

456. *The Retardation of Benzaldehyde Autoxidation. Part IV.* Isolation of Chain-termination Products from 3 : 5 : 3' : 5'-tetramethyl-4 : 4'-diphenoquinone.*

By R. F. MOORE and WILLIAM A. WATERS.

A KINETIC study (Part III *) indicated that when 3 : 5 : 3' : 5'-tetramethyl-4 : 4'-diphenoquinone is used as a retarder of the benzoyl peroxide-catalysed autoxidation of benzaldehyde it acts by combining with the free benzoyl radical, $C_6H_5\cdot CO\cdot$, probably to form 4 : 4'-dibenzoyloxy-3 : 5 : 3' : 5'-tetramethyldiphenyl. However, the true location of the added benzoyl group cannot be deduced by kinetic methods and the direct isolation of the chain-ending product was therefore undertaken. The dibenzoate has in fact been isolated but, as pure product, in the yield of 5% only. There was also produced a considerable quantity of a yellowish amorphous powder of indefinite m. p. (140—190°) which could not be purified. It would seem therefore that the kinetic analysis of this retarded autoxidation leads to a representation which very much simplifies the organic chemistry of the whole processes, and it may be recalled that a similar impression of the validity of kinetic study alone has previously been reached from studies of the retardation of benzaldehyde autoxidation by phenols (compare Parts I and II, *J.*, 1951, 812; 1952, 2420).

Experimental.—3 : 5 : 3' : 5'-Tetramethyl-4 : 4'-diphenoquinone. For the preparation of adequate quantities the following amplification of Auwers and Markovits's method (*Ber.*, 1905, **38**, 226) was used. Chromic oxide (20 g.), dissolved in the minimum of hot water, was diluted to 200 c.c. with glacial acetic acid and added dropwise with stirring during 2 hours to a solution of *m*-2-xylene (20 g.) in the same solvent (100 c.c.). Precipitation of the quinone commenced immediately. The reaction mixture was then warmed to 80° for 1 hour and kept overnight. The red precipitate was then collected, washed with glacial acetic acid, and crystallised from a dilute solution (1 g. in 75 c.c.) in this solvent, forming dark red needles (50%), m. p. 210—215° (decomp.).

4 : 4'-Dibenzoyloxy-3 : 5 : 3' : 5'-tetramethyldiphenyl. The quinone was reduced to the dihydroxydiphenyl by zinc dust in hot acetic acid, as described by Auwers and Markovits, and was crystallised from glacial acetic acid to which had been added a small quantity of a solution of stannous chloride in hydrochloric acid, so as to prevent atmospheric re-oxidation. It formed colourless needles, m. p. 221°. This product was benzoylated by use of benzoyl chloride in pyridine solution, giving the *dibenzoate*, which crystallised from glacial acetic acid in colourless prisms, m. p. 218° (Found : C, 80.1; H, 5.7. $C_{30}H_{26}O_4$ requires C, 80.0; H, 5.8%).

Isolation of products from the retarded benzaldehyde autoxidation. A solution of the quinone (8.7 g.) and benzoyl peroxide (9 g., 1 equiv.) in benzaldehyde (500 c.c.) at 80° was oxidised, under a reflux condenser, with a stream of dry air. After 18 hours the peroxide had all reacted and the solution was pale yellow. Benzaldehyde was then removed under reduced pressure, and the residue, in ether, was repeatedly extracted with 10% sodium hydrogen carbonate solution to remove benzoic acid and then with ice-cold 5% sodium hydroxide solution, which however, removed only a trace of tar. The residue, after drying and evaporation at 100° under reduced pressure, was a dark yellow gum (19.4 g.). In portions this was chromatographed on Brockmann alumina, fractions being eluted with graded light petroleum-benzene mixtures. The first eluates on evaporation yielded a white crystalline solid (0.4 g., from 10 g. of gum), m. p. 195—215°, which after twice recrystallising from glacial acetic acid separated in colourless needles, m. p. 217—218° unchanged after admixture with the above dibenzoate (Found : C, 79.9; H, 5.8%). Further fractions from the column yielded pale yellow amorphous powders which melted over the range 140—190° and separated unchanged as such after dissolving in either methyl alcohol or light petroleum. Separation could not be effected by further chromatography on alumina.

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* Part III, preceding paper.

457. Reaction of Propiolactone with Indoles and Pyrrole.

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REACTION of propiolactone with indole has been shown to give β -3-indolylpropionic acid (Harley-Mason, *Chem. and Ind.*, 1951, 886). The reaction has now been extended to some substituted indoles and to pyrrole. 2-Methyl-, 1-methyl-2-phenyl-, and 5-acetoxy-2-methyl-indole all gave the corresponding propionic acids. 2:3-Disubstituted indoles do not give the Ehrlich colour reaction, and the failure of the three products to give the reaction indicates that the propionic acid residue has entered the 3-position. Under similar conditions, 3-methyl- and 2:3-dimethyl-indole reacted with propiolactone to give acidic products which could not be purified. Pyrrole reacted readily to give a pyrrolylpropionic acid, m. p. 85—86°, differing from the β -1-pyrrolylpropionic acid, m. p. 62°, of Clemo and Ramage (*J.*, 1931, 49). It was therefore very probably β -2-pyrrolylpropionic acid since substitution in the pyrrole nucleus occurs normally in the 2- rather than in the 3-position.

Experimental.— β -2-Methyl-3-indolylpropionic acid. 2-Methylindole (1.3 g.) and propiolactone (0.9 g.) were heated at 110° for 3 hours and then cooled. Ether (50 c.c.) was added with vigorous stirring and shaking. After 2 hours some amorphous material was filtered off and the filtrate extracted with aqueous sodium carbonate (10%; 3 \times 30 c.c.). The aqueous solution was acidified and the precipitated acid collected and recrystallised from water (charcoal). β -2-Methyl-3-indolylpropionic acid formed white needles, m. p. 138° (Found: C, 70.8; H, 6.5. $C_{12}H_{13}O_2N$ requires C, 71.0; H, 6.4%).

β -5-Hydroxy-2-methyl-3-indolylpropionic acid. 5-Hydroxy-2-methylindole (Nenitzescu, *Bull. Soc. chim. Roumania*, 1929, 11, 37) was dissolved in a mixture of acetic anhydride (8 c.c.) and pyridine (8 c.c.). Next day the mixture was poured into ice-water, and the precipitated acetyl derivative collected and dried. The acetyl derivative (1.9 g.) and propiolactone (0.9 g.) were heated for 3 hours at 110°, and then treated with sodium carbonate as above. On acidification, a gummy precipitate was obtained. This was hydrolysed by boiling 5% sodium hydroxide solution (30 c.c.) under nitrogen, and the solution then acidified and extracted with ether. Removal of the ether left β -5-hydroxy-2-methyl-3-indolylpropionic acid which formed small prisms (from benzene-light petroleum), m. p. 182—183° (Found: C, 66.3; H, 6.2. $C_{12}H_{13}O_3N$ requires C, 65.8; H, 6.0%).

β -1-Methyl-2-phenyl-3-indolylpropionic acid. 1-Methyl-2-phenylindole (2 g.) and propiolactone (0.9 g.) were heated at 120° for 6 hours. After cooling the mass was ground and extracted with 2% aqueous sodium hydroxide (100 c.c.). Unchanged starting material was filtered off and the filtrate acidified, giving a sticky precipitate. Two recrystallisations from aqueous ethanol (charcoal) gave β -1-methyl-2-phenyl-3-indolylpropionic acid as colourless prisms, m. p. 114—116° (Found: C, 77.3; H, 6.3. $C_{18}H_{17}O_2N$ requires C, 77.7; H, 6.1%).

β -2-Pyrrolylpropionic acid. Pyrrole (1 g.) and propiolactone (1 g.) were heated for 2 hours at 100°. After cooling the deep red viscous melt was extracted with ether (50 c.c.) with vigorous shaking, and the solution decanted from insoluble gum, then extracted with aqueous sodium carbonate (10%; 3 \times 20 c.c.). The aqueous solution was carefully acidified with acetic acid, (not excess), and then extracted with ether. After drying (Na_2SO_4), removal of the ether left β -2-pyrrolylpropionic acid which formed small plates, m. p. 85—86°, from benzene-light petroleum (Found: C, 60.6; H, 6.5. $C_7H_9O_2N$ requires C, 60.5; H, 6.5%).

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458. The Analysis of Pyridine Bases from Coal Tar by Infra-red Absorption Spectroscopy.

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THE infra-red absorption spectra of the better-known pyridine homologues have been determined at the Chemical Research Laboratory, Teddington, and elsewhere, but no account of the use of these data for the analysis of mixtures of pyridine bases has been published. Infra-red spectroscopy has now been applied to the quantitative analysis of the pyridine, α -picoline, and a higher-boiling fraction obtained commercially from coal tar. No precise information was available on the composition of these products, and it

was found that the pyridine contained 1% of α -picoline, that the α -picoline contained 2.6% of pyridine and 0.2% of pyrrole, and that the higher-boiling fraction was a mixture of all three picolines and 2:6-lutidine.

Table 1 gives a list of the bases expected to be present in these fractions, together with the infra-red absorption bands selected for analysis. The observed wave-lengths of the bands do not agree exactly with previously published values.

TABLE 1. *Bands used for analysis (wave-length in microns).*

Base	Bands used		
Pyridine	14.25	Solution in α -picoline	This work
	14.25	Liquid	C.R.L. No. 7
α -Picoline	9.55	Liquid	This work
	9.55	Liquid	C.R.L. No. 11
	9.49	Liquid	A.P.I. No. 743
	13.34	Solution in paraffin	This work
	13.32	Liquid	C.R.L. No. 11
β -Picoline	13.24	Liquid	A.P.I. No. 743
	12.76	Solution in paraffin	This work
γ -Picoline	12.69	Liquid	C.R.L. No. 10
	12.56	Solution in paraffin	This work
2:6-Lutidine	12.52	Liquid	C.R.L. No. 9
	12.95	Solution in paraffin	This work
Pyrrole	12.90	Liquid	C.R.L. No. 8
	9.85	Solution in CS ₂	This work
	9.83	Liquid	Lord and Miller, <i>J. Chem. Phys.</i> , 1942, 10 , 328
	9.82	Liquid	Randall, Fowler, Fuson, and Dangel, "Infra-red Determination of Organic Structures," 1949

C.R.L. = Chemical Research Laboratory Spectrogram.

A.P.I. = American Petroleum Institute Spectrogram.

Table 2 shows the measured specific extinction coefficients used for the analysis. These have been calculated by assuming that the nominal cell thickness (0.05 mm.) was correct. The spectral slit width varied with wave-length from 10 to 20 cm.⁻¹. All the bases investigated gave linear Beer-Lambert law plots, passing through the origin.

TABLE 2. *Specific extinction coefficients, $E_{1\text{cm.}}^{1\%}$ (w/w).*

Wave-length in microns	9.55	9.85	12.56	12.76	12.95	13.34	14.25
α -Picoline in pyridine	2.4	—	—	—	—	—	—
Pyridine in α -picoline	—	—	—	—	—	—	35.0
Pyrrole in α -picoline	—	7.4	—	—	—	—	—
α -Picoline in white spirit	—	—	0.15	0.05	0.25	19.2	—
β -Picoline ,, ,,	—	—	1.25	9.5	0.95	0.2	—
γ -Picoline ,, ,,	—	—	15.1	1.4	0.55	0.2	—
2:6-Lutidine,, ,,	—	—	0.25	0.75	16.4	0.55	—

Experimental.—The bases used for calibration were purified from the best available starting materials. Pyridine was dried (NaOH) and purified by fractionation through a 100-plate column. α -Picoline as the oxalate was recrystallised from alcohol; the liberated base was dried (KOH) and fractionated through a 50-plate column. β -Picoline, γ -picoline, and 2:6-lutidine were distilled and purified by fractional freezing (recommended by Dr. Herington of the Chemical Research Laboratory) followed by fractionation through a 100-plate column. Pyrrole was distilled shortly before use. No special precautions were taken to keep the bases dry.

Commercial pyridine. A spectrogram of commercial pyridine showed no bands due to impurities, but both α -picoline and pyrrole were expected in small amounts.

Absorption measurements at 9.55 μ showed 1.0 \pm 0.2% of α -picoline. Pyrrole also absorbs strongly at 9.55 μ . However, its boiling point is much closer to that of α -picoline than to that of pyridine, and, since there was so little pyrrole in the α -picoline (see below), it is unlikely that there was any appreciable amount in the pyridine. The pyrrole band at 9.85 μ is not sufficiently sensitive for estimation in pyridine.

Commercial α -picoline. A spectrogram of commercial α -picoline showed a pyridine band at 14.25 μ , but no others. Absorption measurements showed 2.6 \pm 0.1% of pyridine. Pyrrole was expected because of the similarity of the boiling points, but absorption measurements showed only 0.2 \pm 0.15%.

Tests with known additions to α -picoline showed that the limits of detection in a 0.075-mm.

cell were: 0.1% of γ -picoline; 1% of β -picoline, though 0.1% could have been detected at 14.1μ in the absence of pyridines; and 0.8% of 2 : 6-lutidine, a 10% solution in carbon disulphide being used. There was no evidence of any of these in commercial α -picoline.

Higher-boiling fraction. A spectrogram of the higher-boiling fraction showed this to be a mixture of all three picolines and 2 : 6-lutidine.

Extinction coefficients were determined for each of these constituents at each of four selected wave-lengths, solutions in paraffin of boiling range $150\text{--}160^\circ$ being used. This solvent has no absorption bands at the wave-lengths used, and was obtained by stirring commercial white spirit twice with concentrated sulphuric acid, and washing and fractionating the residue.

Analysis then involved the determination of $\log I_0/I$ at the four wave-lengths, a 10% solution of the fraction being used. The solution of the four simultaneous equations can most easily be achieved by successive approximations, starting with the concentrations obtained by ignoring all but the strongest absorbing constituent at each wave-length.

Results for two known mixtures and the higher-boiling fraction are shown in Table 3.

TABLE 3.

Known mixtures :	Composition, % wt./wt.				Total
	α -Picoline	β -Picoline	γ -Picoline	2 : 6-Lutidine	
(1) Actual composition	27.2	33.8	18.4	20.6	100.0
Composition found	26.5	33.1	18.2	21.1	98.9
Error	-0.7	-0.7	-0.2	-0.5	—
(2) Actual composition	18.0	25.5	23.0	33.5	100.0
Composition found	17.2	23.9	21.2	34.2	96.5
Error	-0.8	+1.6	-1.8	+0.7	—
Higher-boiling fraction	13.1	34.1	24.9	25.4	97.5
Duplicate	14.1	34.7	24.7	24.1	97.6
Average	13.6 ± 1	34.4 ± 1.5	24.8 ± 1	24.8 ± 1.5	97.6

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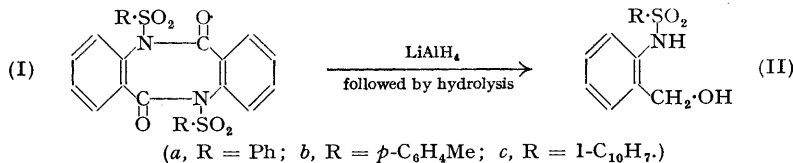
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459. Action of Lithium Aluminium Hydride on (a) *NN'*-Diarylsulphonyl Derivatives of Dianthranilide, and (b) Photo-peroxides of 9 : 10-Diaryl-anthracene.

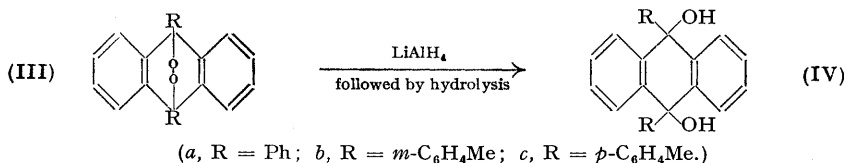
By AHMED MUSTAFA.

WHEN benzene solutions of *NN'*-diarylsulphonyl derivatives (Ia—c) of dianthranilide are treated with excess of lithium aluminium hydride, the corresponding *o*-arylsulphonamidobenzyl alcohols (IIa—c) are obtained in an almost quantitative yield. The structures of these products follow from the identity of (IIa) with a specimen obtained by the action of lithium aluminium hydride on *o*-phenylsulphonamidobenzoic acid (cf. the formation of *o*-aminobenzyl alcohol by the action of lithium aluminium hydride on anthranilic acid; Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197, 2548). The products are colourless, soluble in aqueous sodium hydroxide whence they are regenerated by dilute hydrochloric acid (cf. Mustafa and Gad, *J.*, 1949, 384), contain active hydrogen, and give the expected molecular weights.



The action of lithium aluminium hydride on the photo-peroxides (IIIa—c) of 9 : 10-diarylanthracene, in ether-benzene, yields (IVa—c) respectively in an almost quantitative yield. In an analogous way, the action of lithium aluminium hydride on triphenylmethyl peroxide leads to triphenylmethanol [cf. the reduction of 5 : 6 : 7 : 8-tetrahydro-1-naphthyl

hydroperoxide with lithium aluminium hydride to 5:6:7:8-tetrahydro-1-naphthol (Sutton, *Chem. and Ind.*, 1951, 272)].



The action of lithium aluminium hydride on (I) is an example of the cleavage of the -C-N- linkage by this reagent [cf. the similar cleavage of diethylbenzamide (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738) and of cyclic lactams (Galimovsky and Weiser, *Experientia*, 1950, **6**, 377)] and its action on (III) is an example of the cleavage of the -O-O- linkage.

There is a formal analogy between the action of lithium aluminium hydride and the action of Grignard reagents on (I) and (III) (cf. Mustafa and Gad, *loc. cit.*; Mustafa, *J.*, 1949, 1662).

Experimental.—Action of lithium aluminium hydride on NN'-diarylsulphonyl derivatives (I) of dianthranilide. The action of lithium aluminium hydride on NN'-dibenzene- (Ia) (Heller, *Ber.*, 1916, **49**, 547), NN'-ditoluene-*p*- (Ib) (Schroeter, *Annalen*, 1909, **367**, 104), and NN'-dinaphthalene- α -sulphonyl-dianthranilide (Ic) (see below) was carried out in solvents dried over sodium. To pulverised lithium aluminium hydride (0.7 g.) (from New Metals and Chemicals Ltd., London) was added ether (50 c.c.). After 15 minutes, the NN'-diarylsulphonyl derivative (1 g.) in benzene (30 c.c.) was added in portions. The reaction mixture was refluxed for 3 hours and then set aside overnight at room temperature. After treatment with cold aqueous ammonium chloride solution, the ethereal solution was dried and evaporated; the reaction products were recrystallised from benzene and are reported in Table I.

Preparation of NN'-dinaphthalene- α -sulphonyldianthranilide (Ic). This was prepared as described for the β -derivative (Schroeter, *loc. cit.*).

o-Naphthalene- α -sulphonamidobenzoic acid. This acid is prepared by the action of naphthalene- α -sulphonyl chloride (25 g.) on a boiling solution of anthranilic acid (12.5 g.) in aqueous sodium hydroxide (8% ; 65 g.). It forms colourless crystals, m. p. 226—227°, from dilute ethyl alcohol (Found: C, 62.1; H, 4.0; N, 4.3; S, 9.4. C₁₇H₁₃O₄NS requires C, 62.4; H, 4.0; N, 4.3; S, 9.8%). The yield is almost quantitative. It is easily soluble in hot benzene or xylene, but difficultly soluble in light petroleum (b. p. 40—60°).

o-Naphthalene- α -sulphonamidobenzoyl chloride. The above acid (9 g.), phosphorus pentachloride (6 g.), and benzene (30 c.c.) were heated until the solution became clear (ca. 3 hours). The solid chloride, that separated on cooling, crystallised from benzene as colourless crystals (ca. 60%), m. p. 168° (Found: C, 58.9; H, 3.5; N, 4.1; S, 8.8; Cl, 9.8. C₁₇H₁₂O₃NSCl requires C, 59.0; H, 3.5; N, 4.1; S, 9.2; Cl, 10.2%).

NN'-Dinaphthalene- α -sulphonyldianthranilide (Ic). The acid chloride is boiled with an equal quantity of dry pyridine until the solution became clear. The reaction mixture, on cooling, followed by treatment with a large excess of cold ethyl alcohol, gave colourless crystals; recrystallised from benzene, the disulphonamide had m. p. 248° (Found: C, 66.0; H, 3.6; N, 4.4; S, 10.4%; *M*, 605. C₃₄H₂₂O₆N₂S₂ requires C, 66.0; H, 3.6; N, 4.5; S, 10.4%; *M*, 618). The yield is ca. 65%. (Ic) is soluble in hot benzene or xylene, but difficultly soluble in alcohol. The product (1.5 g.), when refluxed with freshly distilled aniline (20 c.c.) for 3 hours, gave colourless crystals (from benzene) of *o-naphthalene- α -sulphonamidobenzanilide* (ca. 75%), m. p. 156° (cf. Mustafa and Gad, *loc. cit.*) (Found: C, 68.3; H, 4.6; N, 6.9. C₂₃H₁₈O₃N₂S requires C, 68.6; H, 4.5; N, 6.9%).

TABLE I. Substituted *o*-arylsulphonamidobenzyl alcohols (II).

Aryl	M. p.	Yield, %	Formula	Found, % :				Required, % :			
				C	H	N	S	C	H	N	S
Ph	128°	87	C ₁₃ H ₁₃ O ₃ NS ^a	59.2	4.7	5.0	12.1	59.3	4.9	5.3	12.2
<i>o</i> -C ₆ H ₄ Me	150	93	C ₁₄ H ₁₅ O ₃ NS ^b	60.4	5.3	5.0	11.5	60.7	5.4	5.0	11.6
1-C ₁₀ H ₇	108	91	C ₁₇ H ₁₅ O ₃ NS ^c	65.0	4.7	4.4	9.9	65.2	4.8	4.4	10.2

^a Found: Active H, 0.74%; *M*, 258. Req'd.: Active H, 0.76%; *M*, 263. ^b Found: *M*, 269. Req'd.: *M*, 277. ^c Found: *M*, 302. Req'd.: *M*, 313.

Action of lithium aluminium hydride on o-arylsulphonamidobenzoic acids. For comparison, (IIa—c) were prepared by the action of lithium aluminium hydride on *o*-benzene-, *o*-toluene-*p'*-, (Schroeter, *loc. cit.*; Ullmann, Bleier, *Ber.*, 1902, 35, 4274 respectively), and 2-naphthalene- α -sulphonamidobenzoic acids (see above) as described above, *viz.*: *o*-benzenesulphonamidobenzyl alcohol (IIa) (Found: C, 59.1; H, 5.2; N, 5.1; S, 11.9%) (yield, *ca.* 85%); *o*-toluene-*p'*-sulphonamidobenzyl alcohol (IIb) (Found: C, 60.5; H, 5.5; N, 5.1; S, 11.4%); (yield *ca.* 81%); 2-naphthalene- α -sulphonamidobenzyl alcohol (IIc) (Found: C, 65.1; H, 4.8; N, 4.3; S, 10.1%). Identity was proved by m. p. and mixed m. p.

TABLE 2. 9 : 10-Diaryl-9 : 10-dihydro-9 : 10-dihydroxyanthracenes (IV).

Aryl	M. p.	Yield, %	Formula	Found, % :		Required, % :	
				C	H	C	H
Ph	255—256°	85	C ₂₆ H ₂₀ O ₂	85.5	5.3	85.5	5.3
<i>m</i> -C ₆ H ₄ Me	247	83	C ₂₈ H ₂₄ O ₂	85.5	6.1	85.7	6.1
<i>p</i> -C ₆ H ₄ Me	273	87	C ₂₈ H ₂₄ O ₂	85.7	5.9	85.7	6.1

Action of lithium aluminium hydride on 9 : 10-diarylanthracene photo-peroxides (IIIa—c). The action of lithium aluminium hydride on 9 : 10-diphenyl- (IIIa) (Pinnazi, *Compt. rend.*, 1947, 225), 9 : 10-di-*m*-tolyl- (Willemart, *Bull. Soc. chim.*, 1937, 4, 510) (IIIb), and 9 : 10-di-*p*-tolyl-anthracene photo-peroxide (IIIc) (Willemart, *loc. cit.*) was carried out as described above. The 9 : 10-diaryl-9 : 10-dihydro-9 : 10-dihydroxyanthracenes (IVa—c) are identified by m. p. and mixed m. p. and colour reactions with sulphuric acid and are reported in Table 2.

In an analogous way, triphenylmethyl peroxide afforded triphenylmethanol, in an almost quantitative yield, having m. p. 162° (from carbon tetrachloride) (identified by mixed m. p. and colour reaction with sulphuric acid) (Found: C, 87.5; H, 5.9. Calc. for C₁₉H₁₆O : C, 87.7; H, 6.1%).

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460. 3-Nitro-*o*-cresol.

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Two methods for obtaining 3-nitro-*o*-cresol* have been described; Gibson (*J.*, 1925, 127, 44) isolated it from the mixture of mono- and di-nitro-compounds formed in the nitration of *o*-cresol, whilst Deninger (*J. prakt. Chem.*, 1889, 40, 299) and Astle and Cropper (*J. Amer. Chem. Soc.*, 1943, 65, 2395) prepared the compound from *o*-toluidine.

Deninger's and Astle and Cropper's method consisted in treating *o*-toluidine in sulphuric acid with nitrous acid, heating the resulting solution and adding to it more sulphuric acid, and finally isolating the product by steam-distillation. We found that the material so obtained was a mixture of at least two substances. It was, therefore, fractionally steam-distilled; the desired nitrocresol was present in the very early runnings. However, unless large amounts of a mixture of 3-nitro-*o*-cresol and a higher-melting impurity were rejected, subsequent crystallisation was not sufficient to purify the product. The steam-distillation was therefore carried on so long as 3-nitro-*o*-cresol was judged to be present, and the material was then purified by vacuum-distillation. A second component isolated from the distillation was 3 : 5-dinitro-*o*-cresol,* which neither Deninger nor Astle and Cropper (*loc. cit.*) reported.

In a number of large-scale experiments the effect of varying the conditions was studied. The temperature of the actual diazotisation seemed to be relatively unimportant. On the other hand, the temperature of decomposition of the diazonium salt solution was particularly important; it should be at least 70° (65° was indicated by Deninger), and in order to achieve the necessarily rapid decomposition it was essential to have the 50% sulphuric acid initially well above 70°. The quantity of sulphuric acid used for the decomposition appeared to bear a clear relation to the proportions of the two components obtained on steam-distillation; when a large excess was used, mono- and di-nitro-compounds were obtained in about equal amounts, whilst the minimum of sulphuric acid gave an approximate ratio of 5 : 1 in favour of 3-nitro-*o*-cresol. Deninger and Astle and Cropper (*loc. cit.*) added sulphuric acid to the heated diazonium solution; our first

* Me = 1.

experiments were carried out similarly and indicated the formation of mixtures. Later we found it more convenient to carry out the decomposition in the opposite sense. Whilst this reversal may have affected the amount of each product formed, both modes of decomposition provided mixtures. Like Deniger we noticed the formation of nitric oxide during the reaction.

Experimental.—An experiment with *o*-toluidine (10 g.) was carried out roughly as indicated by Astle and Cropper (*loc. cit.*). Diazotisation (with 30% aqueous sodium nitrite) was effected at 5–10°, and the resulting solution was added to sulphuric acid (50%; 250 c.c.) so that the temperature was never greater than 70°. More sulphuric acid (50%; 300 c.c.) was added, and when effervescence slackened the mixture was steam-distilled, the distillate being collected in 250 c.c. fractions. The first fraction gave a product which formed yellow needles (2.8 g.), m. p. 48–50°, after crystallisation from ligroin (b. p. 80–100°). Each of the next six fractions similarly gave almost colourless feathery needles (4.96 g. in all) m. p. in the range 84–87°.

The table records the results of a series of experiments, each of which was conducted as follows. *o*-Toluidine was dissolved in dilute sulphuric acid and diazotised by the addition of ca. 50% aqueous sodium nitrite, with stirring. The resulting solution was poured as rapidly as gas evolution permitted into sulphuric acid (50% vol./vol.), initially at 140°, the temperature during the decomposition being kept above 70° throughout (negligible yields resulted at decomposition temperatures below 70°). The black tarry liquid was then steam-distilled, the distillate was chilled, and the product collected. The yellow solid so obtained was dried (*in vacuo*) and distilled under reduced pressure, the fraction, b. p. 99–104°/7–8 mm. being collected. The reaction liquid remaining from the steam-distillation contained black tarry material which dissolved in alkali to a deep yellow solution.

Distillation of residues after removal of 3-nitro-*o*-cresol gave finally a fraction, b. p. 169–172°/6–8 mm. Recrystallisation of this from benzene–ligroin (b. p. 60–80°) provided almost

<i>o</i> -Toluidine, g.	Amine dissolved in		Sodium nitrite, g.	Moles ^a	Temp. of diazn. (° c.)	50% H ₂ SO ₄ used in decomp., l.	Crude product, g.	Pure product, ^b g.	Yield, %
	H ₂ SO ₄ , l.	water, l.							
100	0.2	0.8	300	4.6	0–5	2	31.9	18.6	14
107	"	"	220	3.2	0–10	1.2	32	20.1	"
214	0.4	1.2	552	4	5–8	1.5	81	63.0	21
"	"	"	"	"	10–15	2.5	56	43.0	14.5
"	"	"	690	5	15–20	2	79 ^c	57.0	19
"	"	"	"	"	10–15	2.5	95 ^c	72.0	24

^a Deniger (*loc. cit.*) mentioned the use of 3 moles but described the use of 4 moles, and Astle and Cropper (*loc. cit.*) used 4.65 moles. ^b Bright yellow crystals, b. p. 99–104°/8 mm., m. p. 68–70°. ^c In the steam-distillation 2–3 l. of distillate were collected.

colourless, feathery needles, m. p. 86–86.5°, of 3 : 5-dinitro-*o*-cresol (Found : C, 43.2; H, 3.3. Calc. for C₇H₆O₅N₂ : C, 42.45; H, 3.1%). Early workers (see "Beilstein," 4th edn.) stated that this compound was yellow, but Gibson (*loc. cit.*) described it as "colourless prisms."

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461. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part X.* The Titration of Small Amounts of Gallium.*

By R. BELCHER, A. J. NUTTEN, and W. I. STEPHEN.

GALLIUM has been determined by titration with ferrocyanide (Kirschman and Ramsey, *J. Amer. Chem. Soc.*, 1928, **50**, 1632; Ato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, **10**, 1). Standard potassium ferrocyanide solution containing a small amount of potassium ferricyanide is added to a weakly acidic solution (ca. 0.005N) of gallium trichloride and the end-point detected electrometrically. The ratio of gallium to ferrocyanide in the precipitated salt is 1.333, corresponding to the formula Ga₄[Fe(CN)₆]₃. Hence, gallium ferrocyanide is a normal salt, whereas the ferrocyanides of zinc, cadmium, calcium, and

* Part IX, *J.*, 1952, 1269.

indium are double salts containing a univalent cation. The above workers determined relatively large amounts of gallium, the titration being carried out at *ca.* 40–50°. Undesirable potential drifts generally occur during potentiometric titrations of metals with ferrocyanide, especially near the end-point; they occur in the direct titration of gallium with ferrocyanide.

Recently, 3 : 3'-dimethylnaphthidine has been used as an internal indicator in the titration of zinc, cadmium, calcium, and indium with ferrocyanide (*J.*, 1951, 1520, 3444). This indicator has also been modified by the introduction of the sulphonic acid group into the molecule and the resulting disulphonic acid applied to the determination of zinc and cadmium (*J.*, 1952, 1269). We now record the use of both these indicators in the titration of gallium with ferrocyanide. Accurate results have been obtained on 0.74–2.94 mg. of gallium with an average error of $\pm 0.25\%$.

When these indicators were used under the conditions of the potentiometric titration sluggish, ill-defined end-points were obtained. Acids and neutral salts completely prevented the formation of the red oxidised indicator complex. Sharp end-points were obtained, however, in weakly acidic solutions containing 30–35% of ethanol, the stoichiometry of the reaction being unaffected. Neither indicator had any advantage over the other. A selection of results obtained with these indicators is listed in the table.

0.01055M-Ga ³⁺ taken (ml.)	0.0075M-K ₄ Fe(CN) ₆ added (ml.)	Ga ³⁺ (mg.)		Indicator	Error, %
		present	found		
1.00	1.06	0.736	0.739	A	+0.41
1.50	1.58	1.103	1.102	B	-0.09
2.00	2.11	1.471	1.471	A	0.00
2.40	2.52	1.765	1.757	B	-0.46
2.80	2.94	2.059	2.050	A	-0.43
3.00	3.17	2.207	2.210	B	+0.11
3.50	3.68	2.575	2.566	A	-0.35
4.00	4.22	2.942	2.942	B	0.00

A = 3 : 3'-Dimethylnaphthidine.

B = 3 : 3'-Dimethylnaphthidinedisulphonic acid.

Experimental.—Solutions required. (a) *Gallium trichloride*, 0.01M. Approximately 0.01M-gallium trichloride was prepared by accurately weighing about 70 mg. of pure metallic gallium in a platinum boat and dissolving it in sufficient 4–5N-hydrochloric acid in presence of the platinum. When the gallium was dissolved, the liquid was carefully evaporated to dryness, the residue dissolved in a small quantity of water, and the solution re-evaporated. The gallium trichloride remaining was diluted to 100 ml. with 0.05N-hydrochloric acid.

(b) *Potassium ferrocyanide*, 0.0075M, and *potassium ferricyanide*, 0.5% aqueous. See *J.*, 1951, 1520.

(c) *Indicator solutions.* 3 : 3'-*Dimethylnaphthidine* : 0.2 g. was dissolved in 100 ml. of ethanol. 3 : 3'-*Dimethylnaphthidinedisulphonic acid*, 0.2% solution : see *J.*, 1952, 1269.

Procedure. Five ml. of 50% ethanol were added for each ml. of 0.01M-gallium solution taken. One drop of 0.5% potassium ferricyanide solution and two drops of indicator were then added, and the solution was titrated rapidly with standard potassium ferrocyanide until the red colour of the oxidised indicator began to fade. The ferrocyanide was then added dropwise with thorough shaking until the colour of the indicator changed to a permanent pale green.

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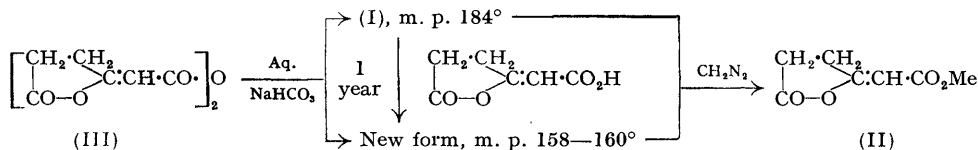
462. A Second Form of γ -Carboxymethylenebutanolide, the Enol-lactone of β -Keto adipic Acid.

By ULLI EISNER, J. A. ELVIDGE, and R. P. LINSTEAD.

We have recently described the lactonisation of β -keto adipic acid to give γ -carboxymethylenebutanolide (I) with m. p. 184° (Eisner, Elvidge, and Linstead, *J.*, 1950, 2223). We now find that this lactone changes slowly into a lower-melting form, m. p. 158–160° unchanged by repeated crystallisation.

The new lactonic acid gives the same analytical figures (C₆H₆O₄) as the original, has the same chemical properties and very similar light-absorption characteristics, but is less

soluble in organic solvents. Its methyl ester, m. p. 109°, prepared by reaction with diazomethane, appeared to be identical (mixed m. p.) with the lactonic ester (II), m. p. 110°, originally made from the lactonic acid of m. p. 184° (Eisner *et al.*, *loc. cit.*) and also obtained *via* the lactonisation of *cis-cis*-muconic acid (Elvidge, Linstead, Orkin, Sims, Baer, and Pattison, *J.*, 1950, 2228). Furthermore, treatment of the previously described anhydride (III), m. p. 164°, with aqueous sodium hydrogen carbonate now yielded the lactonic acid of m. p. 158°, instead of the higher-melting form of (I) as before.



The new, presumably more stable, form of the lactonic acid could be either a second crystal modification or, less probably, a geometrical isomeride.

Experimental.— γ -Carboxymethylenebutanolide, m. p. 158—160°. (a) Separate samples of the lactonic acid (I), m. p. 184° (Eisner *et al.*, *loc. cit.*), had been kept in a sealed tube in the dark, and in a desiccator in the daylight, for 1 year. Repeated crystallisation of these from a large volume of chloroform or from ethyl acetate afforded needles, m. p. 158—160° (decomp.), of the new form (Found: C, 51.05; H, 4.5. $\text{C}_6\text{H}_6\text{O}_4$ requires C, 50.7; H, 4.25%). Light absorption in dioxan: max. at 2260 Å., $\epsilon = 22,700$. The compound dissolved with effervescence in aqueous sodium hydrogen carbonate, and gave the colour reactions described previously for the higher-melting form.

(b) β -Keto adipic acid (10.6 g.) was kept for 3 days with acetyl chloride (80 c.c.; not redistilled). Evaporation of the solution to dryness under reduced pressure gave the anhydride (III) which crystallised from ethyl acetate—light petroleum (b. p. 60—80°) in prisms (5.5 g.), m. p. 164—165°, identical with the anhydride described earlier. The anhydride was dissolved in saturated aqueous sodium hydrogen carbonate, the solution filtered, and the filtrate acidified with aqueous hydrochloric acid. The precipitated acid, m. p. 152—153° (decomp.), crystallised from ethyl acetate as needles, m. p. 158—160° (decomp.) undepressed by the lactonic acid obtained under (a) above.

Esterification. The lactonic acid, m. p. 158—160° (0.2 g.), in ethyl acetate was treated with an excess of ethereal diazomethane, and the solution evaporated under reduced pressure. From ether—light petroleum (b. p. 40—60°), the γ -carbomethoxymethylenebutanolide crystallised as laths, m. p. 109° undepressed when mixed with a specimen of the ester earlier prepared from the lactonic acid of m. p. 184°.

We are indebted to the Department of Scientific and Industrial Research for a maintenance grant (to U. E.).

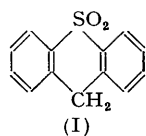
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463. Some Observations on Conjugation in Sulphones.

By E. S. WAIGHT.

THE qualitative molecular-orbital treatment by Moffitt and Koch (*Trans. Faraday Soc.*, 1951, 47, 7) reveals that different kinds and degrees of conjugation can arise in differently substituted unsaturated sulphones, depending on the number (one or two) and the configuration of the unsaturated groups attached to the sulphur atom. Thus it is predicted



that in diphenyl sulphones interaction between the phenyl groups involves a vacant sulphur *d*-orbital and does not affect the sulphur–oxygen bonds. This type of conjugation (known as “Case II”) will be enhanced by substitution of electron-donating groups (*e.g.*, Br, NH_2) in the phenyl rings. On the other hand, in compounds in which the nodal planes of the π -orbitals of the unsaturated and sulphone groups are perpendicular, as for example in divinyl sulphone and thioxanthene 9 : 9-dioxide (I), conjugation will involve the sulphur–oxygen bonds (“Case I”).

In order to test these conclusions the ultra-violet absorption spectra and S–O bond vibration frequencies have been measured for a number of unsaturated sulphones.

Ultra-violet absorption spectra of unsaturated sulphones (in absolute ethanol).¹

Sulphone	$\lambda_{\text{max.}}, \text{\AA}$	ϵ
Diphenyl	2350	15,000
Di- <i>p</i> -bromophenyl	2330, 2530 ²	16,000, 27,000
Di- <i>p</i> -aminophenyl	2610, 2950	18,000, 28,300
Thiaxanthen 9 : 9-dioxide	2350	8,900

¹ Low intensity (benzenoid) absorption in the region 2600—2800 Å not reported.

² Cf. Koch (*J.*, 1949, 408) who reports only one maximum at 2500 Å.

The two intense maxima in di-*p*-bromo- and di-*p*-amino-phenyl sulphones are presumably due to two distinct electronic transitions, which, however, are difficult to identify. Nevertheless, the increasing bathochromic shifts observed in substituting groups of increasing electron-donating powers agree with the theoretical predictions. The wavelengths of the maxima of thiaxanthen 9 : 9-dioxide and diphenyl sulphone are identical, so that conjugation in the former compound must be no stronger than in the latter.

While it has not been possible to measure the position of the absorption maximum for divinyl sulphone (which is below 1900 Å), comparison of the rising parts of the absorption curves of this compound with those of ethyl vinyl sulphone (taken from Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 231) and oct-1-ene indicates considerable electronic interaction, although of unspecified type (see Fig.).

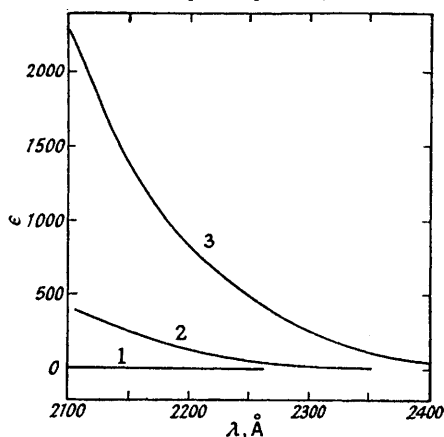
The conjugation of unsaturated groups normally results in decreases in the vibrational frequencies associated with those groups (cf. for example the data for carbonyl compounds given by Hartwell, Richards, and Thompson, *J.*, 1948, 1436). However, the S—O bond vibration frequency is higher in diphenyl sulphone than in dicyclohexyl sulphone and this has been attributed by Barnard, Fabian, and Koch (*J.*, 1949, 2442) to the inductive effect of the phenyl group more than outweighing its conjugative effect (cf. also Gordy, *J. Chem. Phys.*, 1942, **9**, 204). The S—O bond vibration frequency of di-*p*-bromophenyl sulphone is similarly greater than that for diphenyl sulphone, in agreement with the more powerful inductive electron-attraction of the *p*-bromophenyl group. Di-*p*-aminophenyl sulphone is insoluble in carbon tetrachloride and no other suitable solvent could be found. There is again no evidence of strong "Case I" conjugation in thiaxanthen 9 : 9-dioxide, the S—O bond vibration frequency being very similar to the diphenyl sulphone frequency. The S—O bond vibration frequency of divinyl sulphone is not much greater than the frequency of diethyl sulphone, and since the electronegativities of the phenyl and the vinyl group are the same (Moffitt, *Proc. Roy. Soc.*, 1950, **A**, **202**, 548) this is indicative of some degree of conjugation of the vinyl and the sulphone groups.

Valence vibration frequencies of the sulphone group (in carbon tetrachloride) (cm.⁻¹).

	ν_2	ν_1	$\nu_{30} = (\nu_2 + \nu_1)/2$	$\nu_{30} - \nu_{30} \text{ sat.}$
Diphenyl	1329	1160	1245	25
Di- <i>p</i> -bromophenyl	1341	1162	1252	32
Thiaxanthen 9 : 9-dioxide	1321	1167	1244	24
Dicyclohexyl	1305	1134	1220	—
Divinyl	1332	1138	1235	4
Diethyl	1323	1138	1231	—

The data presented support the conclusion that conjugation in diphenyl sulphones occurs by Moffitt and Koch's "Case II" mechanism and does not involve the sulphur-oxygen bonds. The predicted "Case I" conjugation, involving the sulphur-oxygen bonds, is not detectable in thiaxanthen 9 : 9-dioxide but occurs weakly in divinyl sulphone. This result can be understood if it is remembered, as pointed out by Moffitt and Koch (*loc.*

Ultra-violet absorption spectra (in EtOH).



- 1, Oct-1-ene.
2, Ethyl vinyl sulphone.
3, Divinyl sulphone.

cit.), that strong conjugation will be associated with groups of strong conjugating power (*i.e.*, self-atom-polarisability or residual affinity) and that the vinyl group has considerably greater conjugating power than the phenyl group.

Experimental.—Infra-red absorption spectra were determined with a Grubb-Parsons single beam spectrometer. Ultra-violet absorption spectra were determined with a Hilger Uvispek spectrophotometer.

Materials. Diphenyl and di-*p*-aminophenyl sulphone were commercial samples recrystallised from ethanol and methanol and having m. p. 123° and 176° respectively.

Diethyl sulphone was obtained by oxidising the corresponding sulphide in chloroform at 0° with aqueous sulphuric acid and powered potassium permanganate (Barnard, Fabian, and Koch, *loc. cit.*). After crystallisation from ethanol it had m. p. 72°.

Divinyl sulphone, kindly supplied by Mr. E. N. Fettes of the Thiokol Corporation, New Jersey, was redistilled and had b. p. 102–104°/15 mm., n_D^{15} 1.4800. When heated with azobisisobutyronitrile (1%) at 100° for 1 hour, the sulphone polymerised to a yellow, highly insoluble solid.

Pure samples of thioxanthene 9:9-dioxide and di-*p*-bromophenyl sulphone were kindly supplied by Dr. Hans Heymann (Harvard University) and Dr. J. Toussaint (University of Liège) respectively. The ultra-violet spectrum of the former is identical with that determined by Dr. E. A. Fehnel (private communication to the late Dr. H. P. Koch).

Thanks are due to Dr. W. E. Moffitt for helpful discussion of this work which was carried out at the suggestion of the late Dr. H. P. Koch and is derived from a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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464. 9-Ketoferruginol and Its Identity with Sugirol.

By C. W. BRANDT and B. R. THOMAS.

FROM the neutral part of the resin extracted with alcohol from the wood of the New Zealand tree, rimu (*Dacrydium cupressinum*), a crystalline substance $C_{20}H_{28}O_2$ was isolated by Brandt and Thomas (*N.Z. J. Sci. Tech.*, 1951, B, 33, No. 1, 30). Formation of a monoacetate, monobenzoate, and monomethyl ether as well as the slight but definite solubility in aqueous sodium hydroxide and the coupling with diazotized nitroaniline showed the substance to be a monohydric phenol. The second oxygen atom was ketonic, as a crystalline semicarbazone was slowly formed.

The ultra-violet absorption spectrum of the compound indicates a *p*-hydroxyacetophenone grouping, as shown by the following comparisons of λ_{max} . (m μ) (log ϵ in parentheses) in alcohol solution (Morton and Stubbs, *J.*, 1940, 1347) :

<i>o</i> -Hydroxyacetophenone	251, 327	(4.0, 3.5)
<i>m</i> -Hydroxybenzaldehyde	254, 316	(3.9, 3.5)
<i>p</i> -Hydroxyacetophenone	220, 276	(4.0, 4.1)
Keto-phenol $C_{20}H_{28}O_2$	233, 285	(4.2, 4.1)
Ferruginol	— 283	(— 3.5)

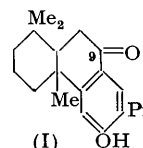
The phenolic diterpenoid, ferruginol, occurs in our resin (Brandt and Neubauer, *J.*, 1939, 1031; Campbell and Todd, *J. Amer. Chem. Soc.*, 1940, 62, 1287; 1942, 64, 928; Brandt and Thomas, *loc. cit.*), and its oxidation at the 9-position would yield a *p*-hydroxyacetophenone grouping. Oxidation of ferruginyl acetate with chromic acid or of ferruginyl methyl ether with alkaline permanganate gave products which were identical (mixed melting points) with the acetate and the methyl ether of our compound $C_{20}H_{28}O_2$.

That oxidation is likely to occur most readily at the 9-position in a compound such as ferruginol is borne out by the work of Jacobsen (*J. Amer. Chem. Soc.*, 1951, 73, 3463, and earlier work quoted by him). Formation of the carbonyl group at any other position in the saturated rings of ferruginol would not have resulted in any significant change in ultra-violet absorption spectrum.

A comparison of 9-ketoferruginol (I) and its derivatives with the hydroxy-ketone sugirol ($C_{20}H_{28}O_2$) isolated from *Cryptomeria japonica* (Keimatsu, Ishiguro, and Fukui, *J. Pharm. Soc. Japan*, 1937, 57, 92; Huzii and Tikamori, *ibid.*, 1939, 59, 116) leaves little doubt that the compounds are identical (see table below). On reduction and dehydrogenation of

sugiol methyl ether, 6-methoxyretene was obtained by the Japanese workers. The position of the ketonic group was however not fixed.

9-Ketoferruginol sugiol		
Keto-phenol	295—297°	283—284°
Acetate	165—167	165
Benzoate	185—186	185—186
Methyl ether	136—137	137
Semicarbazone	242—245	246
$[\alpha]_D^{18-20}$	+20° (in alcohol)	+34° (in pyridine)
λ_{max}	283 m μ	about 286 m μ



Experimental.—9-Ketoferruginol was obtained in approx. 0.01% yield from rimu sawdust, and the benzoate, methyl ether, and semicarbazone were prepared as previously described (Brandt and Thomas, *loc. cit.*).

9-Ketoferruginyl acetate. 9-Ketoferruginol (20 mg.) was kept in acetic anhydride (2 ml.) and pyridine (1 ml.) for 15 hours, and the excess of reagent was decomposed and removed in the usual manner. The product (18 mg.), crystallised from light petroleum and sublimed under reduced pressure, had m. p. 165—167° (Found: C, 77.6; H, 9.0. Calc. for C₂₂H₃₀O₃: C, 77.2; H, 8.8%).

Oxidation of ferruginol with chromic acid. Ferruginyl acetate (500 mg.) and chromic oxide (220 mg.) in acetic acid (10 ml.) were heated on the water-bath for 45 minutes. After dilution with water the product was extracted with ether and recrystallised twice from light petroleum; this gave 170 mg. of m. p. 161—163° alone or mixed with the acetate of the keto-phenol from rimu. The acetate was chromatographed but only a small amount of the pure acetate was recovered. The remainder of the product was obtained from the acetone eluate as free keto-ferruginol.

Oxidation of ferruginyl methyl ether with potassium permanganate. Ferruginyl methyl ether (400 mg.) and excess of alkaline permanganate solution were heated on the water-bath with occasional shaking for 20 hours. The reaction mixture was treated with sulphur dioxide until clear and then extracted with ether. The product, which contained no acid, was crystallised from light petroleum; it (90 mg.) had m. p. 130—132°. Recrystallisation from alcohol gave plates, m. p. 138—139°, λ_{max} . 231 and 279 m μ (log ϵ 4.3, 4.2) (Found: C, 79.9; H, 9.7. Calc. for C₂₁H₃₀O₂: C, 80.2; H, 9.6%). A mixed m. p. with the methyl ether of the compound from rimu resin was undepressed.

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465. Pyridinium Sulphates derived from Cholesterol and Lanostadienol.

By M. J. BIRCHENOUGH and H. BURTON.

SINCE it has been shown that œstrone and related compounds are frequently excreted as sulphates, interest has been aroused in the steroid sulphates. A convenient method has been described by Sobel and Spoerri (*J. Amer. Chem. Soc.*, 1941, **63**, 1259) for the preparation of cholesteryl pyridinium sulphate, by the interaction of cholesterol in benzene solution and pyridine-sulphur trioxide. Cholesteryl pyridinium sulphate gives foaming solutions (probably colloidal) in water, but is only moderately surface-active. *epi*Cholesteryl pyridinium sulphate has been prepared by Sobel's method for comparison, and the salts have been found to have a comparable effect in lowering the surface tension of water. With the du Noüy tensiometer, aqueous solutions of both pyridinium sulphates gave a minimum value of 35—36 dynes/cm. at 25° in the concentration range M/1000 to M/5000. Thus the inversion in configuration at C₃ does not appear to have any effect on surface activity.

The method of preparation can be extended with minor modifications to derivatives of lanostadienol (formerly known as lanosterol), a triterpene alcohol which occurs with cholesterol in wool wax. Although a reference has been made to "lanosteryl pyridinium sulphate" (Sobel, *loc. cit.*), the product was certainly not homogeneous, since lanostadienol

itself has not been isolated by the technique described, and the analytical values reported differed widely from the theoretical. Though it is difficult to isolate lanostadienol from wool wax, the derivatives lanostenol (dihydrolanosterol) and γ -lanostadienol (dihydroagosterol) are readily obtainable pure, and the derivatives prepared from these triterpene alcohols are described below. Like the cholesterol analogue, lanostenyl pyridinium sulphate and the γ -lanostadienyl derivative give precipitates of the alkali-metal salts when aqueous solutions are treated with sodium or potassium chloride solution. The pyridinium salts are much less soluble in water (the lanostenyl salt being the more soluble and dissolving to the extent of approximately 0.05% w/v at 25°) than cholesteryl pyridinium sulphate, and the very low solubility limits a comparison of their surface activity. They have a smaller effect in lowering the surface tension of water, the lowest value obtained for a saturated solution of lanostenyl pyridinium sulphate being 45 dynes/cm. at 25°. None of the pyridinium sulphates appeared to be an effective emulsifying agent.

Experimental.—*epiCholesteryl pyridinium sulphate*, prepared by Sobel's method (*loc. cit.*), had m. p. 163—164° (Found: S, 5.7. $C_{27}H_{46}O_4S, C_5H_5N$ requires S, 5.9%). *Lanostenyl pyridinium sulphate* was prepared as follows: lanostenol (3 g.) in anhydrous benzene (50 ml.) was stirred at 50—55° with pyridine-sulphur trioxide (1.2 g.) for 30 minutes. The reaction mixture was cooled to room temperature and light petroleum (150 ml.; b. p. 60—80°) was added. After 10 minutes the suspension of lanostenyl pyridinium sulphate was decanted from the excess of the reagent, and filtered. The residue was washed with benzene-light petroleum (1:4) and dried in a vacuum (yield, 2 g.). The product dissolved largely in chloroform (50 ml.) and after filtration from traces of pyridine-sulphur trioxide, the solution gradually deposited long needles, which after one crystallisation from chloroform had m. p. 216—217° (sintering at 202°), $[\alpha]_D^{25} +41.7^\circ$ (c, 2.015% in chloroform) (Found: C, 71.0; H, 9.6; S, 5.3. $C_{30}H_{52}O_4S, C_5H_5N$ requires C, 71.55; H, 9.7; S, 5.45%). *γ -Lanostadienyl pyridinium sulphate* similarly prepared, had m. p. 234—235°, $[\alpha]_D^{19} +57.3^\circ$ (c, 0.803% in chloroform) (Found: S, 5.1. $C_{30}H_{50}O_4S, C_5H_5N$ requires S, 5.5%).

We thank Mrs. S. B. David for the preparation of *epicholesteryl pyridinium sulphate* and Professor C. W. Shoppee for a gift of *epicholesterol*.

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466. Preparation of Crystalline Nitrides of Vanadium and Niobium.

By F. H. POLLARD and G. W. A. FOWLES.

THE normal methods used to prepare the nitrides of vanadium and niobium, *viz.*, action of nitrogen on heated mixture of oxide and carbon, yield amorphous products which are not always suitable for chemical studies. Pollard and Woodward's continuous process (*J.*, 1948, 1709) for preparing titanium nitride on a filament from titanium tetrachloride in the presence of nitrogen and hydrogen has been found convenient (with appropriate modifications) also for vanadium and niobium nitrides and provides crystalline products suitable for high-temperature studies (see Pollard and Woodward, *Trans. Faraday Soc.*, 1950, 46, 190). One of the main factors for success is the control of the filament temperature, since this is critical for crystal growth and differs for different nitrides, *viz.*, TiN, 1250—1450°; NbN, 1340—1350°; VN, 1500—1570°. As the nitrides have a lower electrical conductivity than the metal filament, the current has to be continuously increased, to counteract the cooling effect of the outer surface growth of the nitride and maintain the critical temperature. Good growths of vanadium nitride can thus be obtained, but niobium nitride could only be obtained as small crystals, difficult to analyse accurately.

Experimental.—The apparatus and procedure were similar to those already described earlier (*J.*, 1948, 1709).

Vanadium tetrachloride, prepared by passing chlorine over pure vanadium metal powder at 400°, yielded a product free from ferric chloride (Calc.: V, 26.3; Cl, 73.8. Calc. for VCl_4 : V, 26.4; Cl, 73.6%).

Niobium pentachloride was prepared by Alexander and Fairbrother's method (*J.*, 1949, S 223).

Vanadium nitride. The proportion of vanadium chloride in the carrier gas stream (normally equal volumes of nitrogen and hydrogen) was controlled by a bath surrounding the liquid vanadium tetrachloride. Increase of the proportion of vanadium tetrachloride in the gas phase by change of temperature from 0° to 40° resulted in increasing deposits on the filament, but above 40° there was considerable loss of tetrachloride by condensation and decomposition on the walls of the reaction vessel. On the whole, more satisfactory crystals were obtained with the bath at 20°.

Changes in the total pressure of the carrier gas indicated that crystal size was independent of the pressure, though at too high a pressure the weight of the deposit decreased slightly, probably owing to cooling effects on the filament.

Variations in the thickness of the filament showed that for mechanical reasons, *viz.*, breakage and end losses, it was best to use wire of 0.20-mm. diameter. Tungsten wire was generally used though successful growths were also obtained with molybdenum. Tantalum wire absorbed hydrogen too readily, and platinum had too low a melting point and soon fused.

Filament temperatures below 1350° gave amorphous black deposits consisting of metallic vanadium, partly nitrided, and at 1400° crystals began to grow but the deposit was small and rapidly became coated with an amorphous layer. Over a range of temperatures from 1400° to 1570°, the growth of crystals improved, but at higher temperatures the centre of the filament was left bare, although good crystals form on each side. Observations on the changes in current through the filament as the crystals grow show that there is an initial period of nucleation followed by an even rate of current increase corresponding to the growth of the nitride as a "cylinder" (cf. Pollard and Woodward, *loc. cit.*). The rate of increase later slows down perceptibly and at this stage the filament darkens quite suddenly as the amorphous deposit starts to form. Thus, the current changes are a good indication of success.

Optimum conditions are: filament temp., 1540—1570°; total pressure of carrier gas (equal volumes of nitrogen and hydrogen), 50—60 cm. Hg; v. p. of VCl₄, 5—8 mm., *i.e.*, temp. of surrounding bath 20°; tungsten filament, 0.20-mm. diameter.

The product is obtained as yellowish-brown cubic crystals [Found: V (colorimetrically as the H₂O₂ complex), 77.8 ± 1. Calc. for VN: V, 78.4%].

Niobium nitride. As the niobium pentachloride was a solid (m. p. 209.5°) with an appreciable vapour pressure at 150—200°, it was necessary to replace the usual trap for the liquid chlorides by a tube surrounded by an electrically heated furnace. The glass tubing and mercury cut-off leading to the reaction vessel were also heated to about 180° to prevent undue deposition of the pentachloride. The carrier gases were led over the heated niobium pentachloride, a fairly smooth flow of pentachloride vapour being thus obtained.

The temperature of the filament was most critical, amorphous growths being obtained below 1340°, whereas above 1360° there was usually no deposit.

Optimum conditions were: filament temp., 1340—1350°; total pressure of carrier gas, 60 cm. Hg; v. p. of NbCl₅, 40—50 mm. Hg, produced by the electric furnace at 175°.

The product formed silvery-grey crystals, containing a considerable amount of nitrogen, but no satisfactory analysis could be made since the crystal growth was small.

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467. *The Oxidation of 4-Methylcatechol in Aqueous Solution by Ferric Ion.*

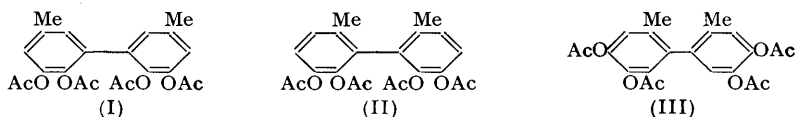
By H. BURTON and H. B. HOPKINS.

THE oxidation of monohydric phenols in aqueous solution has been studied by several workers (see, for example, Cosgrove and Waters, *J.*, 1951, 1726), but there is little reported work on the corresponding oxidation of dihydric phenols. Majima and Takayama (*Ber.*, 1920, 53, 1914) investigated the oxidation of 2:3-dihydroxytoluene with aqueous ferric chloride. Reduction of the oxidation product by zinc and acetic acid, followed by acetylation, yielded 4:5:4':5'-tetra-acetoxy-3:3'-dimethyldiphenyl. The same compound was obtained by the oxidation of 2-hydroxy-3-methoxytoluene under similar conditions, followed by reduction, demethylation, and acetylation. This established the structure of the original oxidation product, for in the oxidation of 2-hydroxy-3-methoxy-

toluene, coupling would necessarily occur in the position *para* to the hydroxy-group, both *ortho* positions being blocked.

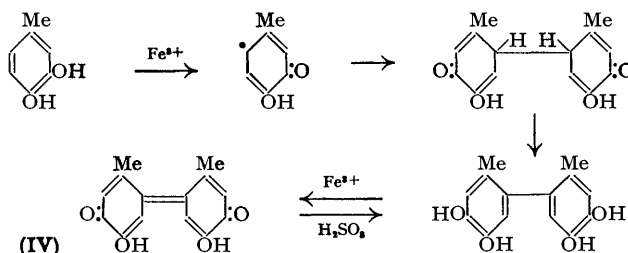
We now report the oxidation of 4-methylcatechol (3 : 4-dihydroxytoluene) in aqueous solution by ferric acetate and by silver oxide. The black iron-containing precipitate obtained on mixing aqueous solutions of 4-methylcatechol and ferric acetate was suspended in dilute sulphuric acid and treated with sulphur dioxide. The product obtained by ethereal extraction was acetylated to yield a colourless crystalline acetate, m. p. 135—136°. On shaking an aqueous solution of 4-methylcatechol with silver oxide a red solution was obtained. The addition of *o*-phenylenediamine, dissolved in dilute acetic acid, to this solution resulted in the immediate formation of a yellow precipitate, indicative of the presence of a 1 : 2-diketone or a 2-hydroxy-1-keto-compound in the solution. It was not possible to identify this precipitate. The red solution was decolorised by sulphur dioxide; the ether-soluble product was acetylated to give a small amount of the above acetate.

Analytical and molecular-weight data indicated that the acetate was a tetra-acetoxy-dimethyldiphenyl. Of the three possible structures (I, II, III) for this compound, (I) is



known to have m. p. 110—112° (Asano and Gisvold, *J. Amer. Pharm. Assoc.*, 1949, **38**, 172). Previous investigations (for example, the above oxidation of 2 : 3-dihydroxytoluene) indicate that when there is a possibility of coupling either *ortho* or *para* to a hydroxy-group, a *para* position is preferred. Further, the formation of (II), in which all four positions *ortho* to the Ph-Ph linkage are substituted, would seem unlikely from steric considerations. We accordingly suggest that the tetra-acetate is (III).

The course of the reaction with ferric ions is presumably as illustrated below



(cf. Cosgrove and Waters, *loc. cit.*); the black precipitate obtained is undoubtedly an iron complex of (IV) (cf. Burton and Stoves, *Nature*, 1950, **165**, 569), and its formation indicates that 2 : 2'-dimethyldiphenyl-4 : 5-4' : 5'-diquinone is not produced. In accordance with expectations no metal complex was formed during the oxidation with silver oxide.

The oxidation of tolu-2 : 5-quinol by ferric ions under similar conditions gave, as expected, after reduction of the intermediate quinone, the original quinol; formation of a metal complex would not be expected to occur.

Experimental.—4-Methylcatechol, m. p. 64.5—65°, was crystallised from benzene-light petroleum (b. p. 60—80°).

Oxidations with Ferric Ion.—(i) Anhydrous ferric chloride (24 g., 0.148 mol.) was dissolved in water (150 ml.), and saturated sodium acetate solution added until Congo-paper just remained red. This solution was then added during 5 minutes to a solution of 4-methylcatechol (4.5 g., 0.036 mol.) in water (50 ml.) with stirring, which was continued for a further hour. The black suspension was then filtered, and the black residue washed with water and suspended in dilute sulphuric acid. Sulphur dioxide was passed for 2 hours, the clear yellow solution being then saturated with sodium chloride and repeatedly extracted with ether. Removal of the ether left a red-black oil which was acetylated by adding acetic anhydride (15 ml.) and a little 60% perchloric acid. After several hours, the solution was poured into water and subsequently

extracted with ether. The yellow oil obtained on evaporation of the ether was freed from acetic acid in a vacuum desiccator over solid sodium hydroxide. The crude acetate (4.6 g., 61%) on repeated recrystallisation from ethanol gave 4 : 5 : 4' : 5'-tetra-acetoxy-2 : 2'-dimethyldiphenyl, m. p. 135—136° (Found : C, 63.9; H, 5.3%; M, 409. $C_{22}H_{22}O_8$ requires C, 63.7; H, 5.4%; M, 414).

(ii) Tolu-2 : 5-quinol (1.5 g.) and ferric chloride (8 g.) under the same conditions gave a dark red solution. From the subsequent treatment, only tolu-2 : 5-quinol diacetate was obtained.

Oxidations with Silver Oxide.—(a) Silver oxide [prepared by the addition of a slight excess of saturated barium hydroxide solution to an aqueous solution of silver nitrate (18 g., 0.094 mol.), followed by repeated washing by decantation with water] was suspended in water (100 ml.), and a solution of 4-methylcatechol (2.9 g., 0.023 mol.) in water (25 ml.) added rapidly. The suspension was shaken in a stoppered bottle for 35 minutes and then filtered. Sulphur dioxide was passed for 2 hours through the red filtrate, which was then treated as previously described; crystalline material (0.08 g.) was obtained on allowing an ethanol solution of the oily product to stand for 2 weeks. Recrystallised from ethanol, the diphenyl had m. p. 134—135° (Found : C, 63.7; H, 5.5%), alone or in admixture with the product from the ferric chloride oxidation.

(b) To one-half of the filtrate obtained by oxidising 4-methylcatechol (3.0 g., 0.024 mol.) as described under (a), was added *o*-phenylenediamine (2 g., 0.018 mol.) in dilute acetic acid. The yellow precipitate was filtered off and washed with dilute acetic acid and then with water. On drying in a vacuum a yellowish-brown solid (0.1 g.) was obtained; this darkened at 143° and changed to a black tar at 157—160°. There was no improvement in m. p. after crystallising the solid from chloroform–light petroleum (b. p. 40—60°).

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468. *The Raney Nickel Desulphurisation of S-Benzyl-N-phthaloyl-L-cysteine.*

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IN our studies on the configuration of amino-acids we needed to desulphurise some optically active amino-acids containing sulphur. Our preliminary investigations with Raney nickel were made on *S*-benzyl-*N*-phthaloyl-*L*-cysteine, and *N*-phthaloyl-*L*-alanine was thus obtained.

Conversion of *L*-cysteine into optically active α -alanine on a preparative scale has hitherto not been described. By thermal decomposition of cysteine hydrochloride Mörner (*Z. physiol. Chem.*, 1904, **42**, 349) obtained, along with other products, *DL*-alanine; and Mauthner (*ibid.*, 1912, **78**, 28) obtained *DL*-alanine by reduction of *L*-cystine with zinc in concentrated aqueous ammonia.

Turner, Pierce, and du Vigneaud (*J. Biol. Chem.*, 1951, **193**, 359) desulphurised oxytocin with Raney nickel and found, on chromatography of the hydrolysate on starch, an increase in alanine content in direct ratio to the amount of cystine present.

Experimental.—*S*-Benzyl-*N*-phthaloyl-*L*-cysteine, $[\alpha]_D^{15} - 151^\circ$ (1.36 g., 0.004 mole) (prepn. *J. Org. Chem.*, in the press) was heated under reflux for 4 hours with Raney nickel C (5 g.) (Hurd and Rudner, *J. Amer. Chem. Soc.*, 1951, **73**, 5157) in absolute ethanol (100 c.c.), and left overnight at room temperature. The nickel was removed by filtration and washed with absolute ethanol (50 c.c.), and the combined filtrate and washings were evaporated to dryness. The dark brown oily residue (450 mg.) was dissolved in benzene (15 c.c.) and shaken with 5% hydrochloric acid (3 × 10 c.c.) and water (10 c.c.). The benzene solution was dried (Na_2SO_4) and evaporated, giving *N*-phthaloyl-*L*-alanine (350 mg., 40%) which, recrystallised from ethanol–water, had m. p. 150—151°, $[\alpha]_D^{20} - 18.3^\circ \pm 0.7^\circ$ (c, 2.63 in ethanol) (Found : C, 60.3; H, 4.5. Calc. for $C_{11}H_9O_4N$: C, 60.3; H, 4.1%). Fischer (*Ber.*, 1907, **40**, 499) reported $[\alpha]_D^{20} - 17.8^\circ \pm 0.2^\circ$ (c, 8.13 in ethanol) and m. p. 150—151° (corr.).

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469. A New Synthesis of $\alpha\gamma$ -Diaminobutyric Acid.

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DL- $\alpha\gamma$ -DIAMINOBTYRIC ACID is of interest because of its isolation from hydrolysates of the antibiotic polypeptide, aërosporin (Catch and Jones, *Biochem. J.*, 1948, **42**, lii). It has been prepared from glutamic acid by the Schmidt reaction (Rothschild and Fields, *J. Org. Chem.*, 1951, **16**, 1080), by Hofmann degradation of glutamine (Synge, *Biochem. J.*, 1939, **33**, 671) and by catalytic hydrogenation of ethyl pyrazolone-3-carboxylate, prepared from ethyl acrylate and diazomethane (Carter, Abeele, and Rothrock, *J. Biol. Chem.*, 1949, **178**, 325).

We found that the amino-acid may be prepared more readily and in good yield by the following method: acraldehyde and phthalimide, in presence of Triton B, give β -phthalimidopropaldehyde, which is converted into the amino-acid by the Strecker method (overall yield, 43% based on acraldehyde).

The corresponding hydantoin was also prepared, but yielded only a small amount of the amino-acid on acid hydrolysis.

Experimental.— β -Phthalimidopropaldehyde. Acraldehyde (224 g., 4 moles) was added to ethyl acetate (2 l.) in a flask fitted with a stirrer and reflux condenser. Phthalimide (588 g., 4 moles) was added, and the mixture heated to 60° with rapid stirring. Triton B (60% benzyltrimethylammonium hydroxide solution) (8 c.c.) was added in two equal portions. The suspended imide rapidly dissolved. The mixture was stirred and heated for a further 15 minutes, and then concentrated to low bulk *in vacuo*. The resultant crystalline aldehyde was washed with ether, dried (796 g., 98%), and recrystallised from hot water, to give silky needles, m. p. 125—126° (uncorr.) (Found: C, 65.0; H, 4.5; N, 6.9. $C_{11}H_9O_3N$ requires C, 65.0; H, 4.5; N, 7.0). The semicarbazone, recrystallised from aqueous alcohol, had m. p. 229° (uncorr.) and the 2:4 dinitrophenylhydrazone, recrystallised from acetic acid, melted at 207° (uncorr.).

DL- $\alpha\gamma$ -Diaminobutyric acid monohydrochloride. The aldehyde (40.6 g., 0.2 mole) was added to sodium metabisulphite (19 g.) in water (150 c.c.), and the mixture stirred and cooled. A solution of sodium cyanide (10 g., 0.2 mole) in water (15 c.c.) was added at such a rate that the temperature did not exceed 30°. After 1 hour the mixture was extracted with ether. The extract was washed with hydrogen sulphite solution, dried (Na_2SO_4), and concentrated, to give a white crystalline mass of the crude cyanohydrin (41.6 g., 90%), m. p. 99—100°. This was added to ethyl alcohol (1 l.) saturated with ammonia, and kept for 3 days at room temperature. Concentration gave the crude semi-solid aminonitrile which was too unstable to heat and too insoluble for purification. Hydrolysis by refluxing hydrochloric acid (200 c.c.) for 6 hours, followed by cooling, removal of phthalic acid, evaporation to dryness, and treatment of the alcoholic extract with pyridine gave the monohydrochloride which, recrystallised from aqueous alcohol, had m. p. 228—230° (uncorr.) (13.4 g., 48.4% calc. on cyanohydrin) (Found: N, 17.8; Cl, 22.8. Calc. for $C_4H_{11}O_2N_2Cl$: N, 18.1; Cl, 23.0%). The dipicrate, crystallised from water, had m. p. 188—189° (decomp.).

5-2'-Phthalimidoethylhydantoin. β -Phthalimidopropaldehyde (120 g., 0.6 mole) was added to sodium metabisulphite (60 g.) in water (400 c.c.). The mixture was stirred rapidly and a solution of sodium cyanide (55 g., 1.1 moles) and ammonium carbonate (264 g., 3 moles) in water (450 c.c.) was added, followed by ethyl alcohol (450 c.c.). The mixture was stirred for 4 hours at 50—55°, cooled, and filtered. The filtrate was acidified, concentrated to one-third of its volume, and filtered, to give the crude hydantoin (94 g., 57.5%), m. p. 183—184°. Recrystallised from hot water it had m. p. 186—187° (uncorr.) (Found: C, 56.5; H, 4.2; N, 14.4. $C_{13}H_{11}O_4N_3$ requires C, 57.1; H, 4.0; N, 15.1%). Hydrolysis by hydrochloric acid for 6 hours at 150° gave only a very small yield of the amino-acid.

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