491. *Oxidative Degradation of Sterculic Acid.*

By J. P. Varma, Bhola Nath, and J. S. Aggarwal.

We have already advanced [1] some evidence that sterculic acid is ω-(2-*n*-hexyl*cyclo*propyl)-dec-9-enoic acid. Support for this assignment has been obtained by potassium permanganate oxidation of the acid. Production of hexyl *n*-methyl ketone, heptanoic acid, and azelaic acid may be explained on the basis of our formulation but not on the *cyclo*propene structure assigned by Nunn.[2] The same products were obtained by Hilditch, O'Meara, and Zaky [3] from permanganate oxidation of the total fatty acids of *Sterculia fœtida oil.*

Experimental.—Sterculic acid (6·2 g.), in dry acetone (98 ml.), was refluxed with powdered potassium permanganate (25 g.) for 1 hr. The solvent was then removed, and the residue suspended in water and saturated with sulphur dioxide. The mixture was then steam-distilled, the distillate neutralised with sodium carbonate and extracted with ether, the ethereal extract dried (Na_2SO_4), and the solvent removed. The neutral product (0·5 g.), b. p. 169—173° (Found: C, 74·5; H, 12·3. Calc. for $C_8H_{16}O$: C, 74·9; H, 12·6%), formed a 2 : 4-dinitrophenylhydrazone, m. p. 59° not depressed when mixed with *n*-hexyl methyl ketone dinitrophenylhydrazone (Found: N, 18·6. Calc. for $C_{14}H_{20}O_4N_4$: N, 18·2%).

The alkaline solution, left after ether extraction, was acidified and extracted with ether, the extract dried (Na_2SO_4), and the solvent removed, yielding a liquid (1·8 g.), b. p. 220°, n_D^{27} 1·4219 (Found: C, 64·9; H, 10·9%; equiv. by titration, 130·5. Calc. for $C_7H_{14}O_2$: C, 64·6; H, 10·8%; equiv., 130). It formed an amide, m. p. and mixed m. p. with authentic heptanoamide, 92°.

The residue from the steam-distillation was thoroughly extracted with ether; the extract, after removal of the solvent, gave a semi-solid which was treated with sodium carbonate solution. The alkaline solution was washed twice with ether, and acidified with dilute hydrochloric acid. The acidic solution was extracted with ether, the extract dried (Na_2SO_4), and the solvent distilled off, leaving a solid, m. p. and mixed m. p. with azelaic acid, 104° (Found: C, 57·6; H, 8·4%; equiv., 94·1. Calc. for $C_9H_{16}O_4$: C, 57·5; H, 8·5%; equiv., 94).

National Chemical Laboratory of India, Poona. [*Received, November 14th*, 1955.]

[1] Varma, Nath, and Aggarwal, *Nature*, 1955, **175**, 84; **176**, 1082.
[2] Nunn, *J.*, 1952, 313.
[3] Hilditch, O'Meara, and Zaky, *J. Soc. Chem. Ind.*, 1941, **60**, 198T.

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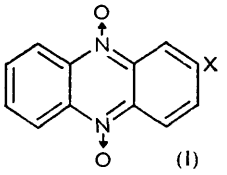
492. *Some Reactions of 2-Chlorophenazine 5 : 10-Dioxide.*

By Justus K. Landquist.

2-Chlorophenazine 5 : 10-dioxide (I; X = Cl) has been shown to give 2-hydroxyphenazine 5 : 10-dioxide (I; X = OH) when heated with aqueous-alcoholic potassium hydroxide.[1] The replacement of the chlorine atom has a limited application in the synthesis of other phenazine *N*-oxides, but with oxidisable reagents reduction of the *N*-oxide



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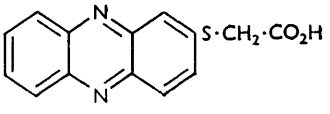

(II)

groups occurs. Thus, with boiling piperidine the chloro-compound (I; X = Cl) gave 2-piperidinophenazine 5 : 10-dioxide (I; X = NC_5H_{10}) and 2-piperidinophenazine mono-*N*-oxide, and with 3-piperidinopropylamine it was reduced to 2-chlorophenazine. With sodium mercaptoacetate it was converted into 2-carboxymethylthiophenazine (II).

[1] Vivian, *J. Amer. Chem. Soc.*, 1949, **71**, 1139.

Experimental.—(a) *Reaction with piperidine.* 2-Chlorophenazine 5 : 10-dioxide (3 g.) and piperidine (30 c.c.) were stirred and refluxed for 1·5 hr., and then poured into water (300 c.c.); the mixture was acidified with hydrochloric acid, and filtered. The product was precipitated by sodium hydroxide and was purified by reprecipitation from a solution in hydrochloric acid. The product was extracted with boiling benzene and the extract concentrated (to 75 c.c.) and treated with light petroleum (250 c.c.; b. p. 60—80°). *2-Piperidinophenazine 5 : 10-dioxide* (1·35 g.) formed violet-black needles (from benzene–petrol), m. p. 174° (Found : C, 68·5; H, 5·8; N, 14·1. $C_{17}H_{17}O_2N_3$ requires C, 69·15; H, 5·75; N, 14·2%). Evaporation of the benzene–light petroleum mother-liquor gave a red solid (1·1 g.), which after three crystallisations from light petroleum (b. p. 100—120°) gave *2-piperidinophenazine* 5- or 10-*oxide* (0·3 g.), as dark red needles with a green reflex, m. p. 159° (Found : C, 72·8; H, 5·9; N, 14·7. $C_{17}H_{17}ON_3$ requires C, 73·1; H, 6·1; N, 15·05%).

(b) *Reaction with 3-piperidinopropylamine.* 2-Chlorophenazine 5 : 10-dioxide (2·5 g.) and 3-piperidinopropylamine (5 g.) were heated to 120° and the exothermic reaction was checked by cooling. The mixture was then heated at 130—135° for 1·5 hr., cooled, and extracted with cold dilute hydrochloric acid. The undissolved material was triturated with dilute sodium hydroxide, filtered and washed with water, giving 2-chlorophenazine (1·3 g.), m. p. 134—136°. The acid extract was made alkaline with sodium hydroxide, and the tar (2·1 g.) was purified by chromatography (benzene–alumina), giving 2-chlorophenazine (0·3 g.), m. p. 135—137°.

(c) *Reaction with mercaptoacetic acid.* 2-Chlorophenazine 5 : 10-dioxide (0·5 g.) and ethanol (10 c.c.) were refluxed with mercaptoacetic acid (0·37 g.) in 10% aqueous sodium hydroxide (3·5 c.c.). After 80 min. the solution was diluted with water (60 c.c.), filtered, and acidified. The precipitated *2-carboxymethylthiophenazine* (0·45 g.) was crystallised from ethanol and then from butanol forming red-brown prisms, m. p. 245—246° (Found : C, 61·9; H, 3·8; N, 9·7; S, 12·7. $C_{14}H_{10}O_2N_2S$ requires C, 62·2; H, 3·7; N, 10·4; S, 11·85%).

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[*Received, December 21st*, 1955.]

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493. *Quinoxaline* N-*Oxides. Part VI.** N-*Oxides of* 2 : 3-*Polymethylenequinoxalines.*

By JUSTUS K. LANDQUIST.

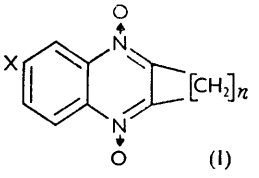
IN addition to the 2 : 3-dialkylquinoxaline 1 : 4-dioxides which were synthesised as potential chemotherapeutic agents,[1] di-*N*-oxides of some 2 : 3-polymethylenequinoxalines were also made. 2 : 3-Tri-, tetra-, and penta-methylenequinoxaline, 6-methyl-2 : 3-trimethylenequinoxaline, and 6-methyl-, 6-chloro-, and 6-methoxy-2 : 3-tetramethylenequinoxaline were conveniently prepared by reaction of cyclic ketones with the appropriate *o*-aminoazo-compounds.[2] 2 : 3-Tetramethylenequinoxaline (1 : 2 : 3 : 4-tetrahydrophenazine) di-*N*-oxide has been described by McIlwain.[3] Bornyleno(2′ : 3′ : 2 : 3)-quinoxaline [4] gave a di-*N*-oxide although by analogy with 2-methyl-3-*iso*propylquinoxaline and 2 : 3-di*iso*propylquinoxaline [1] steric hindrance might have been expected.

In the preparation of 6-chloro-2 : 3-tetramethylenequinoxaline (as I; X = Cl, $n = 4$) from 4-chloro-1 : 2-phenylenediamine and *cyclo*hexane-1 : 2-dione a by-product, $C_{18}H_{18}N_4Cl_2$, was isolated. From its composition and mode of formation it would appear to be (II) or (III). Morley [5] isolated a similar substance, $C_{18}H_{20}N_4$, from the condensation of *o*-phenylenediamine with *cyclo*hexane-1 : 2-dione, and provisionally assigned to it the structure (IV). The evidence for the structure of these compounds is inconclusive; neither of them gave evidence of having diazotisable amino-groups, and neither was hydrolysed to

* Part V, *J.*, 1956, 2058.

[1] Landquist and Stacey, *J.*, 1953, 2822.
[2] King, Clark, and Davis, *J.*, 1949, 3012.
[3] McIlwain, *J.*, 1943, 322.
[4] Singh and Mazumder, *J.*, 1919, **115**, 574.
[5] Morley, *J.*, 1952, 4008.

the parent *o*-phenylenediamine when boiled with hydrochloric acid. The structure (IV) is not possible for the derivative of 4-chloro-1 : 2-phenylenediamine.



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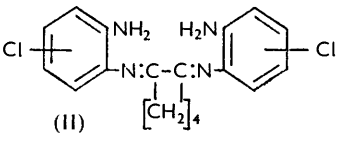

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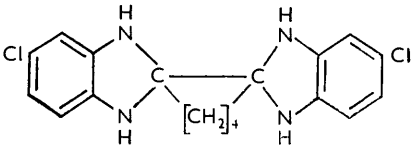

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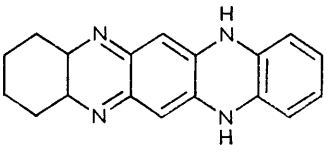

(IV)

Experimental.—2-*Amino*-4-*chloroacetanilide*. 4-Chloro-2-nitroacetanilide (130 g.) was added gradually to iron (pin dust) (110 g.), water (350 c.c.), and glacial acetic acid (10 c.c.), stirred vigorously at 70° ± 2°. The temperature was raised to 80°, calcium carbonate (30 g.) was added, and after 10 min. the hot mixture was filtered. Part of the product (8 g.) crystallised from the filtrate; the remainder (*ca.* 70 g.) was recovered from the filter cake by extraction with boiling ethanol. 2-*Amino*-4-*chloroacetanilide* crystallised from ethanol in needles, m. p. 144° (Found: N, 15·5. $C_8H_7ON_2Cl$ requires N, 15·2%). 2-Amino-4-methoxyacetanilide [6] was made similarly.

2-*Acetamido*-5-*chloroazobenzene*. 2-Amino-4-chloroacetanilide (120 g.) dissolved in ethanol (120 c.c.) and glacial acetic acid (120 c.c.) was treated at room temperature with nitrosobenzene (100 g.). The mixture was shaken at intervals, and after 5 hr. the product (70 g.) was filtered off, washed with ethanol, and crystallised from ethanol (carbon). 2-*Acetamido*-5-*chloroazobenzene* formed yellow needles, m. p. 180° (Found : N, 15·45. $C_{14}H_{12}ON_3Cl$ requires N, 15·4%).

2-*Acetamido*-5-*methoxyazobenzene*, prepared similarly (yield, 24%), formed orange blades, m. p. 174—175°, from ethyl acetate (Found : N, 15·65. $C_{15}H_{15}O_2N_3$ requires N, 15·6%).

2-*Amino*-5-*chloroazobenzene*. The acetyl derivative (68 g.) was refluxed with 5% alcoholic potassium hydroxide (700 c.c.) for 5 hr. The mixture was poured into water (2 l.), and the *product* was crystallised from light petroleum (b. p. 100—120°) (yield, 70%). It formed red needles, m. p. 113° (Found : N, 18·3. $C_{12}H_{10}N_3Cl$ requires N, 18·2%). 2-*Amino*-5-*methoxyazobenzene*, prepared similarly (yield, 69%), crystallised from light petroleum (b. p. 60—80°) in red laminæ with a brassy reflex, m. p. 38—39·5° (Found : N, 18·5. $C_{13}H_{13}ON_3$ requires N, 18·5%).

Preparation of 2 : 3-*polymethylenequinoxalines*. (*A*). A solution of 4-chloro-1 : 2-phenylenediamine (28 g.) in hot 10% aqueous acetic acid (240 c.c.) was heated for 1 hr. at 98—100° with *cyclo*hexane-1 : 2-dione (23 g.), and the mixture cooled and made alkaline with sodium hydroxide solution. The precipitated oil solidified and was washed with water, dried, and extracted with light petroleum (b. p. 60—80°), leaving a by-product which crystallised from ethanol in pale brown prisms, m. p. 274—276° (Found : C, 59·9; H, 4·8; N, 15·55. $C_{18}H_{18}N_4Cl_2$ requires C, 59·8; H, 5·0; N, 15·5%). The petroleum extract afforded 7-*chloro*-1 : 2 : 3 : 4-*tetrahydrophenazine* (11·5 g.), m. p. 94° (Found : C, 66·2; H, 5·0; N, 12·5. $C_{12}H_{11}N_2Cl$ requires C, 65·9; H, 5·0; N, 12·8%). This compound was also prepared by method (*C*).

(*B*). *o*-Aminoazobenzene (10 g.), *cyclo*hexanone (100 c.c.), and concentrated hydrochloric acid (0·5 c.c.) were refluxed for 2 hr. and then distilled until the temperature of the mixture rose to 175°. The residue was dissolved in ether and extracted with N-hydrochloric acid (7 × 100 c.c.). The bases recovered from the acid extract by treatment with sodium hydroxide and extraction with ether were distilled. The fraction of b. p. 125—156°/7 mm. (6·9 g.) gave pure 1 : 2 : 3 : 4-tetrahydrophenazine, m. p. 92—93° [from light petroleum (b. p. 40—60°)].

(*C*). 2-Amino-4′ : 5-dimethylazobenzene (50 g.), *cyclo*hexanone (450 c.c.), and concentrated hydrochloric acid (2 c.c.) were refluxed for 2 hr., made alkaline with sodium carbonate, and

[6] Simonov, *J. Gen. Chem. U.S.S.R.*, **1940**, **10**, 1588.

steam-distilled. The residue was diluted to 500 c.c. with water, and the mixture treated with concentrated hydrochloric acid (100 c.c.), boiled, and decanted from tar. The base precipitated from the aqueous extract by sodium hydroxide solidified on cooling and was separated and extracted with light petroleum (b. p. 40—60°). Distillation of the petrol-soluble material gave 1 : 2 : 3 : 4-tetrahydro-7-methylphenazine [2] (24 g.), b. p. 163—164°/5·5 mm. (m. p. 80—82° after crystallisation from light petroleum).

The following were prepared by these methods :

2 : 3-*cyclo*Pentenoquinoxaline (*B*), b. p. 130—150°/7 mm., m. p. 99—100° (Found : N, 16·5. Calc. for $C_{11}H_{10}N_2$: N, 16·5%).

6-*Methyl*-2 : 3-cyclo*pentenoquinoxaline* (*B*), cream needles from light petroleum (b. p. 60—80°), m. p. 103—104°, b. p. 135—145°/4 mm. (Found : C, 78·2; H, 6·6; N, 15·5. $C_{12}H_{12}N_2$ requires C, 78·2; H, 6·5; N, 15·2%).

1 : 2 : 3 : 4-*Tetrahydro*-7-*methoxyphenazine* (*C*), pale brown prisms, m. p. 115—115·5°, from light petroleum (Found : N, 12·95. $C_{13}H_{14}ON_2$ requires N, 13·1%).

2 : 3-cyclo*Heptenoquinoxaline* (*C*), platelets, m. p. 81°, from light petroleum (b. p. 60—80°) (Found : N, 14·0. $C_{13}H_{14}N_2$ requires N, 14·14%).

Preparation of N-oxides. 2 : 3-*cyclo*Pentenoquinoxaline (4·25 g.) in ether (75 c.c.) was treated with monoperphthalic acid in ether (170 c.c. of 0·35 molar solution) and kept in the dark. After 3 days the *N*-oxide phthalate (5—6 g.) was filtered off, washed with ether, and dissolved in water (100 c.c.) by the addition of sodium carbonate to adjust the pH to 7. The aqueous solution was extracted with chloroform (4 × 50 c.c.), and the extract was dried (Na_2SO_4) and evaporated. The residue (3·1 g.) was twice crystallised from benzene, giving 2 : 3-cyclo*penteno-quinoxaline* 1 : 4-*dioxide* as dull greenish-yellow leaflets, m. p. 179° (decomp.) (Found : C, 64·7; H, 4·8; N, 13·9. $C_{11}H_{10}O_2N_2$ requires C, 65·3; H, 4·95; N, 13·9%). Oxidation of 6-methyl-2 : 3-*cyclo*pentenoquinoxaline gave only tars, and both quinoxalines were unstable to peracetic acid.

The following *N*-oxides were obtained by oxidation with peracetic acid : [1]

1 : 2 : 3 : 4-*Tetrahydro*-7-*methylphenazine* 5 : 10-*dioxide*, yellow needles, m. p. 208—210°, from ethanol (Found : C, 67·3; H, 6·1; N, 12·2. $C_{13}H_{14}O_2N_2$ requires C, 67·8; H, 6·1; N, 12·2%).

7-*Chloro*-1 : 2 : 3 : 4-*tetrahydrophenazine* 5 : 10-*dioxide*, yellow microcrystals, m. p. 186—188°, from ethanol (Found : C, 56·8; H, 4·35; N, 11·0. $C_{12}H_{11}O_2N_2Cl$ requires C, 57·5; H, 4·4; N, 11·2%).

1 : 2 : 3 : 4-*Tetrahydro*-7-*methoxyphenazine* 5 : 10-*dioxide*, brown needles, m. p. 204—206°, from ethanol (Found : C, 63·1; H, 5·8; N, 10·8. $C_{13}H_{14}O_3N_2$ requires C, 63·3; H, 5·7; N, 11·4%).

2 : 3-cyclo*Heptenoquinoxaline* 1 : 4-*dioxide*, yellow prisms, m. p. 172—173°, from benzene (Found : C, 68·0; H, 5·9; N, 11·5. $C_{13}H_{14}O_2N_2$ requires C, 67·8; H, 6·1; N, 12·2%).

Bornyleno(2′ : 3′ : 2 : 3)*quinoxaline di*-N-*oxide*, cream prisms, m. p. 137—139°. from light petroleum (b. p. 80—100°) (Found : C, 71·3; H, 7·0; N, 10·5. $C_{16}H_{18}O_2N_2$ requires C, 71·0; H, 6·7; N, 10·4%).

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[*Received, December 21st*, 1955.]

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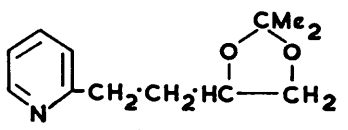
494. *An Attempted Synthesis of Pelletierine.*

By R. E. BOWMAN and D. D. EVANS.

THE alkaloid pelletierine, first isolated by Tanret [1] and later assigned structure (I) by Hess and Eichel,[2] has in spite of its apparent molecular simplicity, resisted all attempts at synthesis.[3] We now report a new approach which, again, has failed to yield the alkaloid. ω-Lithio-2-picoline in ethereal solution with 5-chloromethyl-2 : 2-dimethyl-1 : 3-dioxolan gave smoothly a mixture of the mono- and di-alkyl derivatives (II) and (III), which were readily separated by fractional distillation *in vacuo*. These products were readily hydrolysed by dilute acid to the corresponding di- and tetra-ols but attempts to reduce the pyridine ring of the former with Raney nickel were unsuccessful. However, in the presence

[1] *Compt. rend.*, 1878, **86**, 1270.
[2] *Ber.*, 1917, **50**, 1192, and later papers.
[3] King, Hofmann, and McMillan, *J. Org. Chem.*, 1951, **16**, 1100, and references cited therein.

of one equivalent of ethanolic hydrogen chloride,[4] reduction of the dioxolan (II) took place readily over platinum, to give, after hydrolysis of the protecting group, the piperidine (IV). Reaction of the latter with aqueous periodic acid appeared to take place rapidly at room



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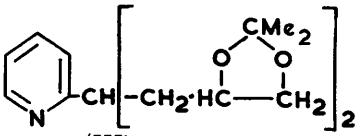

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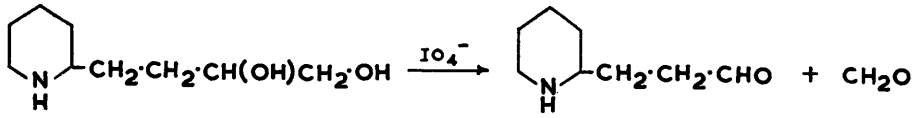

(IV) (I)

temperature, as indicated by evolution of formaldehyde but only a trace of volatile base could be isolated; attempts to isolate pelletierine (I) as its picrate from the reaction mixture were equally unsuccessful.

Experimental.—Alkylation of 2-picoline with 5-chloromethyl-2 : 2-dimethyl-1 : 3-dioxolan. The dioxolan (100 g., 0·66 mole) in ether (200 ml.) was added gradually with stirring and cooling to an ethereal solution of ω-lithio-2-picoline [5] (0·63 mole) during 1 hr. and thereafter the mixture was refluxed for 5 hr. After 2 days at room temperature, the mixture was decomposed with ice-water and the organic extract evaporated to dryness. Fractional distillation furnished 2 : 2-*dimethyl*-4-(2-2′-*pyridylethyl*)-1 : 3-*dioxolan* (II) (25 g.), b. p. 99—101°, n_D^{20} 1·5106 (Found: C, 70·2; H, 8·4; N, 6·8. $C_{12}H_{17}O_2N$ requires C, 69·5; H, 8·3; N, 6·8%), and 1 : 2-6 : 7-*di*(iso-*propylidenedioxy*)-4-2′-*pyridylheptane* (III) (30 g.), b. p. 148—150°, n_D^{20} 1·4927 (Found : C, 67·5; H, 8·5; N, 4·5. $C_{18}H_{27}O_4N$ requires C, 67·3; H, 8·5; N, 4·4%).

4-2′-*Pyridylbutane*-1 : 2-*diol.* The dioxolan (II) (10 g.) was heated in N-sulphuric acid (85 ml.) on the steam-bath for 5 hr. After dilution with water (500 ml.), the mixture was passed through Amberlite resin IRA-400 (OH) to remove sulphate ions, and the percolate evaporated to dryness *in vacuo*, yielding the *diol* (Found : C, 64·6; H, 7·8; N, 8·4. $C_9H_{13}O_2N$ requires C, 64·7; H, 7·8; N, 8·4%). The material appeared to distil (b. p. 148—150°/1·25 mm., n_D^{20} 1·5278) but analytical results (Found : C, 63·9; H, 7·6; N, 7·8%) indicated that some decomposition had occurred.

4-2′-*Pyridylheptane*-1 : 2 : 6 : 7-*tetraol.* Hydrolysis of the bisdioxolan (III) was carried out as in the previous example, to give the *tetraol* (Found : C, 60·1; H, 8·0; N, 5·8. $C_{12}H_{19}O_4N$ requires C, 59·7; H, 7·9; N, 5·8%) which could not be distilled at 0·5 mm. without decomposition.

4-2′-*Piperidylbutane*-1 : 2-*diol* (IV). A solution of the pyridyl derivative (II) (45 g.) in N-ethanolic hydrogen chloride (260 ml.) was hydrogenated over platinum oxide (2·0 g.) until 3 mols. of hydrogen had been taken up. After removal of catalyst, the solution was diluted with 0·2N-sulphuric acid (250 ml.) and set aside overnight. Ethanol and acetone were then removed in steam, and sulphate and chloride ions with ion-exchange resin as previously. Distillation of the eluate furnished the *diol*, b. p. 134—136°/0·3 mm., n_D^{20} 1·5035 (Found : C, 62·4; H, 11·1; N, 8·2. $C_9H_{19}O_2N$ requires C, 62·4; H, 11·1; N, 8·1%).

Periodic acid oxidation of 4-2′-*piperidylbutane*-1 : 2-*diol.* A solution of the diol (10 g.) in water (85 ml.) was mixed with aqueous periodic acid (9%; 170 ml.) at room temperature, a brisk stream of nitrogen being passed through the solution to volatilise the formaldehyde formed. After 3 hr. the solution was concentrated to half-volume under reduced pressure and basified with 10N-sodium hydroxide (10 ml.) in the presence of chloroform (100 ml.). The solution was repeatedly extracted with chloroform and bulked extracts were evaporated to dryness under reduced pressure; the resulting red oil (10 g.) was then distilled *in vacuo* but only a trace of volatile yellow oil (100 mg.), b. p. 65—67°/1 mm., was obtained and gave unexpected

[4] Adams and Voorhees, *J. Amer. Chem. Soc.*, 1922, **44**, 1397.
[5] Walter, *Org. Synth.*, 1943, **23**, 83.

analyses (Found : C, 70·4; H, 10·8; N, 8·7. Calc. for $C_8H_{15}ON$: C, 68·0; H, 10·7; N, 9·9%). Pelletierine [2] is described as an oil, b. p. 106°/21 mm.

In other experiments under the same conditions, samples of reaction mixture were removed at intervals and treated with aqueous picric acid; intractable gummy picrates were obtained.

RESEARCH DEPARTMENT, PARKE, DAVIS & COMPANY, LTD.,
HOUNSLOW, MIDDLESEX.

[*Received, January 9th,* 1956.]

495. epi*Pregnanolone–Benzophenone Adduct.*

By K. R. BHARUCHA.

IN contrast to the chromic acid oxidation, which has been reported [1] to yield the expected *epi*pregnanolone, m. p. 149—151°, oxidation with permanganate of 3α-acetoxy-24 : 24-diphenylchola-20 : 23-diene, obtained from lithocholic acid by the Meystre–Miescher degradation,[1] gave, after hydrolysis, a good yield of a product, m. p. 127—130°. From the ultraviolet absorption spectrum (peak at 2530 Å), identical with that of benzophenone, the product was identified as an adduct of benzophenone and *epi*pregnanolone, the identity being established by comparison (m. p., mixed m. p., [α], spectrum) with a sample prepared from the components in ether.

Elemental analyses, polarimetry, and light absorption indicate a molecular ratio of steroid to benzophenone of 3 : 1. With this stoicheiometry, it is difficult to visualise chemical bonding in the adduct, compatible with its ultraviolet absorption spectrum. The adduct is best considered as a clathrate.

The superior physical and crystallising properties of the adduct and the ready recovery of steroid by steam-distillation suggest its usefulness in the isolation of *epi*pregnanolone (and possibly other 20-keto-steroids) from oxidation mixtures with the aid of extraneous benzophenone. Complex formation may be one of the factors contributing to the low yields generally obtained on oxidation of diphenylcholadienes.

Experimental.—Ultraviolet absorption measurements were carried out with absolute EtOH solutions unless otherwise stated. Optical rotations were measured in alcohol-free chloroform in a 1 dm. tube.

Permanganate oxidation of 3α-*acetoxy*-24 : 24-*diphenylchola*-20 : 23-*diene.* To a stirred suspension of powdered permanganate (20 g.) and hydrated magnesium sulphate (10 g.) in acetone (150 c.c.) and water (10 c.c.) at 27°, the acetoxy-diene (10 g.; $\lambda_{max.}$ 3050 Å, ε 27,300 in "*iso*octane") was added in three lots at 5-minute intervals. An exothermic reaction ensued and acetone refluxed. After 30 min. reduction was complete, additional permanganate (3 g.) was added, and stirring continued at 35—30° for another 4 hr. The mixture was then treated with activated charcoal (1 g.) and filtered through filter-aid, and the residue washed with acetone. Evaporation of the combined filtrates, dissolution of the residue in methanol (25 c.c.), and re-evaporation *in vacuo* left the crude acetoxy-20-ketone as a gum (8·55 g.).

A solution of the gum in methanol (100 c.c.), water (2 c.c.), and concentrated hydrochloric acid (2·5 c.c.) was kept at 27° for 24 hr. After neutralisation with anhydrous sodium carbonate and removal of the solvents *in vacuo* at room temperature, the product was isolated with chloroform as a pale yellow semi-solid (7·65 g.). Crystallisation from ether–hexane furnished the colourless *epi*pregnanolone–benzophenone adduct (4·9 g.), m. p. 126—130° (after sintering). Recrystallisation from hexane gave material, m. p. 127—130°, $[\alpha]_D^{26}$ +83·5° ± 4° (*c* 1·035), $\lambda_{max.}$ 2530 Å ($E_{1\,cm.}^{1\%}$ 185), $\lambda_{min.}$ 2270 Å ($E_{1\,cm.}^{1\%}$ 61). Further crystallisation from aqueous methanol did not alter these constants. The m. p. was not depressed on admixture with the adduct prepared as below.

Concentration of the mother-liquors from the first crystallisation furnished a slightly coloured second crop (1·05 g.), m. p. 112—120° after sintering, $\lambda_{max.}$ 2530 Å ($E_{1\,cm.}^{1\%}$ 158).

epi*Pregnanolone.* An aqueous suspension of the adduct was steam-distilled for 4½ hr. Isolation of the non-volatile residue by filtration and crystallisation from ether–hexane gave pure *epi*pregnanolone as needles, m. p. 149—151°, $[\alpha]_D^{25}$ +109·1° ± 4° (*c* 0·871) (Found :

[1] Meystre and Miescher, *Helv. Chim. Acta*, 1946, **29**, 33.

C, 79·25; H, 10·8; O, 10·25. Calc. for $C_{21}H_{34}O_2$: C, 79·2; H, 10·8; O, 10·1%) (Meystre and Miescher [1] give m. p. 151—154°, $[\alpha]_D^{22}$ +109·5° ± 4°).

epi*Pregnanolone–benzophenone adduct.* A solution of *epi*pregnanolone (240 mg.) and benzophenone (60 mg.) in ether (10 c.c.) was concentrated and then chilled to give colourless needles (197 mg.), m. p. 131—132° (sinters at 128°). Crystallisation from hexane gave the *adduct*, m. p. 131—132° (sinters at 129°), $[\alpha]_D^{26}$ +89° ± 4° (*c* 1·035), $\lambda_{max.}$ 2530 Å ($E_{1\,cm.}^{1\%}$ 176), $\lambda_{min.}$ 2270 Å ($E_{1\,cm.}^{1\%}$ 59) (Found: C, 80·0; H, 10·05; O, 9·9. $3C_{21}H_{34}O_2,C_{13}H_{10}O$ requires C, 80·3; H, 9·9; O, 9·9%. $[\alpha]_D$ +91·5°; $E_{1\,cm.}^{1\%}$ at 2530 Å = 176 *).

Crystallisation of the adduct from very dilute solutions results in partial cleavage (rise in m. p.).

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[*Received, January 9th*, 1956.]

* Based on $\varepsilon_{max.}$ = 20,000 for benzophenone; see Braude, *Ann. Reports*, 1945, **42**, 126.

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496. *Palladised Charcoal as a Catalyst for the Reduction of Aromatic Nitro-compounds by Hydrazine Hydrate.*

By M. J. S. DEWAR and T. MOLE.

HYDRAZINE HYDRATE has for some time been known to reduce aromatic nitro-compounds to amines, but it has not been used extensively since the reaction is very slow. Balcom and Furst [1] recently found that the reduction is catalysed by Raney nickel, and their method has been applied to certain polycyclic nitro-compounds [2] which are difficult to convert into their amines efficiently otherwise. We have now discovered that a wide range of polycyclic aromatic nitro-compounds can be rapidly and smoothly reduced by hydrazine hydrate with a more convenient catalyst, palladised charcoal.

1- and 2-Nitronaphthalene, 1-, 2-, 3-, and 9-nitrophenanthrene, 3-nitropyrene, 2-nitrochrysene, and 3-nitroperylene [3] were thus reduced, in each case to very pure amine, in at least 60% yield after a single recrystallisation. The reduction occurred almost instantaneously with nitro-derivatives of the very reactive hydrocarbons, perylene and pyrene, but appeared to be slower with those of the less reactive hydrocarbons. Nitrobenzene itself reacted very slowly indeed (reaction was incomplete after 1 hour) but *p*-nitroanisole was reduced smoothly to *p*-anisidine. It seems unlikely that the method will be of much value for the reduction of unactivated nitrobenzene derivatives. On the other hand 8-nitroquinoline, the only heterocyclic compound tested, gave 8-aminoquinoline in good yield. The results are summarised in the Table.

Nitro-compound	Concn. of soln. in EtOH (mg./ml.)	Reaction time (min.)	Solvent for recrystn.*	M. p. of amine	Yield (%)
1-Nitronaphthalene	20/20	10	40—60° Pet	49—50°	60
2-Nitronaphthalene	20/20	10	100—120° Pet	109—110	62
1-Nitrophenanthrene	60/20	5	100—120° Pet	144—145	60
2-Nitrophenanthrene	60/20	10	80—100° Pet	82—83	68
3-Nitrophenanthrene	60/20	10	60—80° Pet.	86—87	64
9-Nitrophenanthrene	50/20	5	100—120° Pet	134—135	81
3-Nitropyrene	40/20	5	80—100° Pet	115·5—117	64
2-Nitrochrysene	25/30	10	B	205—206	65
3-Nitroperylene	50/50	10	B	220—230	67
p-Nitroanisole	1000/20	10	40—60° Pet	58—59	63
8-Nitroquinoline	200/20	5	80—100° Pet	62·5—64	65

* B = Benzene. Pet = light petroleum of b. p. indicated.

Experimental.—The experimental method differed from one compound to another only in the time allowed for reaction (5—10 min.) and in the solvent (benzene or light petroleum) for recrystallisation of the product. A typical procedure is as follows.

[1] Balcom and Furst, *J. Amer. Chem. Soc.*, 1953, **75**, 4334.
[2] Bavin, Ph.D., Thesis, London, 1955.
[3] Dewar and Mole, *J.*, 1956, 1441.

1-Nitrophenanthrene (60 mg.), 5% palladium–charcoal (20 mg.), and hydrazine hydrate (0·5 ml.) were refluxed in alcohol (20 ml.) for 5 min. The solution was filtered and the alcohol and excess of hydrazine hydrate were distilled. The residue recrystallised from light petroleum (b. p. 100—120°) in white needles of 1-phenanthrylamine (32 mg.), m. p. 144—145°.

One of us (T. M.) is indebted to the Department of Scientific and Industrial Research for a Maintenance grant.

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497. 3 : 4-*Dihydro*-4-*phenyl-carbostyril and* -iso*carbostyril and Some of their Derivatives.*

By (MISS) E. F. M. STEPHENSON.

FOR purposes of comparison it was necessary to prepare 3 : 4-dihydro-4-phenylcarbostyril and -*iso*carbostyril. 4-Phenylcarbostyril has previously been obtained most conveniently by the cyclisation of *N*-(benzoylacetyl)aniline by various methods;[1] this is now shown to give better results on a small scale when polyphosphoric acid is used. Its reduction to the dihydro-compound could not be effected catalytically but was readily accomplished by using sodium amalgam; and the reverse change was smoothly brought about by palladium black. The dihydro-compound has also been prepared, but in inferior yield, from 3-phenylindanone by the Schmidt reaction; the 3-phenylindanone was obtained by the cyclisation of ββ-diphenylpropionic acid with polyphosphoric acid, which gives better results than concentrated sulphuric acid and, on a small scale, is more convenient than cyclisation of the acid chloride with aluminium chloride. Cyclisation of the ethyl urethane from 2 : 2-diphenylethylamine with polyphosphoric acid gave 3 : 4-dihydro-4-phenyl*iso*carbostyril in fair yield. The preparation of 3 : 4-dihydro*iso*carbostyrils by the cyclisation of the urethanes from phenethylamines has been little used;[2] with polyphosphoric acid as the cyclising agent the method may prove of wider use. Dehydrogenation with palladium black gave 4-phenyl*iso*carbostyril in good yield.

Experimental.—M. p.s marked * were determined on a Kofler hot-stage microapparatus. Microanalyses were made by the C.S.I.R.O. Microanalytical Service. Temperatures quoted for sublimations refer to the heating-bath. The phosphoric acid used in the preparations of polyphosphoric acid had *d* 1·75.

4-*Phenylcarbostyril.* (*a*) To a solution of phosphoric oxide (63 g.) in phosphoric acid (36 ml.) at 105°, *N*-(benzoylacetyl)aniline (2·39 g.) was added rapidly, and the internal temperature of the stirred mixture was raised from 123° to 143° during ½ hr. (oil-bath). The hot, clear yellow solution was poured on crushed ice, and after 5—6 hr. crystallisation of the product was complete. After collection and crystallisation from aqueous ethanol, the carbostyril (1·55 g.), m. p. 259—261°, was obtained. 2-Chloro-4-phenylquinoline prepared therefrom with phosphoryl chloride[1] had m. p. 91—92°. (*b*) A mixture of 3 : 4-dihydro-4-phenylcarbostyril (100 mg.) and palladium black (50 mg.) was heated at 250° (bath) for 35 min. while a steady stream of nitrogen was passed through the apparatus. Much of the product was collected by sublimation during this heating, and the rest was recovered by sublimation at 210°/0·4 mm. After crystallisation from ethanol the product (55 mg.) was identified as 4-phenylcarbostyril by m. p. and mixed m. p. A further 20 mg. was recovered from the filtrate.

3 : 4-*Dihydro*-4-*phenylcarbostyril.* (*a*) To a solution of 4-phenylcarbostyril (0·88 g.) in ethanol (80 ml.) and water (12 ml.) at room temperature, 2% sodium amalgam (55 g.) was added during ¾ hr. with shaking. After 2 hours' further shaking the supernatant suspension was decanted, diluted with water (200 ml.), and acidified with hydrochloric acid. After 4 hr. the precipitate was collected and purified by sublimation at 190—210°/0·2 mm. and by crystallisation from aqueous ethanol. The *product* (0·76 g.) formed colourless prisms, m. p. *180—180·5° (Found: C, 81·0; H, 5·9; N, 6·3; O, 7·6. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·9; N, 6·3; O, 7·2%). The carbostyril was recovered unchanged from attempts to reduce it with hydrogen

[1] Hauser and Reynolds, *J. Amer. Chem. Soc.*, 1948, **70**, 2404.
[2] For references see "Organic Reactions," Wiley, New York, 1951, Vol. VI, p. 78.

(1 atm.) and 20% palladium–charcoal, palladium black, or Raney nickel (W-4 catalyst). Späth *et al.*[3] reduced carbostyril to 3 : 4-dihydrocarbostyril with hydrogen (1 atm.) and a palladium catalyst, and in the present work the same reduction was smoothly effected with hydrogen (1 atm.) and Raney nickel (W-4) catalyst.

(*b*) Powdered sodium azide (0·58 g.) was added with stirring to 3-phenylindan-1-one (1·04 g.) in chloroform (30 ml.) and concentrated sulphuric acid (3 ml.) during 10 min., the temperature rising from 20° to 25°. The mixture was then kept at 40° for 1 hr. The chloroform layer was then decanted and the sulphuric acid layer (which contained the products) decomposed with crushed ice (emulsion formed). After 24 hr. the oily product was washed by decantation, dried, and extracted with boiling benzene (2 × 15 ml.). After some hours the first extract deposited a crystalline product which after sublimation at 190°/0·4 mm. and crystallisation from benzene gave 3 : 4-dihydro-4-phenylcarbostyril (185 mg.), identified by m. p. and mixed m. p. Concentration of the filtrate together with the second benzene extract gave another 90 mg.

3-*Phenylindanone.* To a solution of phosphoric oxide (70 g.) in phosphoric acid (40 ml.) at 105°, ββ-diphenylpropionic acid (4·52 g.) was added rapidly and the mixture was kept at 105—110° for ½ hr. with stirring. The hot mixture was poured on crushed ice, and the emulsion partially neutralised with sodium hydroxide. After 6 hr. the precipitate was collected and stirred with sodium carbonate solution to remove unchanged acid (0·45 g.). The remaining ketone (3·6 g.) was further purified by sublimation at 155°/0·4 mm. and crystallisation from light petroleum (60—80°). The white crystalline product (2·88 g.) had m. p. 78·5—79·5°.

3 : 4-*Dihydro*-4-*phenyl*iso*carbostyril.* To a solution of phosphoric oxide (21 g.) in phosphoric acid (12 ml.) at 110°, the ethyl urethane from 2 : 2-diphenylethylamine (1·47 g.) was added rapidly and the internal temperature of the mixture was raised to 148° during 50 min. with stirring. The hot, pale brown solution was poured on crushed ice. After 6 hr. the product was collected, digested with sodium hydroxide solution, and collected again. The *product* (0·93 g.), after sublimation at 170—180°/0·2 mm. and crystallisation from benzene, was obtained as white crystals, 0·65 g., m. p. *173·5—174° (Found : C, 80·6; H, 5·6; N, 5·9. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·9; N, 6·3%). The 2 : 2-diphenylethylamine was characterised as the hydrochloride, m. p. 259—261°, the ethyl urethane, m. p. *70—71° (Found : C, 76·5; H, 7·0; N, 5·0; O, 12·1. Calc. for $C_{17}H_{19}O_2N$: C, 75·8; H, 7·1; N, 5·2; O, 11·9%), and the *diacetyl derivative* formed from the hydrochloride, anhydrous sodium acetate, and boiling acetic anhydride. The last, after being stirred with a little ethanol, sublimed at 190°/0·4 mm., and crystallised from aqueous ethanol, formed colourless parallelepipeds, m. p. *96—97° (Found : C, 77·5; H, 6·8; N, 5·0; O, 11·7. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8; N, 5·0; O, 11·4%).

4-*Phenyl*iso*carbostyril.* A mixture of the preceding compound (200 mg.) and palladium black (100 mg.) was heated at 255—265° while a steady stream of nitrogen was passed through the apparatus. The *product* (170 mg.), collected mainly by sublimation during this heating and partly by sublimation at 225°/0·4 mm. After sublimation at 190—205°/0·5 mm. and crystallisation from ethanol the *product* formed colourless prisms, m. p. *243·5—244·5° (Found : C, 81·9; H, 5·2. $C_{15}H_{11}ON$ requires C, 81·4; H, 5·0%).

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[*Received, January 16th,* 1956.]

[3] Späth and Galinovsky, *Ber.*, 1936, **69**, 2059.

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498. *Some Derivatives of Kojic Acid.*

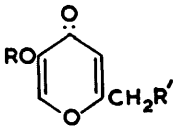
By M. G. BROWN.

THE syntheses described in this Note, and carried out five years ago, were directed more especially to obtain some of the ω-substituted derivatives of kojic acid (I). This work incidentally confirms the m. p. of "*allo*maltol" (III) and 5-benzoylkojic acid (XIII) recently recorded by Beélik and Purves[1] as correcting previous values; also that of one of their new derivatives, ω-benzoylkojic acid (XI). New preparations of "*allo*maltol" and ω-acetyl- (VII) and ω-benzoyl-kojic acid are recorded.

Yabuta[2] reduced chlorokojic acid (II) to "*allo*maltol" (III) with zinc and acetic acid.

[1] Beélik and Purves, *Canad. J. Chem.*, 1955, **33**, 1361.
[2] Yabuta, *J.*, 1924, **125**, 575.

This reduction has now been performed catalytically with hydrogen and Raney nickel or palladised charcoal. The product was identified by its m. p. and the ferric chloride colour and as its 5-methyl ether (IV) and 5-benzoyl ester (V).[1,2,3] Although catalytic reduction of kojic acid itself results in addition of hydrogen to the pyrone ring,[4] it appears that reduction of the chloromethyl group in chlorokojic acid is easy relative to that of the ring. This is in contrast to Campbell, Ackerman, and Campbell's finding [3] that catalytic reduction of ω-chloro-5-methylkojic acid (VI) was not sufficiently selective.



(I) R = H, R′ = OH.
(II) R = H, R′ = Cl.
(III) R = H, R′ = H.
(IV) R = Me, R′ = H.
(V) R = Bz, R′ = H.
(VI) R = Me, R′ = Cl.
(VII) R = H, R′ = OAc.
(VIII) R = Ac, R′ = OAc.
(IX) R = Me, R′ = OAc.
(X) R = Bz, R′ = OBz.
(XI) R = H, R′ = OBz.
(XII) R = Bz, R′ = OAc.
(XIII) R = Bz, R′ = OH.
(XIV) R = Tosyl, R′ = OH.

Hurd and Sims [5] prepared ω-acetylkojic acid (VII) by heating kojic acid with aluminium chloride and acetyl chloride, and by heating the di-*O*-acetylkojic acid (VIII) with aluminium chloride. Partial hydrolysis of the diester may be more conveniently performed by Nierenstein's method.[6] Di-*O*-acetylkojic acid, when treated with one equivalent of piperidine in pyridine, yielded the ω-acetyl ester · the presence of a free phenolic group was shown by the ferric chloride colour and formation of a methyl ether (IX).

Di-*O*-benzoylkojic acid (X), similarly treated, gave ω-*O*-benzoylkojic acid (XI). The m. p. of these two ω-substituted esters are close to those recorded by Beélik and Purves,[1] who carried out analogous partial hydrolyses of ω-*O*-acetyl-5-*O*-benzoylkojic acid (XII) and of the dibenzoyl ester using hydroxylamine hydrochloride.

5-*O*-Benzoylkojic acid (XIII) and 5-*O*-toluene-*p*-sulphonylkojic acid (XIV) were prepared by treating cooled solutions of kojic acid in pyridine with one equivalent of the appropriate acid chloride.

Experimental.—allo*Maltol* (*5-hydroxy-2-methyl-4-pyrone*) (III). Chlorokojic acid [7] (10·2 g.) in ethyl alcohol (150 ml.) was hydrogenated at room temperature and pressure in the presence of anhydrous sodium acetate (8·2 g.) and Raney nickel (uptake, 1350 c.c.; theor., 1435 c.c.) After filtration and removal of the ethanol under reduced pressure, the residue was recrystallised from ethyl acetate, to give colourless prisms of "*allo*maltol," m. p. 152—153° (Found: C, 57·1; H, 4·85. Calc. for $C_6H_6O_3$: C, 57·1; H, 4·8%).

The Raney nickel may be replaced by palladised charcoal.

5-Methoxy-2-methyl-4-pyrone (IV). "*allo*Maltol" (2·5 g.) was added to ethereal diazomethane (from 30 g. of methyl-*N*-nitrosourea). Solvent and excess of diazomethane were removed under reduced pressure after 16 hr. The residue on distillation gave a colourless oil, b. p. 165—167°/20 mm., solidifying on cooling. Recrystallisation from light petroleum (b. p. 40—60°) gave the ether as blades, m. p. 68—69°, which did not give a ferric chloride colour.

5-Benzoyloxy-2-methyl-4-pyrone (V). "*allo*Maltol" in pyridine was refluxed with benzoyl chloride (one equiv.) for 0·5 hr. Addition of the cooled solution to an excess of 2N-hydrochloric acid precipitated the 5-benzoate, needles, m. p. 128—128·5° (from water) (Found: C, 67·8; H, 4·9. Calc. for $C_{13}H_{10}O_4$: C, 67·8; H, 4·35%).

2-Acetoxymethyl-5-hydroxy-4-pyrone (VII). Di-*O*-acetylkojic acid [5] (3·0 g.) and piperidine (1·0 g.) in pyridine (20 ml.) were set aside at room temperature for 20 hr. Addition of the mixture to cooled 2N-hydrochloric acid precipitated ω-*O*-acetylkojic acid, needles, m. p. 136—137° (from ethyl acetate) (Found: C, 52·1; H, 4·5. Calc. for $C_8H_8O_5$: C, 52·2; H, 4·35%).

2-Acetoxymethyl-5-methoxy-4-pyrone (IX). ω-*O*-Acetylkojic acid was added to moist ethereal diazomethane. After 3 hr. at room temperature the ether was removed and the residue recrystallised from ethyl acetate, to give ω-*O*-acetyl-5-*O*-methylkojic acid, prisms, m. p. 125—126° (Found: C, 55·0; H, 5·2. Calc. for $C_9H_{10}O_5$: C, 54·5; H, 5·05%), which did not give a ferric chloride colour.

[3] Campbell, Ackerman, and Campbell, *J. Org. Chem.*, 1950, **15**, 221.
[4] (*a*) Wijkman, *Z. physiol. Chem.*, 1924, **132**, 104; (*b*) Traetta-Mosca, *Ann. Chim. applicata*, 1914, **1**, 477; (*c*) Armit and Nolan, *J.*, 1931, 3023.
[5] Hurd and Sims, *J. Amer. Chem. Soc.*, 1949, **71**, 2440.
[6] Nierenstein, *ibid.*, 1930, **52**, 4012.
[7] Kipnis, *ibid.*, 1948, **70**, 4264.

5-Benzoyloxy-2-benzoyloxymethyl-4-pyrone (X). A solution of kojic acid (3·2 g.) and benzoyl chloride (6·5 g.) in pyridine (20 ml.) was refluxed for 1·5 hr. Addition of the cooled solution to 5N-hydrochloric acid precipitated the di-*O*-benzoylkojic acid, which crystallised from ethyl acetate as prisms, m. p. 134—135° (Found : C, 68·4; H, 4·1. Calc. for $C_{20}H_{14}O_6$: C, 68·5; H, 4·0%).

2-Benzoyloxymethyl-5-hydroxy-4-pyrone (XI). The di-*O*-benzoylkojic acid (1·0 g.) and piperidine (0·24 g.) in pyridine (20 ml.) were kept at room temperature for 20 hr., then added to 2N-hydrochloric acid. The precipitated ω-*O*-benzoylkojic acid recrystallised from ethyl alcohol as prisms, m. p. 176—178° (Found : C, 63·9; H, 3·95. Calc. for $C_{13}H_{10}O_5$: C, 63·4; H, 4·1%). Refluxing the solution, or replacing the pyridine by methanol, did not alter the yield significantly.

5-Benzoyloxy-2-hydroxymethyl-4-pyrone (XIII). Benzoyl chloride (17·2 g.) was added slowly to a cooled solution of kojic acid (18·0 g.) in pyridine (100 ml.) and the solution kept at room temperature for 13 hr., then added to 5N-hydrochloric acid. The precipitated 5-*O*-benzoylkojic acid recrystallised from ethyl acetate as prisms, m. p. 145—146° (Yabuta [8] gives m. p. 136°) (Found : C, 63·8; H, 4·5%).

*2-Hydroxymethyl-5-toluene-*p*-sulphonyloxy-4-pyrone* (XIV) (cf. Tipson [9]). Toluene-*p*-sulphonyl chloride (15 g.) was added to a solution of kojic acid (10 g.) in pyridine (100 ml.) at −5°. The mixture was kept for 2 hr. at 0°, then for 12 hr. at 10°. After dilution at 0° with water (200 ml.) the solution was extracted with ethyl acetate several times, and the combined extracts were dried. After removal of the solvent the residue was recrystallised from ethyl acetate to give the *ester* as prisms, m. p. 145—147° (Found : C, 52·6; H, 3·9; S, 10·75. $C_{13}H_{12}O_6S$ requires C, 52·8; H, 4·05; S, 10·8%), which did not give a ferric chloride colour.

The author thanks the Department of Scientific and Industrial Research for a maintenance grant, Dr. J. A. Barltrop for bringing kojic acid to his attention, and Mr. Tutsuaki Hirai for translating a paper by Yabuta.

THE CHEMISTRY DEPARTMENT, WINCHESTER COLLEGE, HANTS. [*Received, January 25th,* 1956.]

[8] Yabuta, *J. Chem. Soc. Japan*, 1916, **37**, 1185, 1234.
[9] Tipson, *J. Org. Chem.*, 1944, **9**, 235.

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499. 11-*Sulphoundecanoic Acid.*

By W. RIGBY.

ADDITION of sulphurous acid to undecenoic acid yields 11-sulphoundecanoic acid, identical with that resulting from the oxidation of 11-disulphidoundecanoic acid; the acid prepared by Cohen,[1] m. p. 65°, is a hydrate. Some derivatives of the acid are described below.

Experimental.—*11-Sulphoundecanoic acid.* Sulphur dioxide (9 g.) was passed into a solution of undecenoic acid (14 g.) and potassium hydroxide (40 g.) in water (200 ml.). The solution was left overnight, potassium chloride (20 g.) was dissolved in it, and it was then acidified strongly with hydrochloric acid; the product separated as pearly plates. Ether (100 ml.) was added and after a few hours the suspension was filtered and the solid was washed with 10% potassium chloride solution, alcohol, and ether. Recrystallisation from dilute hydrochloric acid containing 5% of potassium chloride gave almost pure potassium hydrogen 11-sulphoundecanoate (9 g.), m. p. 180—182°. Barium chloride dihydrate (40 g.) in water (125 ml.) was added to a solution of this salt (72 g.) in hot water (400 ml.). The precipitated *barium dihydrogen salt* (44·3 g.) was filtered from the warm liquor, washed with water, alcohol, and ether, and dried at 100°; it formed microscopic spherules, m. p. *ca.* 320° (Found : Ba, 20·3. $C_{22}H_{42}O_{10}S_2Ba$ requires Ba, 20·6%). The dried barium salt was suspended in water (1 l.) and was stirred (hot) with the calculated amount of sulphuric acid. Acid-washed charcoal (15 g.) and acid-washed kieselguhr (100 g.) and hydrochloric acid (20 ml.; 2N) were added and the boiling solution was filtered through kieselguhr. The crystalline mass which was obtained on evaporation (there is much charring if traces of sulphuric acid are present) was recrystallised from ethyl acetate–benzene, ether–benzene, or concentrated hydrochloric acid, to give leaflets or needles of

[1] Cohen, *J.*, 1932, 593.

11-*sulphoundecanoic acid hydrate*, m. p. *ca.* 65° (Found: C, 48·3; H, 8·7. $C_{11}H_{22}O_5S,\frac{1}{2}H_2O$ requires C, 48·0; H, 8·4%). Drying in a vacuum at 45—50° gave the *anhydrous acid*, m. p. *ca.* 99° (Found: C, 49·4; H, 8·55%; equiv., 267. $C_{11}H_{22}O_5S$ requires C, 49·6; H, 8·3%; equiv., 266). The *dimethyl ester* (prepared by diazomethane) formed platelets, m. p. 42°, from *cyclo*hexane (Found: C, 52·8; H, 8·7. $C_{13}H_{26}O_5S$ requires C, 53·0; H, 8·9%). The acid gave the following salts: *potassium hydrogen salt*, platelets (from dilute hydrochloric acid), m. p. 195—197° (Found: C, 43·4; H, 6·8; S, 9·4; K, 12·5. $C_{11}H_{21}O_5SK$ requires C, 43·4; H, 6·95; S, 10·5; K, 12·8%) (solubility 2% at 20°, 1·4% at 0° in water; 1·7% at 20°, 1·1% at 0° in 0·5N-hydrochloric acid) (salt may be crystallised from 10N-hydrochloric acid, or even 20N-sulphuric acid with little loss). *Dipotassium salt*, crystallised from aqueous methanol, m. p. >360° (Found: C, 38·8; H, 5·8. $C_{11}H_{20}O_5SK_2$ requires C, 38·6; H, 5·9%). *Sodium hydrogen salt*, platelets (from dilute hydrochloric acid), m. p. 215° (Found: equiv., 291. $C_{11}H_{21}O_5SNa$ requires equiv., 288) (solubility 2·3% at 20° in water; 1·1% at 0° in dilute hydrochloric acid). *Manganese dihydrogen salt* [a solution of the potassium hydrogen salt (0·5 g.) and manganese sulphate (0·8 g.) in water (15 ml.) was acidified with 20N-sulphuric acid (5 ml.). The salt (0·44 g.) crystallised at once as prisms, m. p. 300—305° (Found: C, 44·5; H, 7·4; Mn, 9·4. $C_{22}H_{42}O_{10}S_2Mn$ requires C, 45·1; H, 7·2; Mn, 9·4%) [unlike the potassium hydrogen salt, it gave an immediate precipitate when silver nitrate (1 equiv.) was added to its aqueous solution]. *Disilver salt* [the salt slowly (days) crystallised when a large excess of silver nitrate was added to an aqueous solution of the potassium hydrogen salt], m. p. *ca.* 285° (decomp.) (Found: C, 28·0; H, 4·3; Ag, 44·6. $C_{11}H_{20}O_5SAg_2$ requires C, 27·5; H, 4·2; Ag, 44·95%). *Aniline hydrogen salt*, leaflets (from 2N-hydrochloric acid), m. p. 128° (Found: C, 56·3; H, 8·0; N, 5·1. $C_{17}H_{29}O_5NS$ requires C, 56·81; H, 8·1; N, 3·9%).

The *aniline salt of the anilide* was prepared by boiling the acid with aniline for 1 hr.; it formed needles, m. p. 168—170°, from alcohol [Found: C, 63·5; H, 7·8; N, 6·4%; equiv. (by titration with sodium hydroxide), 434. $C_{23}H_{34}O_4SN_2$ requires C, 63·6; H, 7·9; N, 6·45%; equiv., 434]. The *sodium salt of the anilide*, which crystallised during the titration of the previous substance, formed needles (from alcohol), m. p. *ca.* 250° (decomp.) (Found: C, 56·2; H, 7·2; N, 3·4. $C_{17}H_{26}O_4NSNa$ requires C, 56·2; H, 7·2; N, 3·85%). The *anilide hydrate* crystallised in needles, m. p. 103°, from dilute hydrochloric acid (Found: C, 56·65; H, 7·8; N, 3·65. $C_{17}H_{27}O_4NS,H_2O$ requires C, 56·8; H, 8·1; N, 3·9%).

11-*Chlorosulphonylundecanoic acid.* Potassium hydrogen 11-sulphoundecanoate (3 g.) was boiled with purified thionyl chloride (10 ml.) and pyridine (1 drop) for 2 hr. The excess of thionyl chloride was evaporated, the residue was shaken with hot water and benzene, and the benzene solution was evaporated. Extraction of the residue with boiling light petroleum (b. p. 60—80°) and recrystallisation from ethyl acetate–light petroleum gave 11-*chlorosulphonylundecanoic acid*, as plates, m. p. 62·5—63°; the substance is stable to air. Alternatively the oily impurities could be removed by chromatography on silica with benzene containing 1% of alcohol (Found: C, 47·1; H, 7·4; Cl, 12·4. $C_{11}H_{21}O_4SCl$ requires C, 46·3; H, 7·5; Cl, 12·4%). Reaction of the sulphonyl chloride with aniline gave the *sulphonanilide*, m. p. 113—114° (Found: C, 59·85; H, 7·7; N, 4·1. $C_{17}H_{27}O_4NS$ requires C, 59·8; H, 8·0; N, 4·1%), and with ammonia gave the *sulphonamide*, platelets (from water or aqueous alcohol), m. p. 127—129° (Found: C, 50·1; H, 8·6; N, 6·3. $C_{11}H_{23}O_4NS$ requires C, 49·8; H, 8·7; N, 5·3%). When the sulphonamide was titrated with sodium hydroxide, only approx. half an equivalent of the base was required and an *acid sodium salt* (m. p. 152—154°) of the amide crystallised from the alcoholic solution (Found: C, 50·8; H, 8·9. $C_{11}H_{22}O_4NSNa,C_{11}H_{23}O_4NS$ requires C, 47·8; H, 8·2%).

11-Bromoundecanoic acid [2] (m. p. 49—50°) was converted through 11-disulphidoundecanoic acid (m. p. 91°) into 11-sulphoundecanoic acid by Cohen's method.[1] The product, crystallised from concentrated hydrochloric acid, had m. p. *ca.* 65° as found by Cohen. When this material was dried under reduced pressure with the temperature gradually raised to 90°, the anhydrous acid, m. p. 95—99°, was obtained. There was no depression of m. p. when samples of the hydrated acids, the anhydrous acids, the potassium hydrogen salts, and the dimethyl esters from the two sources respectively were mixed.

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[*Received, January 26th*, 1956.]

[2] Ashton and Smith, *J.*, 1934, 439.

500. *A Crystallographic Study of Trimethylsulphonylmethane.*

By S. C. Abrahams and J. C. Speakman.

The bond distribution in trimethylsulphonylmethane,[1] $CH(SO_2{\cdot}Me)_3$, about the central carbon atom has been investigated by Gibson [2] and by Böhme and Marx [1] by chemical methods, in both cases inconclusively. During a detailed *X*-ray structure analysis of these crystals, we observed an unusual type of diffuse scattering.

The crystals separating from a large volume of hot water consist of elongated hexagonal prisms, belonging to the rhombohedral system and with lattice constants, expressed in terms of hexagonal axes: $a = 12{\cdot}89 \pm 0{\cdot}02$, $c = 9{\cdot}53 \pm 0{\cdot}02$ Å, at 291° K. The measured density is 1·830 g./c.c.; and six molecules in the cell, of volume 1370·3 Å^3, would correspond to a density of 1·820 g./c.c. Reflexions occur in *hkil* only when $h - k + l = 3n$; and in *hh̄0l* only when $l = 2n$. The space group is therefore R3c (C_{3v}^6) or R$\bar{3}$c (D_{3d}^6), the latter being very unlikely on stereochemical grounds. The former space group embodies three-fold axes parallel to [*c*], and the molecules are situated on these axes at intervals of $c/2$ (~4·8 Å). The strict space-group requirement would be for the molecule itself to possess a trigonal axis, along which the unique C–H bond must lie. Either a planar or a pyramidal arrangement of the three $-SO_2{\cdot}Me$ groups would be permissible. The diffuse scattering must imply some deviation from this idealised structure or from its regularity of repetition.

The remarkable diffuse scattering is illustrated in the Plate. It consists of diffuse spots around points in the reciprocal lattice at which reflexions are forbidden by the space group assigned by consideration of the sharp (Bragg) reflexions. These diffuse spots are linked by intense diffuse ridges, forming a honeycomb of diffuse hexagons around the sharp spots. There appears to be no report in the literature of similar diffuse scattering by organic crystals. It might arise either from thermal motions of the atoms, or from disorder in the lattice. The former type of scattering is strongly dependent on temperature; and accordingly *X*-ray photographs were taken at 78° K, with equipment based on a design by Abrahams and Calhoun.[3] Since the diffuse scattering was still as pronounced as at room temperature, it must be due to disorder. The heat-capacity curve (see following Note) shows no anomaly between 20° and 300° K, so that the disorder must be " frozen in " below room temperature.

The lattice constants at 78° K are $a = 12{\cdot}78 \pm 0{\cdot}02$, $c = 9{\cdot}45 \pm 0{\cdot}03$ Å. The lattice therefore undergoes an approximately isotropic contraction from 291° K, the volume falling by about 2½%.

It has recently come to our attention that an investigation of the crystal structure of the ammonium salt of trimethylsulphonylmethane has been undertaken by Dr. K. Hoogsteen.[4]

Thanks are offered to Messrs. G. M. D. Stewart and E. W. Addison who recorded the first *X*-ray diffractions for this crystal, to Messrs. A. O. Brooks and J. Rae for building the low-temperature equipment, to Dr. D. T. Gibson for providing the crystals and for drawing attention to this problem, and to Professor J. M. Robertson, F.R.S., for his interest.

The University, Glasgow, W.2. [*Received, January 30th,* 1956.]

[1] Böhme and Marx, *Ber.*, 1941, **74**, 1667.
[2] Gibson, *J.*, 1931, 2637.
[3] Abrahams and Calhoun, *Acta Cryst.*, 1955, **8**, 257.
[4] Hoogsteen, personal communication.

*Precession photograph of the hki*0 *layer of trimethylsulphonylmethane, with* Cu-$K\alpha$ *radiation.*

[*To face p.* 2562.

501. *Heat Capacity and Entropy of Trimethylsulphonylmethane.*

By T. Davies and L. A. K. Staveley.

Measurements have been made of the molar heat capacity C_p of crystalline trimethylsulphonylmethane between 22° K and room temperature. These measurements were undertaken at the request of Dr. S. C. Abrahams, as *X*-ray diffraction photographs suggested that at room temperature there is some disorder in the crystal, and it was therefore of interest to discover whether it undergoes transitions at a lower temperature.

The measurements were made in a low-temperature adiabatic calorimeter which will be described in detail elsewhere. This calorimeter was constructed to give results of reasonable accuracy from relatively small quantities. The trimethylsulphonylmethane used (4·0475 g.) (Found: S, 38·4%; equiv., 251, 253. Calc. for $C_4H_{10}O_6S_3$: S, 38·4%; equiv., 250·3) had been prepared by Dr. G. T. Gibson at Glasgow; the most likely impurity was considered to be $(CH_3{\cdot}SO_2)_2CH_2$, a very much weaker acid, so that from the equivalent-weight determination it seems certain that the sample used was at least 99% pure.

The heat-capacity results are presented in Table 1, where the thermochemical calorie, 4·1840 abs. joules, is used. Smoothed values at 10° intervals are given in Table 2. The precision is estimated at ±0·3% above 60° K, and ±1% below 60° K.

Table 1. *Measured heat capacity C_p of trimethylsulphonylmethane in cal. mole^{-1} deg.$^{-1}$ [1 cal. = 4·1840 joule (abs.)].*

T (°K)	C_p	T (°K)	C_p	T (°K)	C_p	T (°K)	C_p	T (°K)	C_p	T (°K)	C_p
22·01°	4·29	54·90°	15·12	89·88°	26·24	127·59°	35·50	181·38°	45·85	241·23°	55·40
25·17	5·31	59·56	16·78	95·02	27·47	133·19	36·85	189·36	47·21	250·71	56·64
28·82	6·23	64·00	18·36	100·16	29·02	138·96	38·21	196·21	48·12	260·65	58·30
33·00	7·64	69·20	20·15	105·54	30·22	145·27	39·06	205·27	49·67	270·94	60·08
37·06	9·12	74·21	21·42	110·89	31·68	152·36	40·45	214·13	50·70	281·72	61·85
40·77	10·33	78·85	22·91	116·38	33·09	159·58	42·00	223·07	52·43	292·71	63·65
44·95	11·71	84·20	24·74	121·99	34·33	166·76	43·41	232·10	54·47		
49·69	13·12					173·92	44·37				

Table 2. *Smoothed C_p values at 10° intervals in cal. mole^{-1} deg.$^{-1}$.*

T (°K)	C_p	T (°K)	C_p	T (°K)	C_p	T (°K)	C_p	T (°K)	C_p	T (°K)	C_p
20°	3·78	70°	20·24	120°	33·87	170°	43·85	220°	51·86	270°	59·91
30	6·66	80	23·36	130	36·12	180	45·51	230	53·47	280	61·52
40	9·95	90	26·25	140	38·25	190	47·12	240	55·07	290	63·12
50	13·46	100	28·91	150	40·22	200	48·67	250	56·70	298·16	64·44
60	16·92	110	31·47	160	42·10	210	50·25	260	58·31	300	64·73

A plot of C_p against temperature shows no transition in this range, and no region in which the heat capacity is obviously anomalous. Since Dr. Abrahams has found that the diffuse scattering in the *X*-ray diffraction pattern is just as pronounced at 78° K as at 295° K, disorder must persist in the crystal over the whole range of the C_p measurements, and the solid presumably possesses residual entropy at 0° K. From the C_p results, the value for the entropy difference for the actual crystal between 0° and 298·16° K is 72·8 cal. mole^{-1} deg.$^{-1}$, of which the contribution from 0° to 20° K of 2·4 e.u. was estimated by graphical extrapolation.

We are grateful to Imperial Chemical Industries Limited and to Messrs. Albright and Wilson, Ltd., for financial assistance, and to the Department of Scientific and Industrial Research for a Maintenance Allowance (to T. D.).

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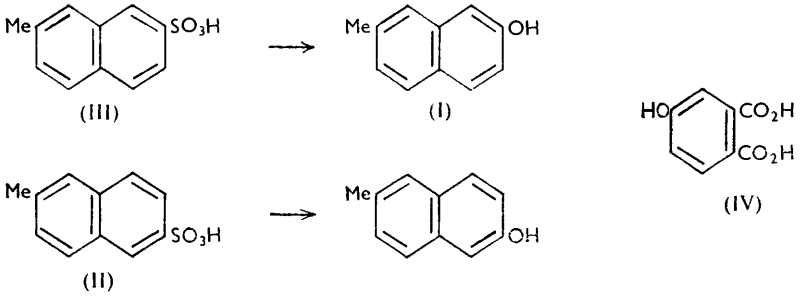
South Parks Road, Oxford.

[*Received, January 30th,* 1956.]

502. *The Preparation of 7-Methyl-2-naphthol.*

By T. G. Halsall and D. B. Thomas.

Recently an authentic sample of 7-methyl-2-naphthol (I) was required for comparison with a methylnaphthol, m. p. 118—120°, which was believed to have this structure.[1] The sole reference to 7-methyl-2-naphthol is by Shreve and Lux [2] who give m. p. 101°. Repetition of their procedure afforded a methylnaphthol, m. p. 105·5—107°. Their method involved sulphonation of 2-methylnaphthalene at 160° and alkaline fusion of the resulting sulphonic acid. By sulphonation at 90—95° Shreve and Lux [2] obtained the known 6-methylnaphthalene-2-sulphonic acid (II). To prove that they had obtained the 7-methyl derivative (III) at 160° the acid was oxidised with potassium permanganate, and the product was fused with potassium and sodium hydroxides at 170—180° to give 4-hydroxyphthalic acid (IV). These results only indicate that the high-temperature sulphonation product was probably either 6- or 7-methylnaphthalene-2-sulphonic acid or a mixture of the two. In view of this, 7-methyl-2-naphthol has been prepared by de-



methylation of 2-methoxy-7-methylnaphthalene which was synthesised by Mitter and De's method.[3]. The melting point of this ether is 87·5—88·5°. Shreve and Lux [2] give m. p. 78°, which is also the melting point (78—79°) given for the methyl ether of 6-methyl-2-naphthol.[3,4]

Experimental.—M. p.s were determined on a Kofler block and are corrected.

2-Methoxy-7-methylnaphthalene. This was prepared according to Mitter and De's method,[3] except that γ-*p*-methoxyphenyl-α-methylbutyric acid was cyclised by thionyl chloride, followed by aluminium chloride. The ether crystallised as plates (from aqueous methanol), m. p. 87·5—88·5°. The 2 : 4-*dinitrophenylhydrazone* of 1 : 2 : 3 : 4-tetrahydro-7-methoxy-2-methyl-1-oxonaphthalene melted at 239° (Found : C, 58·25; H, 4·85; N, 15·05. $C_{18}H_{18}O_5N_4$ requires C, 58·35; H, 4·9; N, 15·1%).

7-Methyl-2-naphthol (I). 2-Methoxy-7-methylnaphthalene (1·6 g.), 46% hydrobromic acid (3 c.c.), and acetic acid (5 c.c.) were heated under reflux for 2 hr. The solid which separated on cooling crystallised from aqueous acetic acid as plates, m. p. 110—115°. These were sublimed under reduced pressure, to give *7-methyl-2-naphthol*, m. p. 118° (Found : C, 83·15; H, 6·45. $C_{11}H_{10}O$ requires C, 83·5; H, 6·4%).

Sulphonation of 2-methylnaphthalene at 160°.[2] 2-Methylnaphthalene (20·5 g.) was heated with concentrated sulphuric acid (20·5 g.) at 160—170° for 5 hr. The mixture was then filtered and the filtrate made alkaline with sodium hydroxide solution. The sodium salt of the sulphonic acid was precipitated and filtered off. The salt (5 g.) was treated with sodium hydroxide (20 g.) and water (2 c.c.) at 250°. The temperature was raised to 315° during 5 min. and after this temperature had been maintained for several minutes the mixture was added to cold water.

[1] Halsall and Thomas, *J.*, 1956, 2431.
[2] Shreve and Lux, *Ind. Eng. Chem.*, 1943, **35**, 306.
[3] Mitter and De, *J. Indian Chem. Soc.*, 1939, **16**, 199.
[4] Dziewoński, Schoeńowna, and Waldmann, *Ber.*, 1925, **58**, 1211.

Hydrochloric acid then precipitated a naphthol which crystallised as plates, m. p. 105·5—107° (after several recrystallisations from aqueous methanol), depressed on admixture with 7-methyl-2-naphthol.

The authors thank the Department of Scientific and Industrial Research for a maintenance grant to one of them (D. B. T.), and Mr. E. S. Morton for the microanalyses.

THE UNIVERSITY, MANCHESTER, 13. [*Received, February 6th*, 1956.]

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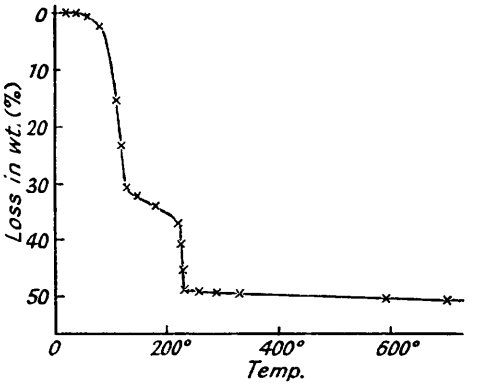
503. *The Preparation and Properties of Some Plutonium Compounds. Part IV.* Crystalline Plutonium Nitrate.*

By J. L. DRUMMOND and G. A. WELCH.

CUNNINGHAM [1] reported that a gummy semicrystalline solid phase is formed when a concentrated solution of quadrivalent plutonium in 1—4M-nitric acid is evaporated, and that neither the anhydrous nitrate nor a hydrate of definite composition is known. Double salts, of the type $M_2Pu(NO_3)_6$ with ammonium or an alkali metal, can be prepared from mixtures of the respective nitrate solutions in the correct proportions.



Thermogravimetric curve for plutonium nitrate crystals.

We have found that a concentrated solution of plutonium tetranitrate in nitric acid will deposit well-formed crystals when it is allowed to evaporate at room temperature over a period of months. When crystal nuclei have formed or have been added, the rate of crystallisation can be increased by evaporating the solution in a current of air.

Chemical and spectrographic analysis has shown that plutonium is the only cation and that nitrate is the only anion present in the crystals. The crystals are not, therefore, related to the double salts referred to above, and were found to be *plutonium tetranitrate pentahydrate*. Plutonium was determined by ignition to oxide at 870°, nitrate by ammonia distillation, and water by Karl Fischer titration corrected for the reduction of the plutonium [Found: Pu, 41·5; NO_3^-, 42·9; H_2O, 15·0. $Pu(NO_3)_4,5H_2O$ requires Pu, 41·4; NO_3^-, 43·0; H_2O, 15·6%].

The small crystals are green but those larger than 1 mm. are shiny black prisms. They give a well-defined but complex *X*-ray diffraction powder photograph of a form which has not yet been identified. The crystals are fairly stable at room temperature, although after some months slight efflorescence was apparent; samples exposed to air dried by silica gel, or to air at normal laboratory humidity, showed less than 0·05% change in weight after 3 days. They are readily soluble in water; a dilute solution is brown, rapidly changing to green as colloidal plutonium is formed.[2] The concentrated aqueous solution remains brown, as the colloid is not formed in solutions of high nitrate-ion concentration. The

* Part III, *J.*, 1956, 781.

[1] Cunningham, "The Actinide Elements," McGraw-Hill Book Co. Inc., New York, 1954, p. 412.
[2] Ockenden and Welch, unpublished work.

crystals form a green solution with concentrated nitric acid, this colour being due to the nitrate complex of plutonium. The solutions in acetone and ether are also green.

The effect of heat on the crystals was studied by using a silica-spiral thermobalance.[3] The sample began to lose weight at 40°, to decompose visibly at 60°, and to melt, or dissolve in the water of crystallisation, at 95—100°. The decomposition became rapid at 100°, and a rather unstable intermediate product was formed between 150° and 220°. At the latter temperature, decomposition was again rapid, and the final product was oxide (see the Figure).

Preparation of the intermediate decomposition product was attempted but no reproducible compound was obtained. A grey-green solid formed at 150—180°, containing 59—64% of plutonium with 1·7—1·4 equivalents of nitrate per mole. It was hygroscopic and became fawn on exposure to moist air. It dissolved completely in water, and the absorption spectrum of the solution was identical with that of plutonyl nitrate, $PuO_2(NO_3)_2$, reported by Hindman.[4] On addition to 5M-nitric acid, it formed a solution of plutonyl nitrate, together with a precipitate of hydrated oxide. This intermediate decomposition product is believed to be a basic plutonyl nitrate.

The possibility of using the plutonium tetranitrate crystals as an analytical standard compound is being considered.

Acknowledgment is made to the Managing Director of this Group of the U.K. Atomic Energy Authority for permission to publish this note.

U.K. Atomic Energy Authority (Industrial Group),
Windscale Works, Cumberland. [*Received, February 29th,* 1956.]

[3] Brown, Ockenden, and Welch, *J.*, 1955, 3932.
[4] Hindman, ref. 1, p. 359.

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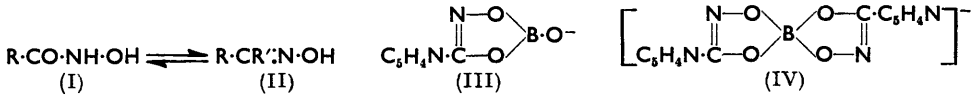
504. *The Formation of Borate Complexes by Hydroxamic Acids.*

By A. L. Green.

Boric acid combines with many 1 : 2-dihydroxy-compounds in aqueous solution to form dissociable cyclic complexes.[1] Although hydroxamic acids (I ⇌ II; R′ = OH) exist predominantly in the hydroxamic form (I),[2] the hydroximic tautomer (II; R′ = OH) possesses two adjacent hydroxyl groups potentially capable of forming cyclic complexes with boric acid. Such complex formation in aqueous solution has now been demonstrated both spectroscopically and titrimetrically.

The Figure shows the ultraviolet spectra of *iso*nicotinhydroxamic acid (I; R = 4-pyridyl) and 4-hydroxyiminopyridine (II; R = 4-pyridyl, R′ = H) in water, in aqueous borax (0·05M), and in aqueous sodium hydroxide (10^{-3}M) in which both compounds are effectively 100% ionised. The absorption spectrum of *iso*nicotinhydroxamic acid in borate buffer differs markedly from those of both the neutral compound and the anion, but it does

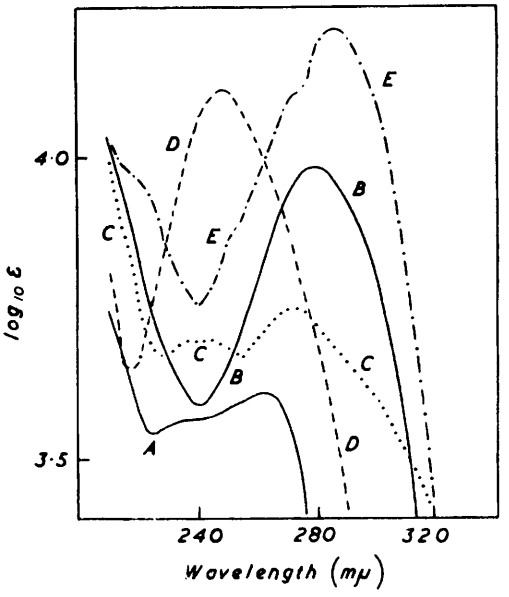


resemble that of 4-hydroxyiminopyridine. The spectrum of *iso*nicotinhydroxamic acid in phosphate buffer at the same pH as that of the borate (9·2) is not shown but is almost identical with that in dilute alkali. This change in the spectrum in the presence of sodium borate is attributed to the formation of a cyclic complex (III).

The formation of a 1 : 1 boric acid–hydroxamic acid complex can be confirmed by

[1] Reviewed by Boeseken, *Adv. Carbohydrate Chem.*, 1949, **4**, 189.
[2] Mathis, *Compt. rend.*, 1951, **232**, 505.

potentiometric titration with sodium hydroxide. The pK_a's of *iso*nicotinhydroxamic acid and boric acid in water are 7·9 and 9·2 respectively, whereas an equimolar (0·005M-)solution of the two acids behaves as a monobasic acid with pK_a 7·4. A second indefinite buffering region, found around pH 10, is possibly due to instability of the complex in more alkaline solution. An aqueous solution of *iso*nicotinhydroxamic acid containing one-third mol. of



iso*Nicotinhydroxamic acid in* (*A*) *water*, (*B*) *aqueous borax*, *and* (*C*) *aqueous sodium hydroxide. 4-Hydroxyiminopyridine in* (*D*) *water and* (*E*) *aqueous sodium hydroxide.*

boric acid gave a potentiometric titration curve consistent with a mixture of the 1 : 1 complex and free hydroxamic acid. There is no evidence under these conditions for a 2 : 1 complex (IV) similar to that demonstrated titrimetrically by Schafer [3] between boric acid and catechol.

Experimental.—*iso*Nicotinhydroxamic acid, m. p. 151—153° (from water) (Found : N, 20·1. Calc. for $C_6H_6O_2N_2$: N, 20·3%), was prepared from ethyl *iso*nicotinate and hydroxylamine in methanolic potassium hydroxide.[4] 4-Hydroxyiminopyridine,[5] m. p. 130° (from water) (Found : N, 22·8. Calc. for $C_6H_6ON_2$: N, 22·9%), was obtained by addition of 4-formylpyridine to hydroxylamine hydrochloride in aqueous sodium hydrogen carbonate.

The ultraviolet spectra were measured at 5 mμ intervals on a Unicam S.P. 600 Spectrophotometer.

Titration experiments. Aqueous solutions of boric acid, *iso*nicotinhydroxamic acid, or mixtures of the two (0·005—0·01M) in a beaker, kept at 25° by a water jacket, were titrated with 0·1M-sodium hydroxide. The beaker was equipped with a magnetic stirrer and contained glass and calomel electrodes connected to an E.I.L. Model 23 pH meter. The pK_a values were calculated by the Henderson–Hasselbach equation from pH's around the half-neutralisation points.

CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT,
PORTON, WILTS.

[*Received, March 6th*, 1956.]

[3] Schafer, *Z. anorg. Chem.*, 1942, **250**, 127.
[4] Sorkin, Roth, and Erlenmeyer, *Helv. Chim. Acta*, 1952, **35**, 1736.
[5] Grammaticakis, *Bull. Soc. chim. France*, 1956, 109.