*). β-*p*-Hydroxyphenyl-α-thiopropionic acid (II*a*) (5 g.) was suspended in water (100 ml.) and shaken with excess of sodium amalgam (120 g.; 4%) for 2 hr. on a water-bath. The solution was filtered, cooled in ice-salt, and acidified with hydrochloric acid. From the resultant gum the *acid* (III*a*) was obtained as a white solid by extraction with light petroleum (b. p. 60—80°). It recrystallised from water in small clusters (1·5 g., m. p. 120—123°) (Found : C, 54·3; H, 4·7. $C_9H_{11}O_3S$ requires C, 54·7; H, 5·1%).

3 : 4-*Dihydroxybenzylidenerhodanine.* Protocatechualdehyde (5 g.), rhodanine (5 g.), and sodium acetate (7·5 g.) were refluxed in glacial acetic acid (20 ml.) for ½ hr. Water (100 ml.)

was added and the mixture warmed on a water-bath for 10 min. The orange-red solid *product* was collected and crystallised from acetic acid [8·7 g.; m. p. 315—319° (decomp.)] (Found: C, 47·45; H, 2·8. $C_{10}H_7O_3NS_2$ requires C, 47·5; H, 2·8%).

β-(3 : 4-*Dihydroxyphenyl*)-α-*thiopropionic acid* (II*b*). The rhodanine (I*b*) (8·5 g.) was heated in 10% aqueous sodium hydroxide (70 ml.) on a water-bath for 15 min. The deep red-violet solution was cooled in a freezing mixture and acidified rapidly with 50% hydrochloric acid, and the bright yellow precipitate (7·1 g.) was collected, reprecipitated from solution in sodium carbonate, and crystallised from methanol. This *acid* had m. p. 281—285° (Found: C, 50·6; H, 3·6. $C_9H_8O_4S$ requires C, 50·9; H, 3·8%).

β-(3 : 4-*Dihydroxyphenyl*)-α-*mercaptopropionic acid* (III*b*). The thio-acid (II*b*) (5 g.), suspended in water (100 ml.), was stirred with sodium amalgam (130 g., 4%) for 2 hr. on a water-bath in an atmosphere of carbon dioxide. After filtration the solution was cooled in a freezing mixture and acidified with hydrochloric acid, and the resulting gum dissolved in chloroform, treated with animal charcoal, and concentrated, the *acid* being obtained as a cream-coloured solid (1·1 g.), m. p. 166—170° (Found: C, 50·7; H, 5·2. $C_9H_{10}O_4S$ requires C, 50·5; H, 4·7%).

p-*Methoxybenzylidenerhodanine and* β-p-*methoxyphenyl*-α-*thiopropionic acid* (cf. Andreasch and Zipser, *Monatsh.*, 1893, **24**, 515). *p*-Anisaldehyde (5 g.), rhodanine (5·5 g.), and sodium acetate (7·5 g.) in glacial acetic acid (20 ml.) were condensed and the product worked up as described for (I*b*), giving orange-red plates (7·4 g.), m. p. 230—234°. The rhodanine (I*c*) (7·2 g.) was hydrolysed as described for (II*b*), and the yellow solid obtained on acidification crystallised from methanol (5·8 g.; m. p. 166—169°).

α-*Mercapto*-β-p-*methoxyphenylpropionic acid* (III*c*). Reduction of the thio-acid (II*c*) (5 g.) with excess of sodium amalgam gave, on acidification, an *acid* (4·6 g.) which crystallised from water in rhombic crystals, m. p. 86—89° (Found: C, 56·9; H, 6·0. $C_{10}H_{12}O_3S$ requires C, 56·65; H, 5·7%).

β-(3 : 4-*Dimethoxyphenyl*)-α-*mercaptopropionic acid* (III*d*) was prepared from β-(3 : 4-dimethoxyphenyl)-α-thiopyruvic acid (II*d*) (5 g.) as described above and crystallised from water in monohydrated prisms (2·3 g.), m. p. 76—78° (Found: C, 50·8; H, 6·1; S, 11·8. $C_{11}H_{14}O_4S,H_2O$ requires C, 50·5; H, 6·2; S, 12·3%).

Oxidation procedure. A slow stream of filtered air was drawn through the mercapto-acid (III*a*) (0·2 g.), distilled water (30 ml.), buffer solution (pH 8; 10 ml.), and tyrosinase solution (4 ml.) for 50 hr. in a thermostat at 20°. The resulting red-brown solution was acidified with acetic acid, filtered, concentrated in a vacuum under nitrogen, saturated with sulphur dioxide, and set aside for 5 hr. before being neutralised with 20% aqueous sodium hydroxide. Further sodium hydroxide solution (10 ml.) was added, followed by methyl sulphate (4 ml.), the resulting solution was refluxed for ½ hr. and then cooled, and a small amount of a dark brown oil was extracted with ether. The solution was acidified and again extracted with ether, on removal of which and distillation β-p-*methoxyphenyl*-α-*methylthiopropionic acid* was obtained as a colourless oil (b. p. 145—147°/0·1 mm.) which crystallised (0·14 g.; m. p. 76—80°) (Found: C, 58·2; H, 5·9. $C_{11}H_{14}O_3S$ requires C, 58·5; H, 6·2%).

β-*p*-Hydroxyphenyl-α-mercaptopropionic acid (III*a*) (1·0 g.) in sodium hydroxide (25 ml.; 10%) was cooled in ice, and methyl sulphate (3 ml.) was added slowly. The solution was heated on a water-bath for ½ hr., cooled, acidified to Congo-red with hydrochloric acid, and extracted with ether. On removal of the solvent a pale yellow oil (b. p. 150—152°/0·2 mm.) was obtained which solidified on cooling (0·8 g.); this had m. p. 77—81°, not depressed by material prepared as in the previous paragraph (Found: C, 58·3; H, 6·0%).

One of us (D. G. B.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

KING'S COLLEGE, NEWCASTLE-ON-TYNE. [*Received, November 24th*, 1953.]

A Statistical Study of Some Olefinic Absorption Bands in the Infra-red Region.

By R. L. WERNER and P. D. LARK.

[Reprint Order No. 4689.]

IN infra-red measurements of some compounds in which *iso*propylidene–*iso*propenyl isomerism was possible, there appeared to be an inverse relation between the C=C stretching frequency of the *iso*propylidene groups (range 1656—1680 cm.$^{-1}$) and the corresponding out-of-plane hydrogen bending frequency (range 812—858 cm.$^{-1}$). Data were collected to investigate this point and a statistical analysis was carried out on values from 31 compounds having the group $R^1R^2C{:}CR_3H$. This was extended to include a skeletal vibration frequency (range 789—810 cm.$^{-1}$) which appeared when the group in question formed part of a *cyclo*hexenyl ring (cf. Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402).

This analysis revealed highly significant correlations between the bands and yielded two sets of regression equations of possible value in structural investigations. If X is the C–H bending frequency in cm.$^{-1}$, and Y the C=C stretching frequency in cm.$^{-1}$, then *

$$X' = 2735{\cdot}0 - 1{\cdot}1401Y \quad . \quad . \quad . \quad . \quad . \quad (1); \ \mathrm{s(e)} = 6{\cdot}49 \text{ cm.}^{-1}$$

[probable (50%) limits of estimate = $\pm 4{\cdot}5$ cm.$^{-1}$; 90% limits = $\pm 11{\cdot}1$ cm.$^{-1}$]

$$Y' = 2033{\cdot}4 - 0{\cdot}4373X \quad . \quad . \quad . \quad . \quad . \quad (2); \ \mathrm{s(e)} = 4{\cdot}02 \text{ cm.}^{-1}$$

[probable (50%) limits of estimate = $\pm 2{\cdot}8$ cm.$^{-1}$; 90% limits = $\pm 6{\cdot}8$ cm.$^{-1}$]

where s(e) is the standard error of estimate based on 29 degrees of freedom. The correlation coefficient between X and Y is $-0{\cdot}706$ which is highly significant, the probability of such a value arising by chance, were there no relation between X and Y, being less than one in 1000 ($P < 0{\cdot}001$). The confidence limits of prediction are rather wide, and it is obvious from them and from the correlation coefficient that factors other than experimental error of measurement have not been allowed for.

For the nine *cyclo*hexenes examined, where the analysis included a skeletal frequency (Z, cm.$^{-1}$) the following were obtained :

$r_{XY} = -0{\cdot}827$ (highly significant, $P < 0{\cdot}01$)	$r_{XY,Z} = -0{\cdot}923$ (highly significant, $P \sim 0{\cdot}001$)
$r_{XZ} = +0{\cdot}627$ (just significant, $P > 0{\cdot}1$)	$r_{XZ,Y} = +0{\cdot}846$ (highly significant, $P < 0{\cdot}01$)
$r_{YZ} = -0{\cdot}194$ (not significant)	$r_{YZ,X} = +0{\cdot}741$ (significant, $P < 0{\cdot}05$)

$X' = 1874{\cdot}6 - 1{\cdot}1252Y + 1{\cdot}0340Z \ . \ . \ . \ (3)$; s(e) = 4·85 cm.$^{-1}$ (probable limits of estimate = $\pm 3{\cdot}5$ cm.$^{-1}$; 90% limits = $\pm 9{\cdot}4$ cm.$^{-1}$).

$Y' = 1711{\cdot}2 - 0{\cdot}7306X + 0{\cdot}7094Z \ . \ . \ . \ (4)$; s(e) = 3·65 cm.$^{-1}$ (probable limits of estimate = $\pm 2{\cdot}6$ cm.$^{-1}$; 90% limits = $\pm 7{\cdot}1$ cm.$^{-1}$).

$Z' = 1019{\cdot}2 + 0{\cdot}6853X + 0{\cdot}7468Y \ . \ . \ . \ (5)$; s(e) = 3·74 cm.$^{-1}$ (probable limits of estimate = $\pm 2{\cdot}7$ cm.$^{-1}$; 90% limits = $\pm 7{\cdot}2$ cm.$^{-1}$).

The X and Y values of the *cyclo*hexenes do not differ from the remainder in range or correlation, but analysis of variance of regression indicates that the improvement in correlation and in the equations, owing to allowance being made for the third variable, cannot be regarded as accidental ($P < 0{\cdot}05$). If, as we believe, the experimental errors

* For description of statistical analysis, see Lyle, " Regression Analysis, etc.," Oliver and Boyd Ltd., Edinburgh, 2nd edn., 1946. In this work accurate equations, allowing for distance from the centre of observed values, are given for computing the confidence limits of prediction.

(standard deviations) are of the order of 3 cm.$^{-1}$ in Y and 2 cm.$^{-1}$ in X and Z, the confidence limits of prediction of (3), (4), and (5) could not be greatly improved. The implication is that, whatever the functional relations may be, the three band frequencies are closely connected in a more or less linear way.

As there was no reason to consider any one band as dependent on the other one or two, all regression equations were computed and, for simplicity, all frequencies were regarded as being of equal weight. In the few cases where two or three experimental values of a C=C stretching frequency were available, these were averaged, and the means regarded as single observations. The analysis did not include data from the few compounds which have the double bond in a *cyclo*pentenyl ring. In these the stretching frequency is much depressed by strain, and the regression equations do not apply to them. The confidence limits quoted are a little low if band frequencies are well away from the middle of the range of values given above, on which the equations are based (see Lyle, *op. cit.*, p. 63).

To the authors' knowledge the methods of correlation and regression analysis have been little applied to spectral data of this type. Here, they have served to indicate the close connection of some absorption bands and have provided empirical equations which might be of use for diagnostic purposes. As an example of their use, consider the compound described as 24-hydroxychol-9(11)-ene, investigated by Bladon *et al.* (*loc. cit.*) and found to have a C–H bending frequency of 827 cm.$^{-1}$. From (2) we deduce that the C=C stretching frequency should be 1671·8 $\pm$ 6·8, say between 1665 and 1679 cm.$^{-1}$ with 90% confidence. Since the value given is 1644 cm.$^{-1}$, we conclude that it is highly exceptional, or the value is incorrect, or the compound has not the supposed structure. Its values were originally included in the analysis and rejected on adequate statistical grounds. Furthermore, unlike the other *cyclo*hexenyl compounds, it has no skeletal band.

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*A Novel Method of Cyanoethylation. Part II.** 10-2′-*Cyanoethyl*-9 : 10-*dihydrophenanthridine.*

By R. J. Bates and J. Cymerman-Craig.

[Reprint Order No. 4717.]

Attempts to cyanoethylate 9 : 10-dihydrophenanthridine with vinyl cyanide resulted only in dehydrogenation to phenanthridine (Smith and Yu, *J. Amer. Chem. Soc.*, 1952, **74**, 1096) which was also the sole product of reaction with 1-bromo-3-chloropropane. Use of the amine-exchange method of cyanoethylation (Bauer, Cymerman, and Sheldon, *J.*, 1951, 3311) was therefore examined.

Phenanthridine readily gave a stable benzenesulphonate and picrate. The corresponding salts of 9 : 10-dihydrophenanthridine were, however, surprisingly unstable, reverting to phenanthridines on recrystallisation. The recrystallised product described by Ritchie (*J. Proc. Roy. Soc. N.S.W.*, 1945, **78**, 177) as 9 : 10-dihydrophenanthridine picrate may thus have been phenanthridine picrate. The constitution of 9 : 10-dihydrophenanthridine benzenesulphonate was proved by its conversion into the known 10-acetyl-9 : 10-dihydrophenanthridine.

Reaction of 9 : 10-dihydrophenanthridine benzenesulphonate and 2-diethylaminoethyl cyanide in commercial nitrogen (containing *ca.* 1% of oxygen) gave 10-2′-cyanoethylphenanthridone, also prepared in quantitative yield by direct cyanoethylation of phenanthridone. In pure nitrogen 10-2′-cyanoethyl-9 : 10-dihydrophenanthridine was obtained. This compound proved unstable on repeated recrystallisation; heating it with acetic anhydride resulted in a 50% conversion into phenanthridine.

* *J.*, 1951, 3311 is regarded as Part I.

9-Methylphenanthridine, like phenanthridine, gave stable salts, and was reduced by lithium aluminium hydride to the known 9 : 10-dihydro-compound whose salts were oxidised on recrystallisation, and it seems possible that the recrystallised 9 : 10-dihydro-9-methylphenanthridine picrate reported by Ritchie (*loc. cit.*) was a mixture with 9-methylphenanthridine picrate. The constitution of the benzenesulphonate of (IV) was proved by conversion into the known acetyl derivative. No cyanoethylation product was obtained from 9 : 10-dihydro-9-methylphenanthridine benzenesulphonate and 2-diethylaminoethyl cyanide, presumably because of the steric hindrance offered to the amino-group by the *ortho*-methyl group; it has been shown that such steric hindrance is an important factor in determining the yield of cyanoethylated product from aromatic amines, both by the amine-exchange reaction (unpublished observations) and direct cyanoethylation (Braunholtz and Mann, *J.*, 1953, 1817).

Experimental.—Phenanthridine. The *benzenesulphonate* crystallised from *iso*propanol as yellow needles, m. p. 218·5—219·5° (Found : N, 4·45. $C_{13}H_9N,C_6H_6O_3S$ requires N, 4·15%), and the picrate formed yellow needles, m. p. 238—240°, from 2-ethoxyethanol (Found : N, 13·5. Calc. for $C_{13}H_9N,C_6H_3O_7N_3$: N, 13·75%). Pictet and Ankersmit (*Ber.*, 1889, **22**, 3339) give m. p. >220° for the picrate, but do not give analytical results.

9 : 10-*Dihydrophenanthridine.* The *benzenesulphonate*, prepared by mixing methanolic solutions of the base (Wooten and McKee, *J. Amer. Chem. Soc.*, 1949, **71**, 2946) and benzenesulphonic acid, formed creamy-white microcrystals, m. p. 178—182°. The product was dried *in vacuo* at room temperature (Found: C, 64·85, 65·05; H, 5·8, 5·75. $C_{13}H_{11}N,C_6H_6O_3S,CH_3{\cdot}OH$ requires C, 64·9; H, 5·65%). Recrystallisation from *iso*propanol gave yellow needles, m. p. 215—216° undepressed on admixture with phenanthridine benzenesulphonate.

A cold methanolic solution of freshly-prepared 9 : 10-dihydrophenanthridine benzenesulphonate and potassium hydroxide was diluted with water (10 volumes) and extracted with ether. The residue from evaporation of the dried (Na_2SO_4) extracts was treated with acetic anhydride, and the mixture poured into ice–water. Crystallisation from aqueous alcohol gave 10-acetyl-9 : 10-dihydrophenanthridine, m. p. 107—108° (Ritchie, *loc. cit.*, gives m. p. 108°).

9 : 10-*Dihydrophenanthridine picrate* was obtained, by mixing cold solutions of the base and picric acid, as bright orange-red needles, m. p. 224—225° (Found : N, 13·75. Calc. for $C_{13}H_{11}N,C_6H_3O_7N_3$: N, 13·65%). The same picrate could also be obtained from 9 : 10-dihydrophenanthridine benzenesulphonate. Ritchie (*loc. cit.*) gives m. p. 238° for this compound. Recrystallisation gave yellow needles, identical (m. p. and mixed m. p.) with phenanthridine picrate, m. p. 238—240°.

10-2′-*Cyanoethylphenanthridone.* (*a*) 9 : 10-Dihydrophenanthridine benzenesulphonate (17 g., 0·05 mole), 2-diethylaminoethyl cyanide (8 g., 0·064 mole), and a few crystals of quinol were refluxed at 180° for 1 hr. in an atmosphere of dry nitrogen (technical). Treatment of the cold melt with acetone at 0° left a white solid (12·6 g.) which was fractionally crystallised from acetone, giving : (i) diethylammonium benzenesulphonate (8 g., 69%), m. p. and mixed m. p. 137°; (ii) 10-2′-*cyanoethylphenanthridone* (3 g., 26%), as needles, m. p. 169—170·5° from acetone (Found : C, 77·4; H, 5·35; N, 10·95. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·85; N, 11·25%). The original acetone filtrate gave on distillation 2-diethylaminoethyl cyanide (2·2 g., 27·5%), b. p. 40—43°/1·2 mm., and extraction of the residue with light petroleum afforded a mixture of phenanthridine and dihydrophenanthridine (5·6 g., 62%).

(*b*) A solution of phenanthridone (2 g.) in pyridine (150 c.c.) was treated slowly in presence of a trace of benzyltrimethylammonium hydroxide with vinyl cyanide (5 c.c.) on the steam-bath. After 4 hr., pyridine (100 c.c.) was distilled off; the residual solution on cooling and dilution with water deposited 10-2′-cyanoethylphenanthridone (2·5 g., 98%) which crystallised as needles from chloroform–light petroleum (b. p. 60—90°), m. p. 170—170·5° undepressed on admixture with material prepared as in (*a*) (Found : N, 11·25%).

The *picrate* crystallised in yellow needles, m. p. 230—232° (decomp.), from 2-ethoxyethanol (Found : N, 14·3. $C_{16}H_{12}ON_2,C_6H_3O_7N_3$ requires N, 14·65%).

(*c*) A solution of phenanthridone (1 g.) in dimethylformamide (25 c.c.) was treated slowly with excess of vinyl cyanide in presence of a trace of potassium hydroxide, and heated (steam bath) for 5 min. 10-2′-Cyanoethylphenanthridone (1·24 g., 97%), m. p. 169·5—170°, was obtained.

10-2′-*Cyanoethyl*-9 : 10-*dihydrophenanthridine.* 9 : 10-Dihydrophenanthridine benzenesulphonate (19·7 g., 0·058 mole), 2-diethylaminoethyl cyanide (11·7 g., 0·09 mole), and a trace of quinol were refluxed at 180° for 1 hr. in an atmosphere of oxygen-free nitrogen. The cooled

melt was extracted with ice-cold acetone, and the residue was washed with hot water and crystallised from chloroform–light petroleum (b. p. 40—60°) giving 10-2′-*cyanoethyl*-9 : 10-*dihydrophenanthridine* (2·7 g., 20%) as needles, m. p. 150—152° (Found : N, 12·05. $C_{16}H_{14}N_2$ requires N, 11·95%). The *benzenesulphonate* formed pale yellow needles, m. p. 213—214° (decomp.), from methanol (Found : N, 7·25. $C_{16}H_{14}N_2,C_6H_6O_3S$ requires N, 7·15%). A mixture with phenanthridine benzenesulphonate (m. p. 218·5—219·5°) had m. p. 191°.

Evaporation of the acetone extract and extraction of the residue with light petroleum (b. p. 40—60°) gave a mixture (3·4 g.) of phenanthridine and dihydrophenanthridine.

9-*Methylphenanthridine*. The *benzenesulphonate* formed needles (from water), m. p. 251·5—252·5° (Found : C, 68·15; H, 4·75; N, 3·65. $C_{14}H_{11}N,C_6H_6O_3S$ requires C, 68·35; H, 4·85; N, 4·0%); the *picrate* separated from 2-ethoxyethanol as yellow needles, m. p. 239·5° (decomp.) (Found : C, 57·4; H, 3·2; N, 12·85. $C_{14}H_{11}N,C_6H_3O_7N_3$ requires C, 56·9; H, 3·3; N, 13·25%).

9 : 10-*Dihydro*-9-*methylphenanthridine*. 9-Methylphenanthridine (17 g.) was introduced into a well-stirred ethereal solution of lithium aluminium hydride (1·6 g.) by a Soxhlet extractor during 10 hr. Addition of moist ether and 2N-hydrochloric acid, followed by basification of the separated hydrochloride and the aqueous layer, and extraction with ether, gave 9 : 10-dihydro-9-methylphenanthridine (10·4 g., 61%), prisms from light petroleum (b. p. 40—60°), m. p. 86—87° (Ritchie, *loc. cit.*, gives m. p. 89°). The *benzenesulphonate* had m. p. 205—207° (Found : N, 4·1. $C_{14}H_{13}N,C_6H_6O_3S$ requires N, 3·95%). After recrystallisation this m. p. rose to 250°, not depressed on admixture with 9-methylphenanthridine benzenesulphonate. 9 : 10-Dihydro-9-methylphenanthridine benzenesulphonate was converted into 10-acetyl-9 : 10-dihydro-9-methylphenanthridine, m. p. 100—101° undepressed on admixture with an authentic specimen (Ritchie, *loc. cit.*, gives m. p. 102°). Prepared from the base or from 9 : 10-dihydro-9-methylphenanthridine benzenesulphonate, the picrate formed red needles, m. p. 232° (decomp.) (Found : C, 56·6; H, 3·6; N, 13·0. Calc. for $C_{14}H_{13}N,C_6H_3O_7N_3$: C, 56·6; H, 3·75; N, 13·2%). Ritchie (*loc. cit.*) reports m. p. 220—240° (decomp.). On recrystallisation the compound was converted into 9-methylphenanthridine picrate, m. p. and mixed m. p. 239·5° (decomp.).

We are indebted to the late Mrs. E. Bielski for microanalyses.

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Preparation of Pentachlorothiophenol and Some Other Sulphur Compounds.

By WADIE TADROS and EZZAT SAAD.

[Reprint Order No. 4722.]

PENTACHLOROTHIOPHENOL and some other sulphur compounds have been prepared and tested for molluscicidal activity against *Biomphalaria boissyi mansoni*. The results of these tests will be published by Dr. Donald O. Hoffman.

When injected subcutaneously in solution in sesame oil (5 mg. in 0·4 c.c.) into groups of 5 ovariectomised 22-g. mice, *as*-di-*p*-ethylthiophenylethylene (4 doses of 0·1 c.c. during 2 days), *as*-di-*p*-ethylsulphonylphenylethylene, and 1 : 1-di-*p*-ethylsulphonylphenyl-2-phenylethylene (doses, as above, but 1·25 mg. in 0·4 c.c.) failed to show œstrogenic activity.

Experimental.—Pentachlorothiophenol. A solution of pentachlorobenzenediazonium chloride (Willgerodt and Wilcke, *Ber.*, 1910, **43**, 2746) (pentachloroaniline, 5 g.; acetic acid, 150 c.c.; concentrated hydrochloric acid, 100 c.c.; sodium nitrite, 10 g.; at 5°) was added gradually to a solution of potassium ethyl xanthate (6 g.) and sodium carbonate (250 g.) in water (500 c.c.), the temperature being kept at 70° during the addition, with subsequent shaking for 15 min. and storage overnight. The residue was filtered off, washed successively with water, dilute hydrochloric acid, water, 3% aqueous sodium hydroxide, and water, and then hydrolysed by refluxing alcoholic sodium hydroxide (sodium hydroxide, 5 g.; water, 10 c.c.; alcohol, 150 c.c.) for 1 hr. Alcohol was distilled off and the residue, after being treated with water, was filtered off. The filtrate was acidified with dilute hydrochloric acid; the precipitated *phenol*, crystallised from

glacial acetic acid, was colourless and had m. p. 240° (yield, *ca.* 20—25%) (Found: C, 26·3; H, 0·7; Cl, 63·1; S, 11·5. C_6HCl_5S requires C, 25·5; H, 0·4: Cl, 62·8; S, 11·3%).

Pentachlorothioanisole was prepared from pentachlorothiophenol (0·2 g.), alcoholic sodium ethoxide (sodium, 0·04 g.; alcohol, 25 c.c.), and methyl iodide (1 g.) on the water-bath during 1 hr. It had m. p. 95—96° (from alcohol) (yield, quantitative) (Found: C, 28·8; H, 1·4; Cl, 59·6; S, 10·4. $C_7H_3Cl_5S$ requires C, 28·3; H, 1·0; Cl, 59·9; S, 10·8%).

Pentachlorothiophenetole, similarly prepared, had m. p. 42—44° (from alcohol) (yield, quantitative) (Found: S, 9·9. Calc. for $C_8H_5Cl_5S$: S, 10·3%). Pollak, Heimberg-Krauss, Katscher, and Lustig (*Monatsh.*, 1930, **55**, 358) do not give a m. p.

Bispentachlorophenyl disulphide. To a solution of pentachlorothiophenol (0·5 g.) in carbon tetrachloride (10 c.c.), phosphorus pentachloride (0·37 g.) was added and the mixture was heated on the water-bath for 10 min. and then left overnight. Carbon tetrachloride was removed and the residue was treated with water, filtered off, washed with a few c.c. of 3% aqueous sodium hydroxide and then water. The *disulphide* (0·45 g.), crystallised from acetic acid, had m. p. 229° (Found: Cl, 63·5; S, 11·4. $C_{12}Cl_{10}S_2$ requires Cl, 63·1; S, 11·4%).

4 : 4′-*Dimercaptobenzophenone* was prepared in the same way as pentachlorothiophenol (4 : 4′-diaminobenzophenone, 25 g.; 12·5% hydrochloric acid, 400 c.c.; ice, 100 g.; sodium nitrite, 25·8 g.; potassium ethyl xanthate, 50 g.; sodium carbonate, 150 g.; water, 300 c.c.). The residue was hydrolysed with alcoholic sodium hydroxide (27 g. of sodium hydroxide in 500 c.c. of alcohol). The solution was filtered and the alkaline filtrate was acidified with hydrochloric acid. The precipitate was redissolved in 5% aqueous sodium hydroxide and reprecipitated with hydrochloric acid, twice. The ketone thus obtained and crystallised from alcohol had m. p. 165° (yield, 15 g.) (Found: C, 62·9; H, 4·3; S, 25·3. $C_{13}H_{10}OS_2$ requires C, 63·4; H, 4·1; S, 26·0%).

4 : 4′-Diethylthiobenzophenone was prepared from the dithiol (30 g.), sodium ethoxide (from 5·75 g. of sodium) in alcohol (200 c.c.), and ethyl iodide (50 g.) or ethyl sulphate (40 g.) at the b. p. for 45 min. It formed pale greenish crystals (30 g.) (from alcohol), m. p. and mixed m. p. 116—118° (cf. Tadros, *J.*, 1949, 442) (Found: C, 67·4; H, 6·2; S, 21·1. Calc. for $C_{17}H_{18}OS_2$: C, 67·5; H, 6·0; S, 21·2%). The dimethyl derivative, similarly prepared, had m. p. and mixed m. p. 125° (cf. Tadros, *loc. cit.*).

4 : 4′-*Diethylsulphonylbenzophenone.* 30% Hydrogen peroxide (12 c.c.) was added dropwise at room temperature to a solution of 4 : 4′-diethylthiobenzophenone (7·55 g.) in glacial acetic acid (25 c.c.). The solution was then heated for 1 hr. on the water-bath. Acetic acid was removed in steam, and the *ketone* recrystallised from alcohol; it had m. p. 142—143° (yield, 8·33 g.) (Found: C, 55·7; H, 5·1; S, 17·4. $C_{17}H_{18}O_5S_2$ requires C, 55·7; H, 5·0; S, 17·5%).

1 : 1-*Di*-p-*ethylsulphonylphenylethanol.* To a Grignard reagent prepared from methyl iodide (22·4 g.), magnesium (3·4 g.), and ether (100 c.c.) was added 4 : 4′-diethylsulphonylbenzophenone (12·2 g.) suspended in benzene (50 c.c.) and after 5 hours' stirring, the mixture was left overnight and then decomposed with aqueous ammonium chloride. The ether–benzene and aqueous ammonium chloride layers were filtered and the residue was washed with water. On removal of solvents, a very small amount of the product was also obtained, and was added to the main residue. The *disulphone* (10 g.) had m. p. 192° (from alcohol) (Found: C. 56·3; H, 5·5; S, 17·3. $C_{18}H_{22}O_5S_2$ requires C, 56·5; H, 5·8; S, 16·8%). 1 : 1-*Di*-p-*ethylsulphonylphenyl*-2-*phenylethanol*, similarly prepared (benzyl chloride, 3·8 g.; magnesium, 0·75 g.; ether, 100 c.c.; 4 : 4′-diethylsulphonylbenzophenone, 5·5 g.; benzene, 50 c.c.) and crystallised from alcohol, had m. p. 200° (yield, 4·5 g.) (Found: C, 62·7; H, 5·8; S, 14·3. $C_{24}H_{26}O_5S_2$ requires C, 62·9; H, 5·7; S, 14·3%).

as-*Di*-p-*ethylthiophenylethylene* was obtained directly from the Grignard reaction (4 : 4′-diethylthiobenzophenone, 1 g.; methyl iodide, 2·4 g.; magnesium, 0·38 g.; ether, 50 c.c.). Crystallised from alcohol it had m. p. 118° (yield, 1 g.) (Found: C, 71·7; H, 7·0; S, 21·1. $C_{18}H_{20}S_2$ requires C, 72·0; H, 6·7; S, 21·3%). as-*Di*-p-*ethylsulphonylphenylethylene* was obtained by refluxing on the sand-bath a solution of the alcohol (3 g.) in acetic acid (30 c.c.) containing concentrated sulphuric acid (0·7 c.c.) for 2 hr. and had m. p. 117—118° (from alcohol) (yield, 2 g.) (Found: C, 59·2; H, 5·4; S, 18·0. $C_{18}H_{20}O_4S_2$ requires C, 59·3; H, 5·5; S, 17·6%). 1 : 1-*Di*-p-*ethylsulphonylphenyl*-2-*phenylethylene*, similarly prepared and crystallised, had m. p. 156° (Found: C, 65·4; H, 5·6; S, 14·5. $C_{24}H_{24}O_4S_2$ requires C, 65·4; H, 5·5; S, 14·6%).

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2-Acetoacetyl-4-methylphenol as a Reagent for Primary Amines.

By J. B. Harborne and A. S. Weaving.

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It has been shown that primary aliphatic amines can be characterised by reaction at room temperature with ω-acetyl-*o*-hydroxyacetophenones to give crystalline *o*-β-alkylaminocrotonylphenols, which show an intense greenish-yellow fluorescence in ultra-violet light (Baker, Harborne, and Ollis, *J.*, 1952, 3215). Previously, only 2-acetoacetylphenol was used for this purpose, but we now suggest the use of the 4-methyl derivative, since it can be obtained more economically than the parent compound (comparative yields from phenol and *p*-cresol are 17 and 63% respectively). A number of amines (see Experimental section) have been characterised by reaction with 2-acetoacetyl-4-methylphenol, and this compound has also been used successfully in place of 2-acetoacetylphenol as a spraying reagent for the detection of primary aliphatic amines in paper chromatography.

The reaction of 2-acetoacetyl-4-methylphenol with other types of amine has been investigated in some detail. It does not react at room temperature with primary aromatic amines (aniline, 2-aminopyridine) or secondary amines (diethylamine), but when heated in ethanol with aniline it gives 2-β-anilinocrotonyl-4-methylphenol, but in a much lower yield than that stated by Wittig and Blumenthal (*Ber.*, 1927, **60**, 1085). When heated with diethylamine in ethanol, it undergoes, not condensation, but cyclisation to 2 : 6-dimethylchromone. On the other hand, 2-acetoacetyl-4-methylphenol reacts slowly at room temperature, or more rapidly on heating, with *o*-, *m*-, and *p*-phenylenediamine. The chief product from the first was the mono-condensation compound, but there was evidence that some of bis-condensation compound was formed. On paper chromatograms, the three phenylenediamines, after spraying with this reagent, appear as bright yellow spots, which can be readily distinguished from the corresponding spot, given by primary aliphatic amines.

The copper complexes which were prepared by Baker, Harborne, and Ollis (*J.*, 1952, 1294) from *o*-β-alkylaminocrotonylphenols and cupric acetate and contained the unusual ratio of one molecule of Schiff's base to each copper atom, were found to be too insoluble for molecular-weight determinations. By increasing the size of the *N*-alkyl group in the Schiff's bases, two copper derivatives have now been prepared which are sufficiently soluble in chloroform for the molecular weight to be determined by ebullioscopic methods. Determinations with the copper derivatives of 2-β-decylamino- and 2-β-dodecylaminocrotonyl-4-methylphenols show that these complexes are dimeric.

Experimental.—*2-Acetoacetylphenol and its 4-methyl derivative.* These two phenols were prepared by known methods (Chattaway, *J.*, 1931, 2495; Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56; Wittig, Bangert, and Richter, *Annalen*, 1926, **446**, 169) and the best yields at each stage were: Phenol ⟶ phenyl acetate (88%) ⟶ *o*-hydroxyacetophenone (35%) ⟶ 2-acetoacetylphenol (53%); *p*-cresol ⟶ *p*-tolyl acetate (91%) ⟶ 2-hydroxy-5-methylacetophenone (88%) ⟶ 2-acetoacetyl-4-methylphenol (78%).

Reaction of 2-acetoacetyl-4-methylphenol with primary aliphatic amines. The general method described by Baker, Harborne, and Ollis (*J.*, 1952, 3215) was used. The products were crystallised from ethanol, with the exception of the ethylenediamine derivative, which was crystallised from benzene.

o-β-*Alkylaminocrotonyl-4-methylphenols.*

Amine	M. p.	Yield (%)	Formula	Found (%) C	H	N	Required (%) C	H	N
Ethyl-	125°	47	$C_{13}H_{17}O_2N$	71·1	7·5	6·6	71·2	7·7	6·4
n-Butyl-	86	54	$C_{15}H_{21}O_2N$	72·5	8·3	5·8	72·8	8·5	5·7
n-Hexyl-	81—82	63	$C_{17}H_{25}O_2N$	73·9	9·0	5·2	74·2	9·1	5·1
Benzyl-	123	66	$C_{18}H_{19}O_2N$	76·4	6·5	5·2	76·9	6·7	5·0
n-Octyl-	67	41	$C_{19}H_{29}O_2N$	—	—	4·6	—	—	4·6
n-Decyl-	62—63	79	$C_{21}H_{33}O_2N$	75·6	9·8	4·0	76·1	10·0	4·2
n-Dodecyl-	65—66	71	$C_{23}H_{37}O_2N$	76·7	10·2	4·1	76·3	10·3	3·9
Ethylenediamine-	236 (decomp.)	41	$C_{24}H_{28}O_4N_2$	70·3	6·7	6·7	70·6	6·9	6·9

Copper derivatives of 2-β-decylamino- and 2-β-dodecylamino-crotonyl-4-methylphenol. These *copper* derivatives were prepared by mixing ethanolic solutions of these compounds with ethanolic cupric acetate; they crystallised from benzene as green needles, m. p. 225° (decomp.) [Found: C, 63·9; H, 8·1; N, 3·8; Cu, 14·4%; *M* (ebullioscopic in chloroform), 763. $(C_{21}H_{31}O_2NCu)_2$ requires C, 64·2; H, 7·9; N, 3·6; Cu, 16·2%; *M*, 785], and m. p. 209—210° [Found: C, 65·4; H, 8·2; N, 3·4; Cu, 15·8%; *M* (ebullioscopic in chloroform), 779. $(C_{23}H_{35}O_2NCu)_2$ requires C, 65·6; H, 8·3; N, 3·3; Cu, 15·2%; *M*, 808], respectively.

The authors thank Professor W. Baker, F.R.S., for his interest in this work.

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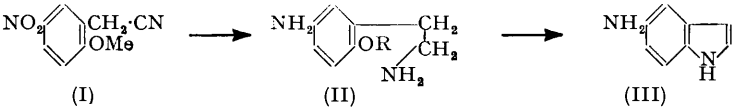
5-*Aminoindole.*

By JOHN HARLEY-MASON and A. H. JACKSON.

[Reprint Order No. 4805.]

OXIDATION of 2-(2 : 5-dihydroxyphenyl)ethylamine has been shown (Cromartie and Harley-Mason, *J.*, 1952, 2525) to give 5-hydroxyindole in high yield. It has now been found that oxidation of 2-(5-amino-2-hydroxyphenyl)ethylamine (II; R = H) gives 5-aminoindole (III), though in lower yield. Of the oxidising agents tried only silver oxide proved to be satisfactory.



(I) (II) (III)

Chloromethylation of *p*-nitroanisole (cf. Quelet, *Bull. Soc. chim.*, 1934, **5**, 539) gave 2-methoxy-5-nitrobenzyl chloride, which with potassium cyanide gave 2-methoxy-5-nitrobenzyl cyanide (I). Hydrogenation of (I) over palladium–charcoal gave 5-amino-2-methoxybenzyl cyanide, while with platinum oxide 2-(5-amino-2-methoxyphenyl)ethylamine (II; R = Me) was formed. Demethylation with hydrobromic acid gave (II; R = H), which was oxidised to the indole (III).

Experimental.—2-Methoxy-5-nitrobenzyl chloride. A mixture of *p*-nitroanisole (50 g.), paraformaldehyde (7·5 g.), finely powdered anhydrous zinc chloride (9 g.), and light petroleum (b. p. 100—120°; 75 c.c.) was stirred vigorously at 70° and saturated (10—15 min.) by a rapid stream of hydrogen chloride. After cooling, the mixture was added to ice-cold water (250 c.c.) and ethyl acetate (200 c.c.) with stirring. The organic layer was separated, washed with sodium carbonate solution, and dried ($MgSO_4$), and the solvent removed. On distillation of the residue, *p*-nitroanisole (15 g.), b. p. 85°/0·1 mm., was followed by 2-methoxy-5-nitrobenzyl chloride (22·5 g.), distilling at 120°/0·1 mm., which solidified (m. p. 75—77°) and was used directly for the next stage.

2-Methoxy-5-nitrobenzyl cyanide. The chloride (10 g.) and potassium cyanide (6 g.) in ethanol (45 c.c.) and water (15 c.c.) were refluxed for 2 hr. The resulting dark brown solution was poured into water (250 c.c.) and filtered from some tarry material, and the product extracted with ethyl acetate (3 × 150 c.c.). The dark reddish-brown extract was decolorised by passage through charcoal, and removal of the solvent then left the crude nitro-cyanide (7·9 g.). *2-Methoxy-5-nitrobenzyl cyanide,* on recrystallisation from aqueous ethanol, formed prisms, m. p. 108—109° (Found: C, 56·3; H, 4·4. $C_9H_8O_3N_2$ requires C, 56·2; H, 4·2%).

Reduction of the nitro-cyanide. (*a*) The nitro-cyanide (1 g.) in ethanol (50 c.c.) and concentrated hydrochloric acid (1 c.c.) was hydrogenated over palladium–charcoal at room temperature and pressure. Absorption ceased when 3 mol. of hydrogen had been taken up:

the catalyst was then filtered off and the filtrate evaporated to dryness under reduced pressure at 40—50°. Recrystallised from ethanol–ether the residue gave *5-amino-2-methoxybenzyl cyanide hydrochloride* as fine white needles, m. p. 230—232° with previous darkening (Found: C, 54·3; H, 5·6. $C_9H_{11}ON_2Cl$ requires C, 54·4; H, 5·5%).

(*b*) The nitro-cyanide (2 g.), dissolved in ethanol (100 c.c.) and concentrated hydrochloric acid (2 c.c.), was hydrogenated over platinum oxide at 4—5 atm. at room temperature. After the catalyst had been filtered off, the solvent was removed under vacuum and the residual solid recrystallised from ethanol–ether, giving 2-(*5-amino-2-methoxyphenyl*)*ethylamine dihydrochloride* as needles, m. p. 267—268° (decomp., with previous darkening) (Found: C, 44·9; H, 6·9. $C_9H_{16}ON_2Cl_2$ requires C, 45·2; H, 6·7%).

5-Aminoindole. The foregoing dihydrochloride (5 g.) was refluxed for 1 hr. with hydrobromic acid (*d* 1·49; 25 c.c.). The solution was diluted with water and evaporated to dryness under reduced pressure of hydrogen. A solution of the dark brown residue in water was boiled with charcoal and evaporated, and the residue recrystallised from ethanol–ether (charcoal), giving 2-(*5-amino-2-hydroxyphenyl*)*ethylamine dihydrobromide* as small prisms, m. p. 247—248° (decomp.) (Found: C, 31·0; H, 4·5. $C_8H_{14}ON_2Br_2$ requires C, 31·6; H, 4·5%).

This dihydrobromide (0·82 g.) and sodium acetate (0·45 g.) were dissolved in water (100 c.c.), and the solution shaken vigorously with silver oxide (1 g.) for 5 min. An intense transient reddish-violet colour appeared at first, but this faded rapidly. The silver and unreacted silver oxide were filtered off and a little sodium dithionite added to the almost colourless filtrate before extracting it with ethyl acetate (3 × 100 c.c.). The dried ($MgSO_4$) extracts were evaporated under reduced pressure of hydrogen, and the residue sublimed at 60—80°/10^{-4} mm., yielding *5-aminoindole* (60—70 mg., 20—25%) as prisms, m. p. 125—127°. On recrystallisation from light petroleum (b. p. 100—120°) fine needles, m. p. 127—129°, were obtained (Found: C, 72·5; H, 6·0; N, 21·0. $C_8H_8N_2$ requires C, 72·7; H, 6·2; N, 21·2%). The ultra-violet absorption spectrum, measured in 95% ethanol ($\lambda_{max.}$ 2720, 3060 Å; $\varepsilon_{max.}$ 5700, 2950: $\lambda_{min.}$ 2500, 2940 Å; $\varepsilon_{min.}$ 3050, 2600), was very similar to that of 5-hydroxyindole. With Ehrlich's reagent, a bright pink colour was given, while diazotisation followed by coupling with β-naphthol gave a deep brick-red precipitate.

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Synthesis of 2-Chloro-6-methylphenoxyacetic Acid.

By J. H. BARNES and P. G. MARSHALL.

[Reprint Order No. 4864.]

DURING a study of methods of assay, by ultra-violet spectroscopic photometry, of technical preparations of the selective herbicide 4-chloro-2-methylphenoxyacetic acid (cf. Grabe, *Acta Chem. Scand.*, 1950, **4**, 806; Hill, *Analyst*, 1952, **77**, 67), the need arose for a specimen of the isomeric 2-chloro-6-methylphenoxyacetic acid. The methods of preparation of the parent 2-chloro-6-methylphenol, described by Huston and Neeley (*J. Amer. Chem. Soc.*, 1935, **57**, 2176) and Sjöberg (*Acta Chem. Scand.*, 1950, **4**, 798) did not give material of sufficient purity. If, however, the intermediate 4-hydroxy-3-methylbenzenesulphonic acid, not isolated in Huston and Neeley's method, was purified through its aniline salt (Tatibouët and Setton, *Bull. Soc. chim.*, 1952, **19**, 382) before chlorination and desulphonation, the resulting 2-chloro-6-methylphenol readily gave pure 2-chloro-6-methylphenoxyacetic acid. A specimen of this phenol, which gave the pure phenoxyacetic acid, was also prepared from 2-methyl-6-nitrophenol (Monti, *Gazzetta*, 1937, **67**, 628), the toluene-*p*-sulphonate of which was reduced to the amine, then converted into 2-chloro-6-methylphenyl toluene-*p*-sulphonate and hydrolysed.

Experimental.—*2-Methyl-6-nitrophenyl toluene*-p-*sulphonate.* A solution of 2-methyl-6-nitrophenol (Monti, *loc. cit.*) (15·3 g., 1 mol.) and toluene-*p*-sulphonyl chloride (38 g., 2 mols.) in anhydrous pyridine, protected from moist air, was heated on the steam-bath for 1 hr., then

cooled and poured into water (600 ml.). The resulting gum gradually solidified and was washed with 2N-hydrochloric acid and with water, and recrystallised from ethanol, giving the *ester* (28·7 g., 94%) as prisms, m. p. 70—70·5° (Found: C, 54·4; H, 4·1; N, 4·8. $C_{14}H_{13}O_5NS$ requires C, 54·7; H, 4·3; N, 4·6%).

2-*Amino*-6-*methylphenyl toluene*-p-*sulphonate*. The above nitro-compound (19·3 g.) in glacial acetic acid (200 ml.) was hydrogenated, at a pressure of 45 atm., in the presence of palladised charcoal (10%; 3 g.) during 3 hr. The suspension was filtered in an atmosphere of carbon dioxide, and the filtrate evaporated to dryness under reduced pressure below 50°. Recrystallisation of the residue from aqueous ethanol gave prisms of the *amine* (14·4 g., 83%), m. p. 89—90° (Found: C, 60·0; H, 5·3; N, 5·35. $C_{14}H_{15}O_3NS$ requires C, 60·6; H, 5·45; N, 5·05%).

Sandmeyer reaction of 2-*amino*-6-*methylphenyl toluene*-p-*sulphonate*. The amine (20·8 g.; finely powdered), concentrated hydrochloric acid (25 ml.), and water (25 ml.) were vigorously stirred, with warming, giving a suspension of the difficulty soluble hydrochloride. To this, stirred at 0°, was added, gradually, sodium nitrite (7 g.) in water (50 ml.), to form a clear solution which was stirred at 0° for 2 hr. After addition of urea to destroy the excess of nitrous acid, the diazonium salt solution was added during 20 min. (chilled funnel) to a stirred solution of cuprous chloride (20 g.) in concentrated hydrochloric acid (50 ml.). The resulting mixture was stirred for a further hr., then extracted three times with ether. The combined extracts were washed with water and dried (Na_2SO_4) and the ether was removed, leaving a mixture (20 g.) of crystalline material and gum. Separation was effected by washing the mixture with ether, in which the gum was very soluble. The solid remaining was recrystallised from ethanol, to give long needles (5·5 g.) of an unidentified substance, m. p. 152—153° [Found: C, 63·9; H, 4·85; S, 13·2%; *M* (Rast), 224]. This material, which was insoluble in aqueous alkali, contained neither nitrogen nor chlorine. The gum was recovered by removal of ether and a portion was distilled; a first, small fraction, b. p. 118—158°/0·1 mm., and a second, main fraction, b. p. 158—168°/0·1 mm., were collected. Redistillation of the second fraction, through a Vigreux column, gave mainly material having b. p. 168°/0·1 mm.; this solidified when chilled and gave, by recrystallisation from ethanol, large prisms of 2-*chloro*-6-*methylphenyl toluene*-p-*sulphonate*, m. p. 53—54° (Found: C, 57·0; H, 4·0; Cl, 12·05. $C_{14}H_{13}O_3SCl$ requires C, 56·65; H, 4·4; Cl, 11·95%).

2-*Chloro*-6-*methylphenoxyacetic acid*. The foregoing ester (1 g.) was heated with ethanol (10 ml.) and aqueous 2N-sodium hydroxide (20 ml.) under reflux. The mixture rapidly became homogeneous but heating was continued for 6 hr. An excess of 2N-hydrochloric acid was then added and the mixture was distilled with steam; the distillate contained 2-chloro-6-methylphenol, which was isolated with ether as an oil (0·46 g., 92%).

2-Chloro-6-methylphenol, obtained as above (0·66 g., 1 mol.), and ethyl bromoacetate (0·77 g., 1 mol.), were added, in a small volume of ethanol, to a solution from sodium (0·11 g., 1 equiv.) and ethanol (20 ml.), and the mixture was heated under reflux for 2 hr. After addition of 2N-sodium hydroxide (25 ml.) refluxing was continued for a further 90 min. The mixture was then acidified and extracted three times with ether; the combined extracts, washed with water and dried (Na_2SO_4), yielded on evaporation the acid, which crystallised from *cyclo*hexane as plates, m. p. 105—108·5° (0·45 g., 48%). Further recrystallisation, from benzene, furnished needles, m. p. 107·5—109° (Sjöberg gives m. p. 108·9—109·3°) (Found: C, 53·9; H, 4·2; Cl, 17·7. Calc. for $C_9H_9O_3Cl$: C, 53·9; H, 4·5; Cl, 17·7%). Light absorption in MeOH: max. at 267 mμ, log ε 2·51; inflexion at 273 mμ, log ε 2·44 (Grabe records a maximum at *ca.* 267 mμ).

2-*Chloro*-6-*methylphenoxyacetic acid from* 4-*hydroxy*-3-*methylbenzenesulphonic acid*. 4-Hydroxy-3-methylbenzenesulphonic acid, m. p. *ca.* 50°, prepared by sulphonation of *o*-cresol at 0—5° (Tatibouët and Setton, *loc. cit.*) (10·7 g.), in dry dioxan (20 ml.), was treated with a slow stream of chlorine, whereupon the temperature of the mixture rose to *ca.* 60°, with evolution of hydrogen chloride. After a few min., the mixture had increased in weight by 3 g. (theor., for 1 Cl, 2 g.). The dioxan was removed under reduced pressure and the dark residue, in ethereal solution, was extracted three times with water. The ethereal layer, after drying (Na_2SO_4) and evaporation, gave an oil (1·1 g.) which crystallised; the m. p., 50—55°, was undepressed on admixture with a sample of 2 : 4-dichloro-6-methylphenol, m. p. 54—55° (Zincke, *Annalen*, 1918, **417**, 206). Evaporation of the combined aqueous extracts, under reduced pressure, gave crude 3-chloro-4-hydroxy-5-methylbenzenesulphonic acid, m. p. 109—112°, decomp. *ca.* 140°. This product, on steam-distillation, gave a steam-volatile oil (0·80 g.), which was discarded, and subsequent distillation with superheated steam gave 2-chloro-6-methylphenol (2·28 g.). This was converted into 2-chloro-6-methylphenoxyacetic acid by the method previously employed. The product, recrystallised from *cyclo*hexane and from benzene, had m. p. 107—109°, un-

depressed on admixture with the acid obtained by the previous route; the yield was 1·2 g. (10·5% based on 4-hydroxy-3-methylbenzenesulphonic acid).

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2 : 6-*Bis*-2′-*hydroxyethylnaphthalene.*

By MORTON MEADOW and WILSON M. WHALEY.

[Reprint Order No. 4813.]

2 : 6-BIS-2′-HYDROXYETHYLNAPHTHALENE, desired as an intermediate for the synthesis of *iso*quinolino(8′ : 7′-7 : 8)*iso*quinoline, has been prepared in 21% overall yield from 2 : 6-dibromonaphthalene. The diol was prepared by the reaction of ethylene oxide with 2 : 6-naphthalenedilithium, the latter compound being formed by the halogen–metal interconversion reaction (Jones and Gilman *Org. Reactions*, 1951, **6**, 339) between 2 : 6-dibromonaphthalene and *n*-propyl- or *n*-butyl-lithium (Gilman, Beel, Brannan, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499). 2 : 6-Dibromonaphthalene would not react with metallic lithium or magnesium in butyl ether or ethyl ether under various conditions. 2-Bromo-6-iodonaphthalene, prepared by a Sandmeyer reaction (Hodgson and Walker, *J.*, 1933, 1620) from 6-bromo-2-naphthylamine, also failed to react with metallic magnesium in ethyl ether, and was less effective in the halogen–metal interconversion than the dibromo-compound.

Unsuccessful attempts were made to prepare a di-Grignard reagent from 1 : 5-dibromonaphthalene (Lock, *Monatsh.*, 1950, **81**, 852; Fries and Köhler, *Ber.*, 1924, **57**, 500) although this reaction is claimed to proceed in excellent yield (Salkind, *Ber.*, 1934, **67**, 1031). Examination of the products obtained by treating the Grignard solutions with ethylene oxide indicated that one bromine atom was completely replaced and the second one to a limited extent.

Experimental.—M. p.s were determined with a calibrated apparatus. Microanalyses are by Galbraith Laboratories, Knoxville 17, Tennessee, U.S.A.

2 : 6-*Bis*-2′-*hydroxyethylnaphthalene.* 2 : 6-Dibromonaphthalene was prepared in 24% yield from 6-bromo-2-naphthylamine (Franzen and Stauble, *J. prakt. Chem.*, 1921—22, **103**, 352, 380, 387 *et seq.*) by a Sandmeyer reaction (Hodgson and Walker, *loc. cit.*). A solution of *n*-propyl-lithium (Gilman *et al.*, *loc. cit.*), prepared from distilled *n*-propyl bromide (15·8 g.) and lithium (2·19 g.) in di-*n*-butyl ether (70 c.c.) at −10° to 10°, was filtered into a dropping funnel and added during 5 min. to a solution of 2 : 6-dibromonaphthalene (4·5 g.) in benzene (50 c.c.) and *n*-butyl ether (100 c.c.). After 3 min. there was slowly added a cold solution of ethylene oxide (22 g.) in butyl ether (50 c.c.). After 10 min., the mixture was hydrolyzed with hydrochloric acid (100 c.c. of water and 100 c.c. of hydrochloric acid, *d* 1·18), and the organic phase was washed with water (4 × 200 c.c.) which precipitated a white solid in the aqueous phase. The collected solid, 2 : 6-*bis*-2′-*hydroxyethylnaphthalene* (0·7 g., 21%), formed shiny white plates, m. p. 147·5—148° [from 50% ethanol (charcoal)] (Found: C, 77·5; H, 7·5. $C_{14}H_{16}O_2$ requires C, 77·7; H, 7·5%). The compound was prepared in 19% yield by using *n*-butyl-lithium; in this case the product was isolated by distilling the organic layer *in vacuo*.

Attempts to prepare 2 : 6-bis-2′-aminoethylnaphthalene from 2 : 6-bis-2′-hydroxyethylnaphthalene through the corresponding dibromide were unsuccessful. Conversion of the diol into the dibromide by refluxing it with phosphorus tribromide in benzene (Kon and Ruzicka, *J.*, 1936, 189) yielded an impure product (m. p. 155·5—157°) which could not be converted into the diamine by treatment with aqueous ammonia in a Parr shaker for 4 days.

2-*Bromo*-6-*iodonaphthalene.* 6-Bromo-2-naphthylamine (111 g.) was diazotized by nitrosyl-

sulphuric acid (Hodgson and Walker, *loc. cit.*), and the diazonium solution slowly poured into a well-stirred solution of potassium iodide (249 g.) in water (500 c.c.). The mixture was stirred for 1 hr., set aside overnight, diluted with an equal volume of water, and filtered. The solid was dissolved in ethanol (8 l.), diluted with water (10 l.), and treated with sulphur dioxide. The solid, after recrystallization from ethanol by the Soxhlet-extractor method, was thoroughly washed with cold sulphuric acid (*d* 1·84) followed by ice-water, and dried. Sublimation at 200—210°/0·2 mm. followed by recrystallization from ethanol afforded pink leaflets (97 g., 57%) of 6-*bromo*-2-*iodonaphthalene*, m. p. 170—171° [Found : C, 35·9; H, 1·8; Br, 53·9. $C_{10}H_6BrI$ requires C, 36·1; H, 1·8; halogen (calc. as Br), 54·0%].

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Some Derivatives of Phenanthrene.

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THE selenium dioxide oxidation of 3-acetylphenanthrene (Mosettig and van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704) was found to yield 3-phenanthrylglyoxal. The glyoxal was apparently a hydrated acetal and was therefore characterized as the quinoxaline and dithiosemicarbazone.

2-Hydroxyiminoacetylphenanthrene was desired as an intermediate for the preparation of 7 : 8-α-naphtho*iso*quinoline. Its preparation from 2-acetylphenanthrene with *n*-amyl nitrite in ethanolic sodium hydroxide has been described (van de Kamp, Burger, and Mosettig, *J. Amer. Chem. Soc.*, 1938, **60**, 1321). However, we could not prepare it by the reported procedure or by variations involving other conditions and other nitrosating agents, such as 2-ethoxyethyl nitrite, 2-*n*-butoxyethyl nitrite, and *N*-nitrosodimethylamine. Starting material was recovered when 2-acetylphenanthrene was treated with acetyl chloride and 2-ethoxyethyl nitrite (Claisen and Manasse, *Ber.*, 1887, **20**, 2194).

The objectionable physiological effects of the volatile alkyl nitrites were circumvented by the use of 2-*n*-butoxyethyl nitrite.

The high-melting impurity obtained by Bachmann (*J. Amer. Chem. Soc.*, 1935, **57**, 555) during the preparation of 1-benzoylphenanthrene was also encountered in the preparation and separation of 2- and 3-acetylphenanthrene. This material, shown to be anthraquinone by comparison with an authentic sample, was formed during the purification of phenanthrene by chromic acid oxidation of 90% phenanthrene.

Experimental.—M. p.s were determined with a calibrated apparatus. Microanalyses are by Galbraith Laboratories, Knoxville 17, Tennessee, U.S.A.

2-3′-*Phenanthrylquinoxaline*. A mixture of 3-acetylphenanthrene (44 g.) and selenium dioxide (87 g.) in ethanol (500 c.c.) was refluxed for 9 hr. and then filtered while hot; the filtrate, on cooling, deposited the impure glyoxal, which formed long silky needles, m. p. 82—83° (from ethanol), and was apparently a hydrated acetal (Found : C, 73·5; H, 5·7%). The *quinoxaline*, prepared by refluxing a solution of equivalent amounts of *o*-phenylenediamine and 3-phenanthrylglyoxal in ethanol for 5 min. and adding water, formed clusters of thin, pale-brown needles, m. p. 189—190° [from ethanol (charcoal)] (Found : C, 86·3; H, 4·6; N, 9·2. $C_{22}H_{14}N_2$ requires C, 86·3; H, 4·6; N, 9·1%).

3-*Phenanthrylglyoxal dithiosemicarbazone*. Prepared by refluxing a mixture of the crude glyoxal (7 g.) and thiosemicarbazide (13·6 g.) in ethanol (500 c.c.) for 20 min., the *dithiosemicarbazone* formed a brown-yellow powder, m. p. 242—244° (decomp.) (from ethyl acetate in a

Soxhlet extractor) (Found: C, 57·3; H, 4·1; N, 21·4. $C_{18}H_{16}N_6S_2$ requires C, 56·8; H, 4·2; N, 22·1%).

2-*Ethoxyethyl nitrite*. The nitrite was prepared from ethylene glycol monoethyl ether and nitrous acid according to Noyes's method (*Org. Synth.*, Coll. Vol. II, p. 108). The light-green *nitrite* distilled at 30—33°/15—20 mm. (Found: C, 39·7; H, 7·5; N, 11·0. $C_4H_9O_3N$ requires C, 40·3; H, 7·6; N, 11·8%).

2-n-*Butoxyethyl nitrite*. Prepared in the same manner, this *nitrite* (70%) was obtained as a yellow liquid, b. p. 65—66°/15—20 mm. (Found: C, 49·1; H, 8·9; N, 9·3. $C_6H_{13}O_3N$ requires C, 49·0; H, 8·9; N, 9·5%).

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3 : 6-*Dicyanocatechol.*

By J. D. LOUDON and D. K. V. STEEL.

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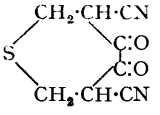
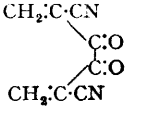
A CRYSTALLINE, sulphur-free compound, produced by the interaction of bis-2-cyanoethyl sulphide and ethyl oxalate in presence of sodium ethoxide, proved to be 3 : 6-dicyanocatechol. Its structure was shown by (*a*) formation of a dimethyl ether and (*b*) hydrolysis and degradation to catechol *via* the 3 : 6- and 3-carboxylic acids. It is presumably formed from the thia*cyclo*heptane derivative (I) by elimination of hydrogen sulphide and cyclisation of the intermediate (II). Condensations of ethyl oxalate with bis-2-cyanoethylamine, with the corresponding *p*-toluenesulphonamide and with *NN*-bis-2-cyanoethylanisidine were attempted but only in the first case yielded a crystalline product, which is possibly 4-cyano-1-2′-cyanoethylpyrrolid-2 : 3-dione.

(I)



(II)



Experimental.—3 : 6-*Dicyanocatechol*. Ethyl oxalate (5·2 g.) and then bis-2-cyanoethyl sulphide (5 g.) were added to an ethereal suspension of sodium ethoxide (from 1·64 g. of atomised sodium and 4·15 c.c. of ethanol). The whole was heated under reflux for 10 hr. and extracted with water. The acidified aqueous extract was exhausted by extraction with ether from which a semi-solid mass was recovered. Gummy material was removed by cautious washing with water, and the residual solid afforded 3 : 6-*dicyanocatechol* as needles, m. p. >330°, from water (Found: C, 60·2; H, 2·8; N, 17·5. $C_8H_4O_2N_2$ requires C, 60·0; H, 2·5; N, 17·5%). It gave a bright green colour with aqueous ferric chloride and in aqueous solution showed a faint blue fluorescence which changed to yellow-green on addition of alkali. Methylation with diazomethane afforded the *dimethyl ether* as needles, m. p. 109—110°, from light petroleum (b. p. 60—80°) (Found: C, 64·1; H, 4·2; N, 15·05. $C_{10}H_8O_2N_2$ requires C, 64·0; H, 4·3; N, 14·9%)

When 3 : 6-dicyanocatechol (0·1 g.) was heated under reflux with aqueous sodium hydroxide (50%; 4 g.) the initially formed yellow sodium salt dissolved, and acidification of the cooled solution gave 3 : 6-dicarboxycatechol, m. p. (decomp.) 290°, from water (Found: C, 44·4; H, 3·8. Calc. for $C_8H_6O_6,H_2O$: C, 44·45; H, 3·7%). This acid, which gave the characteristic blue-purple colour with aqueous ferric chloride, was partially decarboxylated when heated at 240—260° and finally at 300°, affording a sublimate of 3-carboxycatechol, m. p. (in sealed tube) 199—202°, from toluene. Decarboxylation was completed by heating 3-carboxycatechol for 1 hr. in aniline, catechol, (micro-) m. p. and mixed m. p. 98—100°, then being recovered in ether from a solution of the reaction mixture in aqueous acid.

(?)4-*Cyano*-1-2′-*cyanoethylpyrrolid*-2 : 3-*dione*. When bis-2-cyanoethylamine (4·4 g.) replaced the sulphide in the condensation with ethyl oxalate, a yellow sodium salt was formed after 1 hour's heating. This was collected, and its aqueous solution passed through ion-exchange

resin (IR-120H). Concentration of the emergent acidic solution *in vacuo* gave a gum which partly solidified. The solid formed creamy crystals, m. p. 175—177°, from water (Found: C, 49·6; H, 4·7; N, 21·5. $C_8H_7O_2N_3,H_2O$ requires C, 49·2; H, 4·65; N, 21·5%), which were acidic, but non-basic and gave a red colour with aqueous ferric chloride. Reaction with ethereal diazomethane afforded a *monomethyl ether*, m. p. 160—162°, from methanol (Found: C, 56·4; H, 4·7; N, 21·7. $C_9H_9O_2N_3$ requires C, 56·5; H, 4·75; N, 22·0%).

NN-*Bis*-2-*cyanoethyltoluene*-p-*sulphonamide*, m. p. 102° (from ethanol), was formed from bis-2-cyanoethylamine and toluene-*p*-sulphonyl chloride in cold pyridine (Found: C, 56·7; H, 5·0. $C_{13}H_{15}O_2N_3S$ requires C, 56·3; H, 5·45%).

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