NOTES.

248. *The Synthesis of* 2 : 6-*Dicyano*-3 : 5-*dimethylaniline.*

By R. HULL.

A NEW aromatic compound has been obtained during an investigation into the preparation of 2-amino-3-cyano-4 : 6-dimethylpyridine from aliphatic intermediates.

Moir (*J.*, 1902, 113) and Knoevenagel and Cremer (*Ber.*, 1902, **35**, 2393) prepared 3-cyano- and 3-carbethoxy-2-hydroxy-4 : 6-dimethylpyridines by reaction of 1-acetyl-2-aminopropene with cyanoacetamide and malonic ester, respectively. Reaction of 1-acetyl-2-aminopropene and malononitrile, however, has now given two products.

One of these compounds, $C_8H_8ON_2$, m. p. 289—290°, which was soluble in alkali, was 5 : 5-dicyano-2-hydroxy-4-methylpenta-2 : 4-diene, for on hydrolysis with sulphuric acid it gave a degradation product, C_7H_9ON, undepressed in melting point on admixture with 2-hydroxy-4 : 6-dimethylpyridine (Knoevenagel and Cremer, *loc. cit.*). The other product, $C_{10}H_9N_3$, m. p. 211—213°, gave, on acid hydrolysis, a liquid primary arylamine, $C_8H_{11}N$, b. p. 221—222°/752 mm., and a solid, $C_9H_{12}ON_2$, m. p. 160°. The liquid was identified as 3 : 5-dimethylaniline by its physical properties and the formation of 5-*p*-sulphanilamido-*m*-xylene. The product, $C_{10}H_9N_3$, was therefore 2 : 6-dicyano-3 : 5-dimethylaniline, and the solid hydrolysis product, $C_9H_{12}ON_2$, 2-carbamyl-3 : 5-dimethylaniline.

2 : 6-Dicyano-3 : 5-dimethylaniline was probably formed by condensation of the dimer of malononitrile with 1-acetyl-2-aminopropene, with subsequent elimination of cyanamide. 5 : 5-Dicyano-2-hydroxy-4-methylpenta-2 : 4-diene was not an intermediate in the formation of the aniline, because reaction of the aliphatic compound with a further molecular proportion of malononitrile gave no formation of the aromatic compound.

The same products were formed, in the presence of alkali, from acetylacetone and malononitrile. This reaction was mentioned by Östling (*Oversikt Finska Vet. Soc. Forhändl.*, 1915, **57** *A*, No. 11) but no details were given of any compounds isolated.

Experimental.—Condensation of 1-acetyl-2-aminopropene and malononitrile. 1-Acetyl-2-aminopropene (25·7 g., 0·26 mol.) (Combes, *Bull. Soc. chim.*, 1892, **7**, 779) was added to a stirred suspension of malononitrile (18·9 g., 0·268 mol.) in water (200 c.c.), and stirring continued 18 hours. After a further 2 days the solid (25 g.) was collected and washed with water. The material [m. p. 204—225° (sintering 195°)] was extracted with 2N-sodium hydroxide (100 c.c.). The insoluble product (13·5 g.), m. p. 210—212°, on crystallisation from aqueous alcohol gave needles, m. p. 211—213°, of 2 : 6-*dicyano*-3 : 5-*dimethylaniline* (Found : C, 70·0; H, 5·15; N, 24·55. $C_{10}H_9N_3$ requires C, 70·2; H, 5·25; N, 24·6%). The alkaline extract was acidified with 5N-hydrochloric acid, and the precipitate (11·5 g.) crystallised from alcohol, giving needles, m. p. 289—290°, of 5 : 5-*dicyano*-2-*hydroxy*-4-*methylpenta*-2 : 4-*diene* (Found : C, 64·7; H, 5·3; N, 19·3. $C_8H_8ON_2$ requires C, 64·85; H, 5·4; N, 18·9%).

When 1-acetyl-2-aminopropene (9·9 g., 0·1 mol.) and malononitrile (13·2 g., 0·2 mol.) were used 2 : 6-dicyano-3 : 5-dimethylaniline (6·6 g.), m. p. 210—211°, and 5 : 5-dicyano-2-hydroxy-4-methylpenta-2 : 4-diene (4·6 g.), m. p. 289—290°, were again produced.

Condensation of acetylacetone and malononitrile. 5N-Sodium hydroxide (10 c.c.) was slowly run into a stirred mixture of acetylacetone (20 g., 0·2 mol.) and malononitrile (26·4 g., 0·4 mol.) in water (200 c.c.), and stirring was continued for 4 hours. The solid was collected, washed with water, and separated by treatment with dilute alkali, giving 5 : 5-dicyano-2-hydroxy-4-methylpenta-2 : 4-diene (19·8 g.), m. p. 287—288°, and 2 : 6-dicyano-3 : 5-dimethylaniline (3·4 g.), m. p. 213—215°.

Hydrolysis of 2 : 6-dicyano-3 : 5-dimethylaniline. 2 : 6-Dicyano-3 : 5-dimethylaniline (2·9 g.) was heated under reflux with 50% sulphuric acid (15 c.c.) for 6 hours. The reaction mixture was made alkaline with sodium hydroxide and ether extracted. Evaporation of the solvent and distillation gave 3 : 5-dimethylaniline, b. p. 221—222°/750 mm. This was purified for analysis by being refluxed over solid sodium hydroxide and redistilled [Found : C, 79·2; H, 8·9; N, 11·6%; *M* (nitrite titration), 120·6. Calc. for $C_8H_{11}N$: C, 79·35; H, 9·1; N, 11·55%; *M*, 121]. Recrystallisation from alcohol of the residue from the first distillation gave needles of 2-*carbamyl*-3 : 5-*dimethylaniline*, m. p. 160° (Found : C, 65·95; H, 7·6; N, 16·9. $C_9H_{12}ON_2$ requires C, 65·85; H, 7·3; N, 17·1%).

3 : 5-Dimethylaniline (2·05 g.), from a second hydrolysis, *p*-acetamidobenzenesulphonyl chloride (2·74 g.), and pyridine (4 c.c.) were heated, with stirring, at 60—70° for 1 hour and then at 40° for 16 hours. The mixture was diluted with water and stirred for 18 hours, and the aqueous supernatant liquor then decanted off. The solid, after being washed, was refluxed gently with N-hydrochloric acid (20 c.c.) for 7 hours, cooled and filtered, the filtrate was made alkaline with ammonia solution, and the product collected. Recrystallisation from aqueous alcohol gave prismatic needles, m. p. 145—147° undepressed on admixture with authentic 5-*p*-sulphanilamido-*m*-xylene.

Acid hydrolysis of 5 : 5-dicyano-2-hydroxy-4-methylpenta-2 : 4-diene. 5 : 5-Dicyano-2-hydroxy-4-methylpenta-2 : 4-diene (1·0 g.) and 50% sulphuric acid (4·3 c.c.) were heated under reflux for 6 hours. The mixture was neutralised with sodium hydroxide and then made slightly alkaline with ammonia solution. The solid was collected and crystallised from water giving 2-hydroxy-4 : 6-dimethylpyridine as feathery needles, m. p. 173—175°. Sublimation raised the m. p. to 177—178°, undepressed with an authentic specimen (Moir, *loc. cit.*) (Found : C, 68·05; H, 7·2; N, 11·7. Calc. for C_7H_9ON : C, 68·3; H, 7·3; N, 11·4%).

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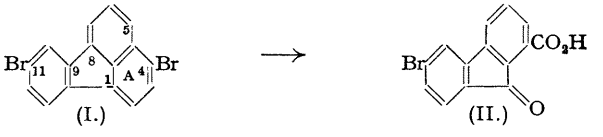
249. *The Oxidation of* 4 : 11-*Dibromofluoranthene.*

By NEIL CAMPBELL, W. H. STAFFORD, and J. F. K. WILSHIRE.

IT was shown (Campbell, Easton, Rayment, and Wilshire, *J.*, 1950, 2784) that chromic acid oxidation of dibromofluoranthene yields 2 : 7-dibromofluorenone-1-carboxylic acid and a monobromo-acid provisionally regarded as 6-bromofluorenone-1-carboxylic acid (II). We have now



confirmed this formulation by decarboxylation of the acid to 3-bromofluorenone, showing that the acid (II) is formed by oxidation of the ring A (I) and providing further evidence that the original compound is 4 : 11-dibromofluoranthene (cf. Holbro and Tagmann, *Helv. Chim. Acta*, 1950, **33**, 2178).

Experimental.—The mixture of acids obtained by oxidation of dibromofluoranthene was boiled with successive 500-ml. portions of calcium hydroxide solution and the hot solutions were filtered. The cold filtrates deposited the calcium salt of the dibromo-acid and the filtrate on acidification gave 6-bromofluorenone-1-carboxylic acid, which crystallised in yellow rosettes, m. p. 253—255°, from glacial acetic acid and gave a *methyl* ester, m. p. 126—127° (Found : Br, 25·8. $C_{15}H_9O_3Br$ requires Br, 25·2%).

The acid on decarboxylation with quinoline and copper-bronze afforded 3-bromofluorenone, yellow leaflets (from light petroleum), m. p. 162—163°, undepressed on admixture with an authentic sample Found: Br, 31·2. Calc. for $C_{13}H_7OBr$: Br, 30·9%). This substance was prepared from *o*-(4-bromobenzoyl)benzamide by Miller and Bachman's method (*J. Amer. Chem. Soc.*, 1935, **57**, 2443), but we were unable to attain the high yields reported by them. By adding a benzene solution of the acid chloride to saturated methanolic ammonia we prepared the substituted benzamide, and after repeated crystallisation from xylene, xylene–acetone, and acetic acid obtained it as needles, m. p. 224° (Found: N, 4·4; Br, 24·1. Calc. for $C_{13}H_{10}O_2NBr$: N, 4·6; Br, 26·3%). The substance is clearly not quite pure (probably owing to adhering solvent), but nevertheless it melts nearly 40° higher than Miller and Bachman's product (m. p. 184·5—185°), which we think was a mixture of acid and amide. The amide was converted *via* 2-amino-4′-bromobenzophenone, m. p. 112°, into 3-bromofluorenone, which had the m. p. given by other workers (*e.g.*, Heilbron, Hey, and Wilkinson, *J.*, 1938, 113).

Thanks are expressed to the Carnegie Trust for the Universities of Scotland for the award of a scholarship to one of us (W. H. S.), and to the Anglo-Iranian Oil Co. Ltd. for a grant.

UNIVERSITY OF EDINBURGH. [*Received, January 9th*, 1951.]

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250. *Some Hydroxyanthraquinones and Derivatives.*

By LINDSAY H. BRIGGS and G. A. NICHOLLS.

IN connection with investigations of the anthraquinone pigments from the bark of *Coprosma* species (cf. Briggs and Thomas, *J.*, 1949, 1246, and earlier papers) and the systematic study of the polarographic behaviour of anthraquinone derivatives (forthcoming communications) we have prepared the following compounds by new or modifications of existing methods.

2 : 6-*Dihydroxyanthraquinone.*—Although insoluble in acids, 2 : 6-diaminoanthraquinone may be diazotised and converted into the 2 : 6-dihydroxy-compound. An ice-cold aqueous solution (50 c.c.) of sodium nitrite (7 g., 2 mols.) was added to an ice-cold suspension of 2 : 6-diaminoanthraquinone (12 g., 1 mol.) in sulphuric acid (20 g. diluted with 100 c.c. of water; 4 mols.), and the mixture shaken for 10 minutes, warmed on the water-bath until most of the frothing had ceased (20 minutes), and finally boiled for 20 minutes. The yellowish-brown product was filtered off, boiled with barium hydroxide solution (17 g. in 250 c.c.) and filtered whilst hot. The precipitate was again extracted with boiling water (250 c.c.) and filtered. On acidification of the combined filtrates a yellow precipitate was formed which was well washed with water (yield, 4 g., 33%) and purified by chromatography of its acetone solution on magnesia from which it was recovered by dissolution of the magnesia in dilute hydrochloric acid. The product was crystallised twice from alcohol (charcoal), forming golden-yellow rods, m. p. >330° [Schunck and Roemer, *Ber.*, 1876, **9**, 379, and Heller, *Angew. Chem.*, 1929, **42**, 170, record m. p. >330° and 360° (decomp.), respectively].

The diacetate, prepared by acetylation of the above compound (37 mg.) with acetic anhydride (0·75 c.c.) and 60% perchloric acid (1 drop), crystallised from acetic anhydride in almost colourless plates of constant m. p. 233—234° (Perkin, *J.*, 1873, **26**, 19, records pale yellow crystals, m. p. 228—229°, for this derivative).

2 : 6-*Dimethoxyanthraquinone.*—2 : 6-Dihydroxyanthraquinone (43 mg.), in dry acetone (8 c.c.), was heated at 100° with methyl sulphate (0·5 c.c.) and anhydrous potassium carbonate for 2 hours. The mixture was poured into cold water (15 c.c.), the acetone removed by distillation, and the product collected as almost colourless plates, m. p. 257° unchanged on recrystallisation from glacial acetic acid. Schunck and Roemer (*loc. cit.*; cf. also D.R.P. 167699 1905) record yellow needles, m. p. 250°, from benzene.

Attempted Synthesis of 1 : 3 : 5-*Trihydroxyanthraquinone.*—A mixture of *m*-hydroxybenzoic acid (4·6 g., 1 mol.) and 3 : 5-dihydroxybenzoic acid (5·1 g., 1 mol.) was heated with concentrated sulphuric acid (18 c.c., 10 mols.) for an hour at 100°. Next morning, the mixture was heated at 140—150° for 10 minutes and the cooled reddish-brown solution poured into boiling water (300 c.c.). The green precipitate (2·6 g., 30%) was extracted with acetone leaving a black residue. Chromatography of the acetone solution on magnesia gave two main red and orange bands; decomposition of the red band with hydrochloric acid gave a bright green precipitate which, on being rechromatographed, afforded red and orange bands identical in appearance with those of the first chromatogram, a phenomenon which was reproduced on repeating the cycle. However, by repeated dissolution of the green precipitate in aqueous sodium hydroxide solution, and reprecipitation from the hot solution with glacial acetic acid, a yellow product was finally obtained, giving an orange band on a magnesia column. After rechromatographing the material from the combined orange bands, pure anthrachrysone (1 : 3 : 5 : 7-tetrahydroxyanthraquinone) was obtained, crystallising from alcohol in yellow needles which sublimed, but did not melt below 350° (Noah, *Ber.*, 1886, **19**, 751, records yellow needles, m. p. >360°). The sodium hydroxide, sodium carbonate, and concentrated sulphuric acid solutions were red; and a brown colour was given with ferric chloride solution.

The tetra-acetate, prepared by acetylation with acetic anhydride and 60% perchloric acid, crystallised from acetic anhydride in pale-cream rods which slowly decomposed at 239°, but when heated quickly melted at 259° (decomp.) (Noah, *loc. cit.*, and Lauer, *J. pr. Chem.*, 1932, **135**, [ii], 361, record m. p. 254—256°).

Anthrachrysone tetrabenzoate was obtained as pale-cream rods, m. p. 280—283·5°, from dioxan (Found : C, 72·55; H, 3·9. $C_{42}H_{24}O_{10},0{\cdot}5H_2O$ requires C, 72·3; H, 3·6%).

Anthrachrysone Tetramethyl Ether.—This was prepared as described above for 2 : 6-dimethoxyanthraquinone, the mixture being heated under reflux for 2 hours. The m. p. of the product (291—293°) confirms that given by Fischer and Ziegler (*J. pr. Chem.*, 1912, **86**, [ii], 297) but is not in agreement with that recorded by Heller (" Elsevier's Encyclopædia of Organic Chemistry," Vol. 13, p. 607). This derivative is insoluble in alkali and almost insoluble in acetone.

Anthrachrysone 3 : 7-*Dimethyl Ether.*—Anthrachrysone (214 mg.), dry acetone (15 c.c.), anhydrous potassium carbonate (4 g.), and methyl sulphate (0·5 c.c.) were heated under reflux for 10 minutes. The product (100 mg.), obtained in this case from the carbonate by treatment with acid, formed, after two crystallisations from nitrobenzene, intensely yellow plates, m. p. 287—288° (with sublimation) (Found : C, 64·0; H, 4·3. Calc. for $C_{16}H_{12}O_6$: C, 64·0; H, 4·0%). The compound forms an insoluble sodium salt with aqueous sodium hydroxide solution. Fischer and Ziegler (*loc. cit.*) record bronze prisms, forming a yellowish-red solution in alkali, but they give no m. p.

Purpurin trimethyl ether. Purpurin (240 mg.) was similarly methylated with methyl sulphate (1 c.c.), more methyl sulphate (0·5 c.c.) being added after an hour and the heating then continued for 3½ hours. The crude product (300 mg.) was purified by chromatography on magnesia; and the *ether* was obtained as yellow rods, which were recrystallised from 80% alcohol and ethyl acetate. It had m. p. 169—171° (Found : C, 68·2; H, 4·6. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%).

The analyses are by Drs. Weiler and Strauss, Oxford, and Dr. T. S. Ma, Microchemical Laboratory, Otago University, Dunedin.

The authors are indebted to the Chemical Society, the Australian and New Zealand Association for the Advancement of Science, the Royal Society of New Zealand, and the Research Fund Committee of the University of New Zealand for continued grants, and to Imperial Chemical Industries Limited for gifts of chemicals; one of them (G. A. N.) expresses gratitude for a Research Fellowship of the University of New Zealand.

AUCKLAND UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND. [*Received, December 29th*, 1950.]

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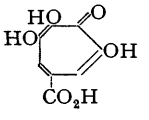
251. *Puberulic and Puberulonic Acids. Part III. The Structure of Puberulonic Acid.*

By A. W. JOHNSON, N. SHEPPARD, and A. R. TODD.

IN previous publications (Corbett, Johnson, and Todd, *Chem. and Ind.*, 1949, 626; *J.*, 1950, 6) evidence was presented showing that puberulic acid had structure (I), and it was suggested on the then available facts that puberulonic acid might be represented by one of the lactonic structures (II) or (III). Structures of this type were advanced to explain (*a*) the yellow colour of the acid, (*b*) its condensation with *o*-phenylenediamine to a highly-coloured product, $C_{15}H_8O_5N_2$, considered to be a quinoxaline derivative (Corbett, Hassall, Johnson, and Todd, *J.*, 1950, 1), (*c*) its ready conversion into puberulic acid on being heated with water or dilute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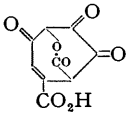
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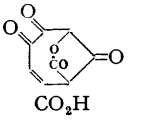
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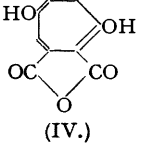
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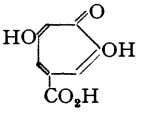
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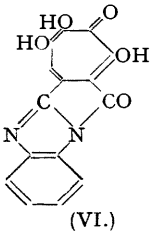
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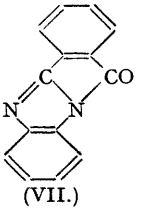
(VII.)

acids, and (*d*) its failure to acetylate with acetic anhydride under conditions which readily effected acetylation of puberulic acid (Birkinshaw and Raistrick, *Biochem. J.*, 1932, **26**, 441). The titration curve of puberulonic acid suggested the presence in it of a lactone or other potential acid group. Lack of material prevented further work on puberulonic acid until recently, and in the meantime, Aulin-Erdtman, on the basis of an extensive study of the ultra-violet absorption of the acid at various pH values, maintained that it must contain an actual, rather than a

potential, tropolone system, and suggested for it the anhydride structure (IV) (Chemical Society Symposium on Tropolones, London, 2nd November, 1950).

In collaboration with Dr. P. W. Brian and Mr. P. J. Curtis of Imperial Chemical Industries Limited, Butterwick Research Laboratories, Welwyn, we have prepared a further quantity of puberulonic acid and find that its infra-red spectrum supports Aulin-Erdtman's structure (IV) in every respect. The main strong frequencies in the 1500—1900-cm.$^{-1}$ region were as follows, the values for puberulic acid and stipitatic acid (V) being given for comparison.

Puberulonic acid	1545	1615	—	1770	1830
Puberulic acid	1535	1595	1690	—	—
Stipitatic acid	1570	1610	1705	—	—

The first two absorption bands have been assigned (Scott and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 240; see also Bartels-Keith and Johnson, *Chem. and Ind.*, 1950, 677) to the basic tropolone structure; the frequency range 1720—1680 cm.$^{-1}$ is generally considered to be characteristic of the C=O group in an acid (*i.e.*, absent in puberulonic acid), and the two bands above 1750 cm.$^{-1}$ are characteristic of the anhydride system (Randall, Fowler, Fuson, and Dangl, " Infra-red Determination of Organic Structures," New York, 1949, p. 20). Confirmatory evidence is available in the 3000-cm.$^{-1}$ region characteristic of O–H groups. Unlike puberulonic acid, puberulic and stipitatic acids show weak, broad absorption bands centred near 2700 cm.$^{-1}$, which may be the strongly bonded O–H groups of the acid dimer. Furthermore, puberulonic acid shows an absorption band between 3100 and 3200 cm.$^{-1}$ which is consistent with the presence of hydroxy-groups in the tropolone nucleus.

The absorption spectra leave little doubt as to the correctness of structure (IV) for puberulonic acid, and the evidence on which the lactone structures (II) and (III) were based must be reconsidered. The anhydride structure (IV) accommodates the required potential acid grouping just as well as a lactone structure and gives an equally ready explanation for the conversion into puberulic acid; that the anhydride ring always re-forms immediately when alkaline solutions of puberulonic acid are acidified is unusual but no more. The yellow colour of puberulonic acid can be ascribed to the anhydride grouping, and it may be recalled that similar deepening of colour in passing from a dicarboxylic acid to its anhydride has been observed in the fulgenic acid–fulgide series (*e.g.*, Stobbe, *et al.*, *Annalen*, 1908, **359**, 2; 1911, **380**, 120). The condensation product with *o*-phenylenediamine is clearly not a quinoxaline. Its structure has not been determined but is probably of type (VI); this would account for our failure to decarboxylate it (cf. Corbett, Johnson, and Todd, *loc. cit.*). Compounds [*e.g.*, *o*-benzoylene-1 : 2-benziminazole (VII)] analogous to (VI) have been isolated from the products of reaction of *o*-phenylenediamine with various anhydrides (Lieb, *Monatsh.*, 1918, **39**, 873; Bistrzycki and Fässler, *Helv. Chim. Acta*, 1923, **6**, 519). The failure of puberulonic acid to acetylate is rather unexpected on the basis of structure (IV), and it seems possible that the preparation of an acetyl derivative may yet be effected under special conditions.

While this note was in preparation, we learned from Woodward, Hassall, and Sondheimer that they had independently reached the same conclusion regarding the correctness of structure (IV) and on the same evidence. We thank Professor R. B. Woodward for his courtesy in sending us an account of his findings. Correspondence with Mrs. G. Aulin-Erdtman revealed that she, too, has determined the infra-red spectrum of puberulonic acid and her results are in the course of publication.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, January 8th*, 1951.]

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252. *The* N-*Toluene*-p-*sulphonyl Derivatives of the* p-*Halogenoanilines.*

By J. RATCLIFFE.

THE melting point of toluene-*p*-sulphon-4-chloroanilide has been reported as 95° (Chattaway, *J.*, 1904, **85**, 1181) and 119° (D.R.-P. 164,130; *Chem. Zentr.*, 1905, II, 1476). The higher m. p. is also recorded by Curd and Rose (*J.*, 1946, 734), but had been disputed by Halberkann (*Ber.*, 1921, **54**, 1846). This compound and the bromo- and iodo-analogues have been prepared in another connection with the following result. The chloro-compound formed prismatic needles, m. p. 95°, from aqueous ethanol in the cold (cf. Chattaway and Halberkann, *locc. cit.*), but had m. p. 122° when formed (as needles) from hot ethanol or when grown slowly (as large colourless

prisms) from cold ethanol; the bromo-compound had m. p. 102°, small colourless prismatic needles from aqueous ethanol, or m. p. 149°, colourless prismatic needles from hot ethanol and large prisms from cold ethanol; the iodo-compound had m. p. 96°, fine needles from aqueous ethanol, or m. p. 171°, fine needles from ethanol. As noted by Halberkann, a change of solvent altered the crystal habit.

On storage, the lower-melting forms changed in all three cases to the higher-melting variety but no corresponding changes in crystal form were revealed under the microscope. Lower-melting forms could not be produced from apparatus contaminated with the corresponding form of higher m. p. Toluene-*p*-sulphon-4-bromoanilide, m. p. 102°, dissolved readily in cold sodium hydroxide solution, but the solution frequently deposited a less soluble sodium derivative of the higher-melting form which furnished the form of m. p. 149° on treatment with mineral acid, and reverted to the insoluble sodium derivative, which did not melt below 300°, in alkali. The higher-melting form did not respond to attempts to reconvert it into the one of lower m. p.

Experimental.—The lower-melting forms could be obtained as follows: The appropriate *p*-halogenoaniline (0·1 g.-mol.) in solution in 30 ml. of pyridine was slowly treated with the calculated amount of toluene-*p*-sulphonyl chloride. Heat was generated and a red fluorescence developed which diminished during 30 minutes' heating on a water-bath. After removal of pyridine by hydrochloric acid, the residual oil or paste was taken up in cold ethanol, water was added to faint turbidity, and the solution refrigerated. The crystalline deposits from several such dilutions were collected (total yield 80—90%) and recrystallised to attain the m. p.s quoted. Dissolution of the crude products in cold sodium hydroxide solution with the object of eliminating the ditoluene-*p*-sulphonyl derivatives contributed little to the purity of the products and involved the risk of change to the higher-melting form, particularly for the bromo-compound as indicated above.

To prepare the forms of higher m. p., it is only necessary to contaminate the apparatus beforehand with this form and proceed as before, the deposits then solidifying readily on dilution of the pyridine and stirring.

Toluene-*p*-sulphon-4-chloroanilide had m. p. 122° (Found: Cl, 12·5; S, 11·4. Calc. for $C_{13}H_{12}O_2NClS$: Cl, 12·6; S, 11·4%); the *bromoanilide* had m. p. 149° (Found: Br, 24·4; S, 9·7. $C_{13}H_{12}O_2NBrS$ requires Br, 24·5; S, 9·8%), and the *iodoanilide* m. p. 171° (Found: I, 33·9; S, 8·5. $C_{13}H_{12}O_2NIS$ requires I, 34·05; S, 8·6%). These analyses relate to forms of low m. p. which had been left to attain the higher m. p.

By stopping the condensation of *p*-bromoaniline at an early stage, dilution with water, and extraction with ethanol, hair-like red needles were deposited, m. p. 131°. At the m. p. these red needles lose colour, which is partly restored by immediately stopping the heating, but further heating results in a colourless product, m. p. 149°, identified as toluene-*p*-sulphon-4-bromoanilide. The red needles appear to be an intermediate product containing pyridine which is driven off by heat. The amount of this red compound which could be isolated was too small for fuller investigation.

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253. *The Preparation and Properties of* tert.-*Butyl Bromide.*

By D. BRYCE-SMITH and K. E. HOWLETT.

IN connection with another research, pure *tert.*-butyl bromide was required; but none of the methods of preparation described in the literature (Norris, *Amer. Chem. J.*, 1907, **38**, 641; *Org. Synth.*, Coll. Vol. 1, p. 38) appeared entirely satisfactory. In particular, Norris has reported a yield of 90%, but in our hands his procedure has given about 40% yield of impure product. We have found the following to be a superior method of preparation.

Experimental.—*tert.*-Butyl alcohol (118 g., 1·6 g.-mols.) was added with stirring during 15 minutes to a mixture of hydrobromic acid (370 c.c. of 48% w/w solution; 3·2 g.-mols.) and concentrated sulphuric acid (100 c.c.), and the temperature was maintained at 20°. After a further 30 minutes, the organic layer was separated, washed twice with water, and dried (calcium chloride plus a trace of calcium oxide). On distillation, the first fraction (a few c.c.) contained dissolved *iso*butene and was rejected. The bulk (186 g., 85%) of the distillate had b. p. 53°/400 mm., and there was no appreciable distillation residue. The product showed no unsaturation when tested with bromine in carbon tetrachloride and had f. p. −16·4° to −16·7°. The use of twice the quantity of sulphuric acid increased the yield to 90%, but this slight increase scarcely justifies the use of such an excess.

The product obtained at this stage is of suitable purity for normal synthetic work. Further purification was, however, effected by fractional crystallisation. This process, repeated four times raised the f. p. to −16·3°, whilst the purified product and rejected matter differed in n_D^{25} values by only 0·0002. Good freezing "flats" were obtained in the last two crystallisations. These determinations show that no appreciable isomerisation occurs in the preparation since the isomeric bromobutanes differ markedly from the tertiary compound in freezing point and refractive index. The yield of pure product was 65%, based upon the *tert.*-butyl alcohol used. Pure *tert.*-butyl bromide slowly decomposes when

kept; the decomposition appears to be retarded by the addition of about 0·1% of calcium oxide and storage in the dark at a low temperature.

The following physical constants were obtained for pure *tert.*-butyl bromide (cf. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, 1950, p. 268): b. p.$_{760}$ 72·8° (with slight decomp.); f. p. −16·3° (sulphur dioxide vapour-pressure thermometer); d_4^{25} 1·2125 g./c.c.; n_D^{25} 1·4249.

T°.	Vapour pressure.	T°.	Vapour pressure.	T°.	Vapour pressure.
0·0	42·8	22·7	121·9	40·0	243·4
6·8	59·0	25·0	135·3	49·3	344·5
10·6	70·7	28·4	155·4	56·6	450·4
15·7	90·0	31·3	174·5	63·5	567·6
20·8	112·9	35·7	209·3	72·8	758·0

The vapour pressure of *tert.*-butyl bromide was measured, an isoteniscope being used, over the range 0—73°. The results, given in the table, can be expressed by the equation $\log_{10} p = 7·627 - 1640/T$, whence the Trouton constant is 21·1.

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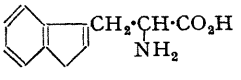
254. *A Synthesis of α-Amino-β-3-indenylpropionic Acid.*

By L. H. GROVES and G. A. SWAN.

3-BROMOMETHYLINDENE (Clemo, Groves, Munday, and Swan, *J.*, 1951, 863) was condensed with ethyl formamidomalonate and the product hydrolysed and decarboxylated to give α-amino-β-3-indenylpropionic acid (inset), an analogue of tryptophan.



Mr. T. K. Miller, of the Department of Bacteriology, King's College, Newcastle-on-Tyne, kindly investigated the effect of this amino-acid on the growth of *Lactobacillus arabinosus*, for which tryptophan is an essential metabolite, and found that it could neither replace nor antagonise tryptophan, the latter even in concentration ratios of 12 : 1 with respect to the indene-acid and tryptophan.

Experimental.—Ethyl α-carbethoxy-α-formamido-β-3-indenylpropionate. To a solution of sodium (0·25 g.) in absolute ethanol (20 ml.) were added ethyl formamidomalonate (2·23 g.) (Galat, *J. Amer. Chem. Soc.*, 1947, **69**, 965) and 3-bromomethylindene (2·3 g.), and the mixture kept at room temperature for 18 hours. It was then heated on the water-bath for a further 18 hours, the bulk of the ethanol removed by distillation, the residue treated with water, the mixture extracted with chloroform, the extract dried (Na_2SO_4), and the solvent removed. The residue (2·3 g.) on recrystallisation from dilute ethanol gave the *diester* as short colourless needles (1·95 g.), m. p. 102—103° (Found: C, 65·1; H, 6·3. $C_{18}H_{21}O_5N$ requires C, 65·25; H, 6·35%).

The above ester (1·0 g.) in 10% ethanolic potassium hydroxide (10 ml.) was heated under reflux for 30 minutes in an atmosphere of nitrogen. After cooling, water (50 ml.) was added and the solution washed successively with chloroform and ether. The ether was removed in a stream of air at room temperature, and the mixture was cooled in ice and acidified (dilute hydrochloric acid), giving the *dicarboxylic acid* (0·65 g.), m. p. 128—130° (decomp.). Recrystallisation from a small volume of ether afforded colourless plates, m. p. 133—134° (decomp.) (Found: C, 57·75; H, 4·8. $C_{14}H_{13}O_5N,H_2O$ requires C, 57·35; H, 5·1%).

α-Formamido-β-3-indenylpropionic acid. An almost theoretical yield of this *acid*, m. p. 161—163°, was obtained when the above dicarboxylic acid was heated at 100°/15 mm. for 1 hour. Recrystallisation from hot water afforded pale yellow needles, m. p. 163—164° (Found: C, 67·6; H, 5·95. $C_{13}H_{13}O_3N$ requires C, 67·55; H, 5·65%).

α-Amino-β-3-indenylpropionic acid. The formamido-acid (1·0 g.) in 4N-sulphuric acid (16 ml.) with a crystal of stannous chloride was heated on the water-bath for 3 hours in an atmosphere of nitrogen. The solution was diluted with water to 120 ml., boiled with charcoal, neutralised to pH 6—7 while hot with barium hydroxide, filtered from barium sulphate, and concentrated under reduced pressure until precipitation of the *amino-acid* (0·8 g.) occurred. The product was purified by dissolution in a large volume of water, boiling with charcoal, filtration, and concentration. It crystallised in granular clusters, m. p. 226—228° (decomp.) (Found: C, 70·8; H, 6·25. $C_{12}H_{13}O_2N$ requires C, 70·95; H, 6·4%).

The amino-acid (0·1 g.) was heated in anhydrous formic acid (0·3 ml.) for 3 hours at 100°, the solvent removed under reduced pressure, and this procedure twice repeated. The brown syrup remaining was boiled with water (5 ml.). The formyl derivative crystallised on cooling, and had m. p. 161—163°, not depressed on admixture with the amido-acid prepared as above.

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