

## 816. The Decomposition of Some Esters of Toluene-*p*-sulphonic Acid.

By W. J. HICKINBOTTOM and N. W. ROGERS.

THE literature contains references to the instability of sulphonic esters of benzyl and allyl alcohol and to the relatively unstable esters of some secondary alcohols.<sup>1</sup> In all these decompositions, the free sulphonic acid is formed together with dark resin: from the esters of some secondary alcohols, formation of olefin has been reported.<sup>2</sup>

To aid another investigation, *cyclohexyl*, *cyclopentyl*, and 1 : 3 : 3-trimethylbutyl toluene-*p*-sulphonate were examined. The pure esters can be preserved for months in the absence of moisture or acid: less pure samples decompose after a week or so with the formation of toluene-*p*-sulphonic acid and olefins and their polymers. The decomposition is hastened by heat and by addition of free sulphonic acid. At 120° the *cyclohexyl* ester decomposes completely in 1 hr. if sulphonic acid is added. The neutral product is resolved by distillation into well-defined portions corresponding to the C<sub>12</sub> and the C<sub>18</sub> hydrocarbon and a considerable amount of higher polymers. The C<sub>12</sub> fraction contains a high proportion of saturated hydrocarbons: *dicyclohexyl* is present, and hydrocarbons which could not be dehydrogenated completely to aromatic hydrocarbons and presumably contain methyl*cyclopentane* rings. The C<sub>18</sub> fraction was obviously a mixture and contained unsaturated hydrocarbons. Decomposition of the *cyclopentyl* ester gave similar products. The third ester gave a dimer which was largely unsaturated and still retained in part the original structure of the alcohol; trimers and polymers were also formed.

*Experimental.*—*Preparation of cyclohexyl toluene-p-sulphonate.* Attention to detail is necessary for the best yield: in particular the pyridine should be dry and freshly distilled over barium oxide; the sulphonyl chloride also should be dry and free from toluene-*p*-sulphonic acid and from hydrochloric acid.

*cycloHexanol* (180 g., 1.8 moles) and pyridine (650 c.c.) were mixed in a 1.5-l. round-bottomed three-necked flask fitted with a Hirschberg stirrer driven by a heavy-duty motor. At -8° toluene-*p*-sulphonyl chloride (323 g., 1.7 moles) was added in three equal portions to the stirred solution, sufficient time being allowed to elapse between each addition to keep the temperature below -3°. The mixture became deep pink; it was stirred for 4 hr. after the chloride had been added and the temperature allowed to rise to 0°. The whole was stored at 0° overnight. The mixture, which had become solid, was removed with cold water (1500 c.c.) and treated with concentrated hydrochloric acid (1 l.). The crude ester was a golden-yellow oil which solidified (410 g., average of 15 preparations).

Purification is best effected by dissolving the crude ester in the minimum amount of light petroleum (b. p. 40—60°), separating the clear upper layer, and chilling it while stirring. *cycloHexyl toluene-p-sulphonate* separates as a white powder, m. p. 45.5—46° (380 g.) (Tipson *et al.*<sup>3</sup> give m. p. 45—46°).

*Thermal decomposition.* *cycloHexyl toluene-p-sulphonate* (350 g.) and toluene-*p*-sulphonic acid (50 g.) were heated with occasional shaking at 120° under reflux for 1 hr. After about 45—50 min., there was separation into two layers. Toluene-*p*-sulphonic acid was removed by neutralisation of the cooled mixture with a slight excess of aqueous sodium hydroxide (150 g. in 500 c.c. of water), and the neutral product taken up in ether, washed, dried, and distilled through a short Vigreux column, giving fractions, (a) b. p. 68—74°/1.2 mm.,  $n_D^{20}$  1.4973 (16.1 g.), (b) b. p. 140—160°/1.2 mm.,  $n_D^{20}$  1.5020 (6.2 g.), (c) b. p. 185—205°/0.1 mm.,  $n_D^{20}$  1.5265 (6.0 g.), and (d) black residue (60 g.). No appreciable amount of *cyclohexene* was obtained. Redistillation of fraction (a) over sodium gave considerable material of b. p. 109—110°/17 mm.,  $n_D^{20}$  1.4775 (Found: C, 86.8; H, 13.4%; *M*, 155. Calc. for C<sub>12</sub>H<sub>22</sub>: C, 86.7; H, 13.3%; *M*, 166. Calc. for C<sub>12</sub>H<sub>20</sub>: C, 87.7; H, 12.3%). It was evident from the refractive indices of consecutive

<sup>1</sup> Földi, *Ber.*, 1920, **53**, 1836; 1927, **60**, 656; 1928, **61**, 1609; Gilman and Beaber, *J. Amer. Chem. Soc.*, 1925, **47**, 523; Medwedew and Alexejewa, *Ber.*, 1932, **65**, 131.

<sup>2</sup> Drahowzal and Klamann, *Monatsh.*, 1951, **82**, 467.

<sup>3</sup> Tipson, Clapp, and Cretcher, *J. Org. Chem.*, 1947, **12**, 133.

small fractions that more than one compound was present and that a clean separation could not be effected. The fractions were relatively stable in dilute aqueous potassium permanganate but were attacked by bromine in carbon tetrachloride. On treatment in chloroform with ozonised oxygen, 7 g. of the redistilled fraction gave 6.6 g. of recovered hydrocarbon, b. p. 109—115.5°/15 mm.,  $n_D^{20}$  1.4758—1.4783. Dehydrogenation (0.8 g.) over palladised charcoal at 400° gave diphenyl, m. p. and mixed m. p. 70° (0.25 g.), and a liquid apparently resistant to further dehydrogenation.

Fraction (b), redistilled over sodium, also gave no material of sufficiently constant b. p. or refractive index to indicate the separation of pure compound; all the fractions were unsaturated towards permanganate. A fraction, b. p. 118—122°/0.4 mm.,  $n_D^{20}$  1.5050, contained C, 87.2; H, 12.6%, and had  $M$ , 230 (Calc. for  $C_{18}H_{30}$ : C, 87.7; H, 12.3%;  $M$ , 246. Calc. for  $C_{18}H_{32}$ : C, 87.0; H, 13.0%).

cycloPentyl toluene-*p*-sulphonate. This ester was prepared as was the cyclohexyl ester: it is best purified by chilling its concentrated solution in light petroleum (b. p. 40—60°), then having m. p. 27° (Drahowzal and Klamann<sup>2</sup> give m. p. 28°). 280 g. of this ester, heated at 90° with 52 g. of toluene-*p*-sulphonic acid, gave a considerable amount of polymer and a fraction, b. p. 80—86°/26 mm.,  $n_D^{20}$  1.476—1.480 (18.9 g.) (Found: C, 87.1; H, 12.8. Calc. for  $C_{10}H_{16}$ : C, 86.9; H, 13.1. Calc. for  $C_{10}H_{16}$ : C, 88.2; H, 11.8%). It slowly decolorises permanganate solution and reacts more rapidly with bromine in carbon tetrachloride.

1 : 3 : 3-Trimethylbutyl toluene-*p*-sulphonate, colourless crystals (from light petroleum), m. p. 46° (Found: C, 61.6; H, 8.1; S, 11.8.  $C_{14}H_{22}O_3S$  requires C, 62.1; H, 8.2; S, 11.8%), decomposed at 90° after addition of toluene-*p*-sulphonic acid. The neutral product from 130 g. of ester was resolved by distillation into fractions, (i) b. p. 70—90°,  $n_D^{20}$  1.3950—1.4032 (5 g.), (ii) b. p. 95—106°/16 mm.,  $n_D^{20}$  1.4455—1.4513 (20 g.), (iii) b. p. 150—160°/16 mm.,  $n_D^{20}$  1.458 (5 g.), and (iv) a higher-boiling residue. The main fraction was unsaturated and is evidently a dimer from the 2 : 2-dimethylpentenes (Found: C, 85.7; H, 14.4%;  $M$ , 177. Calc. for  $C_{14}H_{26}$ : C, 85.6; H, 14.4%;  $M$ , 196). On ozonolysis it gave a mixture of carbonyl compounds in which only 4 : 4-dimethylpentan-2-one was identified with certainty (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 97—98°). No formaldehyde was detected. Fraction (iii) was unsaturated and consists essentially of trimerised 2 : 2-dimethylpentenes. Fraction (i) was evidently a mixture and contained some saturated hydrocarbon.

The authors thank the Hydrocarbons Research Group of the Institute of Petroleum for support.

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[Received, May 14th, 1957.]

### 817. Complex Fluorides. Part X.\* The Magnetic Moment of Hydrated Cobalt(III) Fluoride.

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THE only strongly paramagnetic complexes of trivalent cobalt are the blue complex fluorides  $M_3CoF_6$  (where  $M = Li, Na, K, Rb, \text{ or } Cs$ ),<sup>1</sup> for which the magnetic moment is about 5.2 B.M. (Bohr magnetons), close to the "spin-only" value for four unpaired electrons (4.90 B.M.). As the hydrated cobaltic ion  $Co_6H_2O_3^{3+}$ , which is also blue, is diamagnetic,<sup>2</sup> the magnetic properties of the blue hydrated fluoride  $CoF_3 \cdot 3.5H_2O$  have now been investigated. This unstable compound, obtained by electrolytic oxidation of a solution of cobaltous fluoride in 40% hydrofluoric acid,<sup>3</sup> might have two types of cobalt atom in a structure such as  $[Co_6H_2O][CoF_6] \cdot H_2O$ , or might be a simple aquo-compound  $[CoF_3 \cdot 3H_2O] \cdot 0.5H_2O$ . There is no solvent in which its conductivity can be measured, but magnetic data can provide structural information.

The hydrated fluoride obeys the Curie-Weiss law, and from measurements over the

\* Part IX, *J.*, 1957, 3761.

<sup>1</sup> Hoppe, *Rec. Trav. chim.*, 1956, **75**, 569; for an earlier report on  $K_3CoF_6$  see Grey, *J. Amer. Chem. Soc.*, 1946, **68**, 605.

<sup>2</sup> Friedmann, Hunt, Plane, and Taube, *ibid.*, 1951, **73**, 4028.

<sup>3</sup> Barbieri and Calzolari, *Z. anorg. Chem.*, 1928, **170**, 109; Birk, *ibid.*, 1927, **166**, 284.

range 189—326° K the moment was calculated as 4.47 B.M. on the basis of the formula  $\text{CoF}_3 \cdot 3.5\text{H}_2\text{O}$  in which all cobalt atoms are identical. The doubled formula, with the assumption that half of the cobalt ions had no unpaired electrons, leads to a moment, 6.3 B.M. per paramagnetic cobalt ion, far in excess of that for the  $\text{CoF}_6^{3-}$  ion (the discrepancy appears relatively small because of the dependence of magnetic moment on the square-root of the molar susceptibility), and the formulation of the compound with both dia- and para-magnetic cobaltic ions must therefore be rejected. The divergence between 4.47 B.M. and the value calculated for four unpaired spins may be due to antiferromagnetic interaction (we are indebted to a Referee for comments on this matter); however,  $\mu$  (doubled formula) must be  $\sqrt{2} \mu$  (single formula), and if the moment calculated on the single formula is too low and ought to be about 5 B.M., that calculated on the double formula would be no less than 7 B.M. per paramagnetic cobalt ion. No decomposition occurred during the measurements.

It thus seems that when three of the fluoride ions in the  $\text{CoF}_6^{3-}$  ion are replaced by water, the ligand field is still not strong enough to bring about any appreciable degree of spin-coupling, a result in direct contrast to that reported for the complex  $[\text{CoF}_3 \cdot 3\text{NH}_3]$ , which is said to be diamagnetic.<sup>4</sup>

*Experimental.*—Hydrated cobaltic fluoride was made according to Barbieri and Calzolari's instructions;<sup>3</sup> cobalt was determined by decomposition with acidified potassium iodide solution, and titration of the liberated iodine with standard thiosulphate [Found: Co, 32.6. Calc. for  $\text{CoF}_3 \cdot 3.5\text{H}_2\text{O}$ : Co, 32.9%]. This analysis (the mean of several concordant determinations) together with earlier ones<sup>3</sup> leave no doubt concerning the presence of  $3\frac{1}{2}$  molecules of water. Magnetic-susceptibility measurements were made as described by Clark, Curtis, and Odell,<sup>5</sup> correction being made for the diamagnetism of the fluoride ions and water. A plot of  $1/\chi_m$  against temperature gave a straight line and a value of 60° for the Curie constant, from which the value  $\mu = 4.47$  B.M. (calculated on the single formula) was obtained.

Temp. (°K)	$10^6 \chi_g$	$10^6 \chi_m$	$10^6 \chi_m$ (corrected)
198	52.7	9476	9556
273	41.0	7371	7451
298	38.0	6833	6913
326	35.1	6293	6373

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[Received, April 15th, 1957.]

<sup>4</sup> Cartledge, quoted by Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 1939, p. 117.

<sup>5</sup> Clark, Curtis, and Odell, *J.*, 1954, 63.

## 818. *Some Maleimides, Maleamic Acids, and Phthalimides.*

By M. Z. BARAKAT, S. K. SHEHAB, and M. M. EL-SADR.

In a recent paper<sup>1</sup> we reported condensation of succinic or phthalic acid with aromatic primary amines and 2 : 4-dinitrophenylhydrazine by means of phosphoric oxide or zinc chloride in boiling dioxan to give imides and hydrazides respectively. Extension of this method to maleic acid has given 40—50% yields of various maleimides.

Hydrolysis by hot 5% aqueous sodium hydroxide or cold 10% alcoholic potassium hydroxide converts *N*-phenylmaleimide into maleanilic acid,<sup>2</sup> and this reaction is reversed by heating the acid with phosphoric oxide in boiling dioxan or by fusion at 212°. Hydrolysis by dilute hydrochloric acid converts the imide into aniline and fumaric acid, isomerisation of maleic to fumaric acid by hydrogen halides being well known.<sup>3</sup> The

<sup>1</sup> Barakat, Shehab, and El-Sadr, *J.*, 1955, 3299.

<sup>2</sup> Cf. Moore and Miller, *J. Amer. Chem. Soc.*, 1942, **64**, 1572.

<sup>3</sup> Anschütz, *Annalen*, 1889, **254**, 175; Fittig, *ibid.*, 1877, **188**, 91; Kekulé, *Annalen Suppl.*, 1861, **1**, 129.

reversible ring opening proves the cyclic structure of the imides and this is confirmed by insolubility of the substances in alkali and by absence of an aromatic amino-group in them.

*N*-Arylmaleimides are distinguished from the corresponding succinimides and phthalimides by a sensitive colour test: a crystal of the maleimide develops an intense pink colour in a few drops of 10% alcoholic potassium hydroxide; the colour is stable for an hour, then fades and disappears in about three hours. Acidifying the pink solution affords the maleamic acid. The colour is very faint when an alcoholic solution of the imide is treated with the reagent.

Formation of maleamic acids from maleic anhydride and amines has been reported previously.<sup>4</sup> With aromatic primary amines this reaction occurs readily in chloroform or, if the amine is insoluble therein, in acetic acid.

Fusing phthalic acid with aromatic primary amines or arylhydrazines at 180° for fifteen minutes gives the phthalimide or *NN*-phthaloylhydrazine respectively in 65—70% yields.

*N'*-Phenyl-*NN*-phthaloylhydrazine is converted into the 2:4:6-trinitrophenyl derivative when treated with oxides of nitrogen in boiling acetic acid. Phenol similarly yields picric acid.

*Experimental.*—All the *N*-arylmaleimides were insoluble in 10% aqueous sodium carbonate (except *N-p*-carboxyphenylmaleimide) and gave no colour with sodium 1:2-naphthaquinone-4-sulphonate (test for primary aromatic amines<sup>5</sup>).

*N-Phenylmaleimide.* (a) Maleic acid (1.16 g., 0.01 mole), freshly distilled aniline (0.93 g., 0.01 mole), and phosphoric oxide (3 g.) in dioxan (25 ml.) were refluxed for 2 hr., becoming intensely yellow. The cooled mixture was poured on ice, and the precipitated imide filtered off. The filtrate, on concentration, gave a further crop. The whole product recrystallised from water (charcoal) as pale yellow needles (0.87 g.), m. p. 90—91° (Found: C, 69.4; H, 4.25; N, 8.2. Calc. for C<sub>10</sub>H<sub>7</sub>O<sub>2</sub>N: C, 69.4; H, 4.05; N, 8.1%).

(b) The imide (1 g.) and 5% aqueous sodium hydroxide (20 ml.) were refluxed for 5 min., cooled, and then treated with dilute hydrochloric acid until just acid. Maleanilic acid separated and recrystallised from aqueous alcohol as faintly yellow prisms (0.8 g.), m. p. 206—208° (decomp.) (Found: C, 63.1; H, 4.6; N, 6.85. Calc. for C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>N: C, 62.8; H, 4.7; N, 7.3%). M. p.s recorded are 198° and 187—187.5°. The acid gave no colour in 10% alcoholic potassium hydroxide but with one drop of sulphuric acid gave a bright yellow colour.

(c) *N*-Phenylmaleimide (1 g.) was treated with cold 10% alcoholic potassium hydroxide (10 ml.). An intense pink colour immediately appeared which gradually faded during 1 hr. Acidification then precipitated maleanilic acid, m. p. and mixed m. p. 206° (decomp.).

(d) Maleanilic acid was also prepared by treating aniline (1 mol.) with maleic anhydride (1 mol.) in chloroform at room temperature.

(e) *N*-Phenylmaleimide (1 g.) was refluxed with 12% hydrochloric acid (20 ml.) for 20 min., dissolving gradually. Aniline was detected in the mixture by means of sodium 1:2-naphthaquinone-4-sulphonate and the carbylamine test. The rest of the mixture was concentrated to 5 ml. and allowed to cool. Fumaric acid, m. p. and mixed m. p. 302° (0.2 g.), separated.

(f) Maleanilic acid was converted into *N*-phenylmaleimide when heated under reflux (boiling ethyl benzoate bath; 212°) for 30 min. or when heated with phosphoric oxide in dioxan for 1 hr.

The following new *N-arylmaleimides* were prepared similarly:

*N-p*-Carboxyphenyl-, very pale yellow (from water), m. p. 234° (Found: C, 60.8; H, 3.4; N, 6.6. C<sub>11</sub>H<sub>7</sub>O<sub>4</sub>N requires C, 60.8; H, 3.2; N, 6.45%); *N-o*-methoxyphenyl-, cream-coloured (from water; charcoal), m. p. 139° (Found: C, 64.5; H, 4.25; N, 6.25. C<sub>11</sub>H<sub>9</sub>O<sub>3</sub>N requires C, 65.0; H, 4.4; N, 6.9%); *N-p*-acetylphenyl-, pale yellow needles (from water; charcoal), m. p. 196° (Found: C, 66.9; H, 4.3; N, 6.5. C<sub>12</sub>H<sub>9</sub>O<sub>3</sub>N requires C, 67.0; H, 4.2; N, 6.5%); *p*-acetamidophenyl-, pale yellow (from water; charcoal), m. p. 217—218° (decomp.) (Found: C, 62.1; H, 4.4; N, 11.5. C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub> requires C, 62.6; H, 4.35; N, 12.2%); *N-2-naphthyl*-, yellow (from aqueous alcohol; charcoal), m. p. 169° (red melt) (Found: C, 75.0; H, 3.9; N, 6.2. C<sub>14</sub>H<sub>9</sub>O<sub>2</sub>N requires C, 75.3; H, 4.0; N, 6.3%).

<sup>4</sup> Bergmann and Shapiro, *J. Org. Chem.*, 1942, **7**, 419; Werbin and Spoerri, *J. Amer. Chem. Soc.*, 1947, **69**, 1681.

<sup>5</sup> Vonesch and Velasco, *Arch. farm. bioquím. Tucumán*, 1944, **I**, 241.

*N*-2-Naphthylmaleimide (1 g.) with 10% alcoholic potassium hydroxide (10 ml.) at room temperature gave in 1 hr., after acidifying the pink solution, *N*-2-naphthylmaleamic acid, m. p. 203° (lit.,<sup>6</sup> 190°). The maleamic acid was also prepared from 1 mol. each of 2-naphthylamine and maleic anhydride in chloroform at room temperature.

*N'*-2:4-Dinitrophenylmaleoylhydrazine. Maleic acid (1.16 g., 0.01 mole), 2:4-dinitrophenylhydrazine (1.98 g., 0.01 mole), and phosphoric oxide (3 g.) in dioxan (50 ml.) were refluxed for 2 hr. The red colour faded to brown. The mixture was allowed to cool and poured on ice. The product was filtered off and crystallised from acetic acid (charcoal) in orange-red crystals, m. p. 226° (decomp.) (0.5 g.) (Found: C, 43.0; H, 2.1; N, 20.5. C<sub>16</sub>H<sub>8</sub>O<sub>6</sub>N<sub>4</sub> requires C, 43.2; H, 2.2; N, 20.1%).

*Colour test.* To 1—5 mg. of an *N*-arylmaleimide were added 2 drops of 10% alcoholic potassium hydroxide; an intense pink colour developed at once. *N*-Aryl-succinimides and -phthalimides gave no colour, except the *p*-nitrophenylphthalimide which gave an orange colour. Hydrazides of maleic, succinic, and phthalic acids gave at once a bluish-green colour, and 2:4-dinitrophenylmaleoylhydrazine gave a blue colour which changed to yellowish-green with a purplish tint. Maleic acid gave no colour; the anhydride gave a faint orange-red colour; 2:4-dinitrophenylhydrazine gave a brown colour.

*N*-Acylmaleamic acids. All the maleimide derivatives dissolved in 10% aqueous sodium carbonate.

Sulphadiazine (2.5 g., 0.01 mole) in hot glacial acetic acid (70 ml.) was filtered into a solution of maleic anhydride (0.98 g., 0.01 mole) in hot chloroform (40 ml.), and the mixture kept at 0°. The maleamic acid (2.1 g.), recrystallised from acetic acid, had m. p. 218—220° (decomp.) (Found: C, 48.3; H, 3.5; N, 16.1; S, 8.7. C<sub>14</sub>H<sub>12</sub>O<sub>5</sub>N<sub>4</sub>S requires C, 48.3; H, 3.45; N, 16.1; S, 9.2%).

Similarly acids were prepared, with the named properties, from sulphacetamide, pale yellow (from alcohol), m. p. 210—212° (decomp.) (Found: C, 46.0; H, 4.0; N, 8.8; S, 10.35. C<sub>12</sub>H<sub>12</sub>O<sub>6</sub>N<sub>2</sub>S requires C, 46.15; H, 3.85; N, 9.0; S, 10.3%); sulphamerazine, colourless (from acetic acid), m. p. 222—224° (decomp.) (Found: C, 49.6; H, 3.6; N, 15.4; S, 8.5. C<sub>15</sub>H<sub>14</sub>O<sub>5</sub>N<sub>4</sub>S requires C, 49.7; H, 3.9; N, 15.5; S, 8.8%); sulphamethazine, colourless (from alcohol), m. p. 209° (decomp.) (Found: C, 50.9; H, 4.3; N, 15.15; S, 8.6. C<sub>16</sub>H<sub>16</sub>O<sub>5</sub>N<sub>4</sub>S requires C, 51.1; H, 4.3; N, 14.9; S, 8.5%); *p*-aminophenol, olive-green (from acetic acid-chloroform), m. p. 218—220° (decomp.) (Found: C, 57.9; H, 4.7; N, 6.4. C<sub>10</sub>H<sub>9</sub>O<sub>4</sub>N requires C, 58.0; H, 4.35; N, 6.8%); methionine, colourless (from acetic acid-chloroform), m. p. 158—160° (decomp.) (Found: C, 43.5; H, 5.0; N, 6.25; S, 13.35. C<sub>9</sub>H<sub>13</sub>O<sub>5</sub>NS requires C, 43.7; H, 5.3; N, 5.7; S, 13.0%); *p*-bromoaniline, pale yellow (from acetic acid), m. p. 202—204° (decomp.) (Found: C, 44.45; H, 2.9; N, 4.8; Br, 30.05. C<sub>10</sub>H<sub>8</sub>O<sub>3</sub>NBr requires C, 44.4; H, 3.0; N, 5.2; Br, 29.6%).

*N*-Arylphthalimides. Phthalic acid (1.66 g., 0.01 mole) was heated with aniline (0.93 g., 0.01 mole) under reflux for 15 min. at 180°, cooled, and crystallised from benzene, giving *N*-phenylphthalimide (m. p. and mixed m. p.) (2.1 g.). Similarly were obtained, in ca. 70% yield, *N*-*p*-tolylphthalimide, and *N'*-phenyl- and *N'*-2:4-dinitrophenyl-*NN*-phthaloylhydrazine (m. p.s and mixed m. p.s).

*NN*-Phthaloyl-*N'*-2:4:6-trinitrophenylhydrazine. *N'*-Phenylphthaloylhydrazine (1 g.) was refluxed in acetic acid (60 ml.) while oxides of nitrogen (from copper and nitric acid, *d* 1.45) were passed in for 1 hr. The mixture was allowed to cool, then poured on ice. The trinitro-derivative was filtered off and recrystallised from acetic acid; it was bright yellow and had m. p. 298—300° (decomp.) (yield 0.65 g.) (Found: C, 45.5; H, 1.9; N, 18.7. C<sub>14</sub>H<sub>7</sub>O<sub>8</sub>N<sub>5</sub> requires C, 45.0; H, 1.9; N, 18.8%).

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[Received, March 25th, 1957.]

<sup>6</sup> La Parola, *Gazzetta*, 1934, **64**, 919.



From this the chemical reactivity can also be expected to be analogous. For example the most reactive positions in radical reactions are the "meso"-positions in all three compounds.

I acknowledge the help of Dr. M. Levy in the calculations.

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[Received, April 5th, 1957.]

## 820. The Ammines of Nickel(II) Cyanide.

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INFORMATION in the literature on the ammines of nickel cyanide is both confused and contradictory. The following compounds are reported to have been prepared by treating nickel cyanide with concentrated ammonia solution:  $[\text{Ni}(\text{CN})_2, \text{NH}_3]_2, \text{H}_2\text{O}$ ; <sup>1</sup>  $\text{Ni}(\text{CN})_2, \text{NH}_3$  with variable quantities of water; <sup>2</sup>  $\text{Ni}(\text{CN})_2, 4\text{NH}_3, 2\text{H}_2\text{O}$ ; <sup>3</sup>  $\text{Ni}(\text{CN})_2, \text{NH}_3, 0.2\text{H}_2\text{O}$ , and  $\text{Ni}(\text{CN})_2, 2\text{NH}_3, 3\text{H}_2\text{O}$ .<sup>4</sup> Hofmann and Höchtlen,<sup>5</sup> on the other hand, reported the formation of  $\text{Ni}(\text{CN})_2, 4\text{H}_2\text{O}$  on dissolution of nickel cyanide in ammonia and storage for several days. This statement is repeated in several standard works.<sup>6</sup>

We have attempted to prepare these compounds by the methods described in the literature, and find that nickel cyanide forms two ammines, *viz.*, unstable  $\text{Ni}(\text{CN})_2, 4\text{NH}_3, 2\text{H}_2\text{O}$  and stable  $\text{Ni}(\text{CN})_2, \text{NH}_3, \text{H}_2\text{O}$ . The former is stable under concentrated ammonia solution, but on exposure to air quickly crumbles to a powder and loses ammonia and water, at first rapidly and then slowly, leaving the pale blue, stable monoammoniate monohydrate. The latter compound can also be prepared as a pale blue precipitate when the ammoniacal solution of nickel cyanide is acidified with acetic acid. It remains unchanged in air or on prolonged boiling with water, but loses ammonia in boiling dilute potassium hydroxide. At 160° it is converted into  $\text{Ni}(\text{CN})_2, \text{NH}_3$  although this change cannot be effected completely without slight loss of ammonia.

*Experimental.—Preparations of  $\text{Ni}(\text{CN})_2, 4\text{NH}_3, 2\text{H}_2\text{O}$ .* The method of Hofmann and Höchtlen<sup>5</sup> was used. No crystals had been formed at the end of a week, but when the mixture was kept overnight at 5° large deep blue needles separated. Nickel was determined (a) by ignition to oxide and (b) as nickel dimethylglyoxime, total nitrogen by Kjeldahl digestion in a sealed tube, and ammonia by distillation from 0.1N-sodium hydroxide. In each case the *compound* was weighed under water to prevent decomposition [Found: Ni, 27.7; N, 39.6;  $\text{NH}_3$ , 31.5.  $\text{Ni}(\text{CN})_2, 4\text{NH}_3, 2\text{H}_2\text{O}$  requires Ni, 27.2; N, 39.0;  $\text{NH}_3$ , 31.6%].

The preparation reported by Hertel, Rissel, and Riedel<sup>2</sup> was repeated using (a) cold and (b) hot ammonia (*d* 0.88). When either solution was kept at 5°, crystals of  $\text{Ni}(\text{CN})_2, 4\text{NH}_3, 2\text{H}_2\text{O}$  were deposited [Found: Product from (a), Ni, 27.4; N, 39.4;  $\text{NH}_3$ , 31.4. Product from (b), Ni, 26.8; N, 39.3;  $\text{NH}_3$ , 31.5%].

*Preparations of  $\text{Ni}(\text{CN})_2, \text{NH}_3, \text{H}_2\text{O}$ .* A few large crystals of  $\text{Ni}(\text{CN})_2, 4\text{NH}_3, 2\text{H}_2\text{O}$  were spread out in a porcelain boat and a slow stream of dry air was drawn over them. Ammonia and water were evolved and the crystals crumbled to a pale blue powder of the *monohydrate* [Found: Ni, 40.0; N, 28.2;  $\text{NH}_3$ , 11.2.  $\text{Ni}(\text{CN})_2, \text{NH}_3, \text{H}_2\text{O}$  requires Ni, 40.1; N, 28.8;  $\text{NH}_3$ , 11.6%]. In a further experiment, the loss in weight was determined [Found: 32.2%, corresponding to 100% conversion into  $\text{Ni}(\text{CN})_2, \text{NH}_3, \text{H}_2\text{O}$ ].

A portion of the ammoniacal solution of nickel cyanide prepared as above<sup>5</sup> was made just acid with glacial acetic acid.<sup>4</sup> A blue gelatinous precipitate was formed which could not be filtered and had to be washed by centrifugation (Found: Ni, 41.0; N, 27.9%).

*Effect of heat on  $\text{Ni}(\text{CN})_2, \text{NH}_3, \text{H}_2\text{O}$ .* No change in weight occurred when the compound was heated for 12 hr. at 140°, but at 150° water was driven off, and a maximum decrease in weight of

<sup>1</sup> Bernouilli and Grether, *Chem.-Ztg.*, 1901, **25**, 436.

<sup>2</sup> Hertel, Rissel, and Riedel, *Z. anorg. Chem.*, 1929, **178**, 202.

<sup>3</sup> Kocsis, *Magyar Chem. Folyóirat*, 1934, **40**, 147; *Chem. Zentr.*, 1935, II, 494.

<sup>4</sup> Cambi, *Gazzetta*, 1934, **64**, 758.

<sup>5</sup> Hofmann and Höchtlen, *Ber.*, 1903, **36**, 1149.

<sup>6</sup> Sidgwick, "The Chemical Elements and their Compounds," Oxford, 1950, Vol. II, p. 1434; Newton Friend, "A Textbook of Inorganic Chemistry," Griffin, London, 1920, Vol. IX, Pt. I, p. 132.

10.5% was observed (Calc. for loss of one molecule of water: 12.3%). On exposure of the dried material to air for 1 hr., moisture was absorbed equal to that lost at 150° and Ni(CN)<sub>2</sub>.NH<sub>3</sub>.H<sub>2</sub>O was re-formed.

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[Received, April 15th, 1957.]

## 821. A Method for the Identification of Pentitols and Hexitols.

By J. BADDILEY, J. G. BUCHANAN, and B. CARSS.

POLYOLS have been separated from each other and identified by paper chromatography in a variety of solvents,<sup>1,2</sup> and by paper electrophoresis in the presence of borate.<sup>3</sup> The polyols are usually detected on the paper by the application of oxidising agents. In the paper-chromatographic method the degree of separation of individual pentitols and hexitols from other members of the series is not large and it is frequently difficult to achieve more than a broad classification into the groups tetrityls, pentitols, and hexitols. As a result of work on the chemistry of nucleotides containing polyol residues,<sup>4</sup> and from the behaviour of polyol phosphates under acidic conditions,<sup>5</sup> we have developed a convenient paper-chromatographic method for the identification of all the pentitols and hexitols.

It is known that tetrityls, pentitols, and hexitols and their derivatives are converted into anhydro-compounds containing 5-membered rings when heated with concentrated acids, frequently under anhydrous conditions. We found, however, that polyol phosphates and even the free polyols were converted, at least in part, into anhydro-compounds in dilute acid. Wide variation in the ease of cyclisation occurred with different polyols.

	$R_F$ of polyol	$R_F$ of coloured spots			
		blue	yellow → green	magenta	
Erythritol .....	0.65	0.75	—	—	
Ribitol .....	0.62	0.71	—	—	
Arabitol .....	0.63	0.68, 0.73	—	—	
Xylitol .....	0.61	0.72	—	—	
Allitol .....	0.63	—	0.71	—	
Talitol .....	0.61	0.74	0.70	—	
			0.77 (v. faint)		
Sorbitol .....	0.58	—	0.68	0.72	
Mannitol .....	0.59	—	0.68	—	
Dulcitol .....	0.58	—	0.72	0.72	
Iditol .....	0.61	—	—	0.74	

Under conditions which bring about extensive decomposition of ribitol to 1 : 4-anhydro-ribitol,<sup>5</sup> arabitol and xylitol were only slightly affected. It was possible to identify the three pentitols by treatment with 2*N*-hydrochloric acid at 100° for 17 hours, evaporation, and examination of the products by paper chromatography in *n*-propyl alcohol-ammonia (*d* 0.88)-water (6 : 3 : 1). Unchanged polyols and the anhydro-compounds were detected by spraying the paper with the periodate-Schiff reagents for glycols.<sup>2</sup>

Hexitols were also converted to various extents into anhydro-compounds under similar conditions. Allitol was completely converted into an anhydro-compound which appeared as a yellow spot, gradually becoming green. Ribitol and talitol were largely decomposed, the former giving a blue spot and the latter a yellow spot, which became green, and a blue spot. The tetrityl, erythritol, was also partly converted into a single product giving a blue spot. Although other pentitols and hexitols were only slightly affected, the number and colour of the spots observed were characteristic in all cases. The products are almost certainly anhydro-compounds containing 5-membered rings.<sup>5</sup> The  $R_F$  values on Whatman No. 4 paper (ascending chromatography) and colours observed for the products are given in the Table.

<sup>1</sup> Hough, *Nature*, 1950, **165**, 400.

<sup>2</sup> Buchanan, Dekker, and Long, *J.*, 1950, 3162.

<sup>3</sup> Gross, *Nature*, 1955, **176**, 362.

<sup>4</sup> Baddiley, Buchanan, Carss, and Mathias, *J.*, 1956, 4583.

<sup>5</sup> Baddiley, Buchanan, and Carss, *J.*, 1957, 4058.



The amount of anhydro-compounds formed in some cases is probably small. However, the characteristic colours produced by the periodate-Schiff spray were readily observed from samples of about 100  $\mu\text{g}$ . of the original polyol. Considerably smaller samples of certain polyols, *e.g.*, ribitol, may be identified by this method. The quality of dye used in the preparation of the Schiff reagent is most important. We have obtained reliable results with reagent prepared from "pararosaniline hydrochloride" supplied by Hopkin and Williams, but other preparations of magenta or pararosaniline are frequently unsatisfactory.

The polyols which were converted most readily into anhydro-compounds, allitol, ribitol, and talitol, are those in which at least three consecutive secondary hydroxyl groups are conventionally depicted on the same side of the carbon chain. It would seem that these polyols in acid solution are in a particularly favourable steric conformation for cyclisation. The reason for this is not known but may be related to the degree of hydrogen bonding between hydroxyl groups in the chain.

The intensity of the coloured spots formed may not be a reliable guide to the extent of anhydropolyol formation. Those anhydro-compounds formed from pentitols and containing *trans*-glycol groups in the ring react slowly with periodate, and the sensitivity of the test in such cases will be lower. More reliable estimates of the extent of reaction were obtained by observing the intensity of the spot corresponding to unchanged polyol. The sensitivity of the reagents is approximately equal for all the acyclic polyols.

Samples of threitol have not been available to us, but it is probable that this tetritol would yield a single anhydro-compound slowly. The *trans*-glycol grouping in the anhydro-compound would result in the production of a weak blue spot on the paper.

The value of this method for the identification of polyols has already been demonstrated in the determination of the structure of cytidine diphosphate ribitol, (CDP)-ribitol. Moreover, it has now been shown in a similar manner that D-mannitol 1(6)-phosphate isolated from *Lactobacillus arabinosus*<sup>6</sup> contains a small amount of ribitol phosphate. When the analytically pure hexitol phosphate sample was examined by the above method a spot corresponding to 1:4-anhydribose was clearly visible on the paper. Synthetic mannitol phosphate (kindly supplied by Dr. N. O. Kaplan) did not give this spot. The method has also been used to demonstrate the presence in *L. arabinosus* of a polymer containing ribitol phosphate and glycerophosphate residues.<sup>7</sup>

We are indebted to Professor T. Reichstein for samples of allitol, talitol, and iditol, to the Council of King's College for the award of a George Angus Studentship (to B. C.), and to the Rockefeller Foundation for a grant.

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[Received, April 26th, 1957.]

<sup>6</sup> Baddiley, Buchanan, Carss, Mathias, and Sanderson, *Biochem. J.*, 1956, **64**, 599.

<sup>7</sup> Baddiley, Buchanan, and Greenberg, unpublished work.

## 822. *Synthesis of 3-Nitro-2-naphthol.*

By D. WOODCOCK and D. R. CLIFFORD.

IN connection with work on plant-growth regulating substances 3-nitro-2-naphthol, the only unknown mononitro-2-naphthol, was required. The obvious preparative route, from 3-nitro-2-naphthylamine<sup>1</sup> by diazotisation and subsequent decomposition, failed in our hands, as did various attempts to replace the diazonium group of diazotised 3-methoxy-2-naphthylamine by a nitro-group. The possibility of oxidising 3-methoxy-2-naphthylamine to the corresponding nitro-compound with peroxytrifluoroacetic acid<sup>2</sup> was also examined without success.

<sup>1</sup> van Rij, Verkade, and Wepster, *Rec. Trav. chim.*, 1951, **70**, 236; Ward, Coulson, and Hawkins, *J.*, 1954, 2974; Curtis and Viswanath, *Chem. and Ind.*, 1954, 1174.

<sup>2</sup> Eamons and Ferris, *J. Amer. Chem. Soc.*, 1954, **76**, 3468.

2-Naphthol was reduced to the 5 : 6 : 7 : 8-tetrahydro-compound by Raney nickel and hydrogen<sup>3</sup> in 50% yield. Nitration by means of liquid nitrogen tetroxide afforded 5 : 6 : 7 : 8-tetrahydro-3-nitro-2-naphthol<sup>4</sup> which on dehydrogenation should give 3-nitro-2-naphthol. Whilst bromine has recently been successfully employed in a similar conversion of 5 : 6 : 7 : 8-tetrahydro-2 : 3-dinitronaphthalene,<sup>5</sup> in the present work dehydrogenation was found to be accompanied by bromination of the nucleus. *N*-Bromosuccinimide, however, gave a gummy brominated tetrahydro-compound which by a two-stage dehydrobromination in a manner similar to that used in the latest preparation of 3-nitro-2-naphthylamine<sup>6</sup> gave 3-nitro-2-naphthol. Its identity was confirmed by methylation and subsequent reduction to the known 3-methoxy-2-naphthylamine.

*Experimental.*—5 : 6 : 7 : 8-Tetrahydro-2-naphthol. 2-Naphthol (200 g.) was shaken with Raney nickel (*ca.* 5 g.) in a rocking autoclave at 200° and an average hydrogen pressure of 33 atm. for 2 hr. On cooling, the resultant mass was dissolved in ether and filtered from catalyst, and naphtholic material extracted by 2*N*-sodium hydroxide. The product obtained on acidification was extracted with ether, the extract dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent removed. Distillation of the residue gave *ar*-tetralol (106 g.), *b. p.* 120—122°/2.5 mm., which crystallised from light petroleum (*b. p.* 60—80°) in plates, *m. p.* 58—61° (Stork<sup>3</sup> gives *m. p.* 59—60°).

5 : 6 : 7 : 8-Tetrahydro-3-nitro-2-naphthol. Nitration of *ar*-tetralol (48 g.) by the method of Thoms and Kross<sup>4</sup> gave the nitro-compound (17.2 g., 27%) which crystallised from aqueous methyl alcohol in golden-yellow prisms, *m. p.* 89—90° (Found: N, 7.25. Calc. for C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>N: N, 7.25%). Thoms and Kross<sup>4</sup> give *m. p.* 88—89°. The acetyl derivative crystallised from methyl alcohol in monoclinic prisms, *m. p.* 102—103° (Found: C, 61.4; H, 5.8; N, 6.2. Calc. for C<sub>12</sub>H<sub>13</sub>O<sub>4</sub>N: C, 61.3; H, 5.5; N, 6.0%). Thoms and Kross<sup>4</sup> give *m. p.* 100°.

1-Bromo-5 : 6 : 7 : 8-tetrahydro-3-nitro-2-naphthol. (a) The above nitronaphthol (1 g.) was treated with bromine (0.5 ml., 2 mols.), and heated at 100° until evolution of hydrogen bromide ceased, and then at 180° for 0.5 hr. After cooling, the dark *product* was extracted with ether and removal of the solvent gave yellow prisms, *m. p.* 129.5—130° [from ether—light petroleum (*b. p.* 40—60°)] (Found: C, 44.4; H, 3.7; N, 5.2. C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>NBr requires C, 44.1; H, 3.7; N, 5.1%). The *acetyl derivative* crystallised from methyl alcohol in prisms, *m. p.* 96—97° (Found: C, 46.1; H, 3.9; N, 4.4. C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>NBr requires C, 45.9; H, 3.8; N, 4.5%).

(b) A solution of 5 : 6 : 7 : 8-tetrahydro-3-nitro-2-naphthol (1 g.) in glacial acetic acid (10 ml.) was stirred during the addition of bromine (0.3 ml., 1.2 mol.) and for a further 1 hr. Dilution with water (10 ml.) gave a yellow product which crystallised from aqueous dioxan in prisms, *m. p.* and mixed *m. p.* 128—129°.

1 : *x*-Dibromo-3-nitro-2-naphthol. The above monobromonaphthol (0.5 g.) and bromine (0.3 ml., 2 mols.) were heated at 100° until the evolution of hydrogen bromide ceased and then at 180° for 0.5 hr. Crystallisation of the *product* from ethyl alcohol gave deep orange-red prisms, *m. p.* 170—171° (Found: C, 34.8; H, 1.5; N, 4.2. C<sub>10</sub>H<sub>8</sub>O<sub>3</sub>NBr<sub>2</sub> requires C, 34.6; H, 1.4; N, 4.0%).

3-Nitro-2-naphthol. A solution of 5 : 6 : 7 : 8-tetrahydro-3-nitro-2-naphthyl acetate (2.5 g.) in carbon tetrachloride (40 ml.) was treated with *N*-bromosuccinimide (recrystallised from water, finely powdered, and dried *in vacuo* for 12 hr.; 3.8 g.) and benzoyl peroxide (0.12 g.) and boiled for 4 hr. The carbon tetrachloride was removed *in vacuo* from the filtered solution and the gummy residue refluxed in methyl alcohol (30 ml.) with fused potassium acetate (3 g.) for 15 min. The solution, when poured into ice-water, gave a slightly sticky orange product which, after trituration with glacial acetic acid, was collected, washed with water, and dried. It had *m. p.* 131—133° (Found: N, 4.9. C<sub>10</sub>H<sub>8</sub>O<sub>3</sub>NBr requires N, 5.2%). This *monobromo-compound* was usually extracted with ether and after removal of the solvent, refluxed for 3 hr. with 96% ethyl alcohol (40 ml.) and hydrochloric acid (*d* 1.2; 15 ml.). Pouring the solution into water gave 3-nitro-2-naphthol which was washed with water and dried. Crystallisation from ether—light petroleum (*b. p.* 60—80°) gave rosettes of orange-red prisms, *m. p.* 103—104° (Found: C, 63.1; H, 3.8; N, 7.6. C<sub>10</sub>H<sub>7</sub>O<sub>3</sub>N requires C, 63.5; H, 3.7; N, 7.4%). The *acetyl derivative* crystallised from aqueous methyl alcohol in pale yellow prisms, *m. p.* 97—98° (Found: C, 62.6; H, 3.8; N, 6.1. C<sub>12</sub>H<sub>9</sub>O<sub>4</sub>N requires C, 62.3; H, 3.9; N, 6.1%). The *methyl ether* crystallised from

<sup>3</sup> Adkins and Krsek, *J. Amer. Chem. Soc.*, 1948, **70**, 412; Stork, *ibid.*, 1947, **69**, 576.

<sup>4</sup> Thoms and Kross, *Arch. Pharm.*, 1927, **265**, 336.

<sup>5</sup> Ward and Coulson, *J.*, 1954, 4545.

<sup>6</sup> Curtis, personal communication.

light petroleum (b. p. 40—60°) in lemon-yellow prisms, m. p. 81—82° (Found: C, 65.2; H, 4.7; N, 7.1.  $C_{11}H_9O_3N$  requires C, 65.0; H, 4.4; N, 6.9%).

*3-Methoxy-2-naphthylamine.* The above methyl ether (0.5 g.) was shaken in tetrahydrofuran (10 ml.) with Raney nickel in hydrogen until no further gas was absorbed. Removal of the solvent from the filtered solution and crystallisation of the residual oil from aqueous methyl alcohol gave stout prisms, m. p. 107—108°, undepressed by admixture with 3-methoxy-2-naphthylamine, m. p. 109—110°, prepared by the method of Jambuserwala, Holt, and Mason.<sup>7</sup>

The authors thank Professor W. Baker, F.R.S., for making available the high-pressure reactor, and also Dr. R. F. Curtis.

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<sup>7</sup> Jambuserwala, Holt, and Mason, *J.*, 1931, 376.

### 823. *Some Experiments with Di-indolyls.*

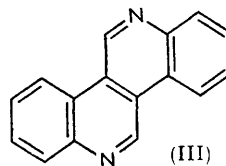
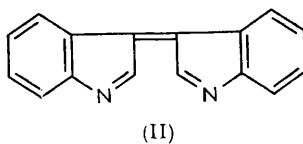
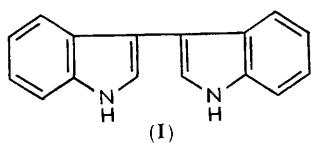
By S. A. FASEEH and JOHN HARLEY-MASON.

3 : 3'-DI-INDOLYL (I), m. p. 286—287°, was first obtained by Gabriel, Gerhard, and Wolter,<sup>1</sup> who found that, when boiled with hydrobromic acid, it was converted into an isomer, m. p. 207—208°, designated "β-di-indolyl." A more convenient preparation of the 3 : 3'-isomer was devised by Oddo and Raffa,<sup>2</sup> who suggested an (unlikely) bisindolenine structure for the lower-melting isomer obtained by the German workers.

Schmitz-Dumont, Hamann, and Geller<sup>3</sup> prepared 2 : 3'-di-indolyl, m. p. 206°, which was converted by nitrous acid into a hydroxyimino-derivative. We have now found that "β-di-indolyl" is similarly converted into a hydroxyimino-derivative whose properties agree precisely with those given by Schmitz-Dumont *et al.*, and it is clear that "β-di-indolyl" is in fact the 2 : 3'-isomer. Evidently its formation from the 3 : 3'-compound (I) is an acid-catalysed rearrangement analogous to the long-known conversion of 3-phenyl- into 2-phenyl-indole by heating with zinc chloride.<sup>4</sup>

In our hands, Seidel's<sup>5</sup> modification of Madelung's<sup>6</sup> synthesis of 2 : 2'-di-indolyl proved unsuccessful, but the compound was obtained satisfactorily by heating di-*o*-tolylamide with sodamide.

Oxidation of 3 : 3'-di-indolyl with lead dioxide gave a highly coloured crystalline dehydro-compound (II), which is isomeric with 6 : 12-diazachrysene (III), reported<sup>7</sup> to be the structure of calycanine, a degradation product of the alkaloid calycanthine. However, the di-indoleninylidene (II) could not be isomerised to the diazachrysene (III). Similar oxidations of 2 : 3'- and 2 : 2'-di-indolyl gave coloured solutions, but attempts to isolate crystalline dehydro-derivatives were unsuccessful.



*Experimental.*—3 : 3'-Di-indolyl. This compound (I) [absorption spectrum in ethanol:  $\lambda_{\max}$ , 234, 291 m $\mu$  ( $\log \epsilon$  4.59, 3.91);  $\lambda_{\min}$ , 218, 265 m $\mu$  ( $\log \epsilon$  4.41, 3.75)] was obtained in 59% yield by heating indole with sulphur as described by Oddo and Raffa.<sup>3</sup> It was rearranged to "β-di-indolyl" [absorption spectrum in ethanol:  $\lambda_{\max}$ , 224, 312 m $\mu$  ( $\log \epsilon$

<sup>1</sup> Gabriel, Gerhard, and Wolter, *Ber.*, 1923, **56**, 1032.

<sup>2</sup> Oddo and Raffa, *Gazzetta*, 1939, **69**, 562.

<sup>3</sup> Schmitz-Dumont, Hamann, and Geller, *Annalen*, 1933, **504**, 1.

<sup>4</sup> Fischer and Schmidt, *Ber.*, 1888, **21**, 1812.

<sup>5</sup> Seidel, *Ber.*, 1944, **77B**, 787.

<sup>6</sup> Madelung, *Annalen*, 1914, **405**, 61.

<sup>7</sup> Woodward and Clark (unpublished) quoted by Saxton, *Quart. Rev.*, 1956, **10**, 119.

4.52, 4.36);  $\lambda_{\min.}$  217, 266  $m\mu$  ( $\log \epsilon$  4.49, 3.85)] as described by Gabriel *et al.*<sup>1</sup> Treatment of the latter with nitrous acid gave the hydroxyimino-derivative, m. p. 243° (decomp.) (Found: C, 73.7; H, 4.0; N, 16.0. Calc. for  $C_{16}H_{12}ON_3$ : C, 73.3; H, 4.5; N, 16.0%). Schmitz-Dumont *et al.* give m. p. 241°.

2: 2'-Di-indolyl.—A finely-powdered intimate mixture of thoroughly dried di-*o*-tolyl-oxamide (2.68 g.) and sodamide (1.17 g.) was heated on an oil-bath with stirring. The temperature was raised to 280—290° and kept there for an hour. After cooling the mass was ground under water, and kept overnight. The product was then filtered off and twice recrystallised from ethyl acetate giving plates (0.51 g.), m. p. 308—310°. Absorption spectrum in ethanol:  $\lambda_{\max.}$  224, 270, 333, 351  $m\mu$  ( $\log \epsilon$  4.57, 3.82, 4.71, 4.68);  $\lambda_{\min.}$  267, 277, 345  $m\mu$  ( $\log \epsilon$  3.79, 3.78, 4.49).

3: 3'-Di-indoleninylidene. To a boiling solution of 3: 3'-di-indolyl (0.5 g.) in ethyl acetate (100 ml.) lead dioxide (5 g.) was added, and the boiling mixture was shaken vigorously for 4 min., and immediately filtered hot. On cooling, the filtrate deposited 3: 3'-di-indoleninylidene (0.3 g.) as lustrous bronze plates, which decomposed indefinitely without melting when heated (Found: C, 83.3; H, 4.5; N, 12.0.  $C_{16}H_{10}N_2$  requires C, 83.5; H, 4.35; N, 12.2%). The product was sparingly soluble in the common organic solvents giving golden yellow solutions, which soon decomposed when heated. Absorption spectrum in ethyl acetate:  $\lambda_{\max.}$  269, 302, 469  $m\mu$  ( $\log \epsilon$  4.32, 4.25, 4.21);  $\lambda_{\min.}$  249, 303, 424  $m\mu$  ( $\log \epsilon$  4.06, 3.12, 4.18).

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[Received, May 10th, 1957.]

## 824. Preparation of 2:3:5-Trimethoxy- and 2:3:6-Trimethoxybenzaldehydes.

By J. R. MERCHANT, R. M. NAIK, and A. J. MOUNTWALLA.

2:3:5-TRIMETHOXYBENZALDEHYDE has been prepared by Baker *et al.*<sup>1</sup> by the Elbs persulphate oxidation of *o*-vanillin, and subsequent methylation. A modification of the method using pyridine<sup>2</sup> gave a better yield than that previously reported.

The hitherto unknown 2:3:6-trimethoxybenzaldehyde has now been synthesised from the known<sup>3</sup> 2-hydroxy-6-methoxy-3-methoxycarbonylbenzaldehyde. This was hydrolysed and the acid subjected to Elbs persulphate oxidation, 3-carboxy-2:5-dihydroxy-6-methoxybenzaldehyde being obtained in a fairly good yield. Attempts to decarboxylate this acid with hot quinoline or quinaldine, or with glass powder resulted only in the formation of tar. Decarboxylation, however, occurred with water at 135—140° giving 3:6-dihydroxy-2-methoxybenzaldehyde which was methylated to 2:3:6-trimethoxybenzaldehyde.

*Experimental.*—2:3:5-Trimethoxybenzaldehyde. Potassium persulphate (40.0 g.) in water (1000 c.c.) was dropwise added to a cooled, stirred solution of *o*-vanillin (20.0 g.) in pyridine (20 c.c.) and sodium hydroxide (200 c.c.; 2N). The mixture was left overnight at room temperature, then just acidified (hydrochloric acid), and extracted with ether. More concentrated acid (75 c.c.) and sodium sulphite (32 g.) were added to the aqueous portion which was then heated at 80° for  $\frac{1}{2}$  hr. The ether extract of the cooled solution furnished 2:5-dihydroxy-3-methoxybenzaldehyde, as yellow brown needles (3.2 g.), m. p. 142—143° (from benzene). Baker *et al.*<sup>1</sup> give the same m. p.

The aldehyde was methylated with dimethyl sulphate and potassium carbonate in acetone solution to give 2:3:5-trimethoxybenzaldehyde, m. p. 61—62° (from light petroleum).

2-Hydroxy-6-methoxy-3-methoxycarbonylbenzaldehyde. 2:6-Dihydroxy-3-methoxycarbonylbenzaldehyde (12 g.), dimethyl sulphate (6 c.c.), anhydrous potassium carbonate (30 g.), and dry acetone were gently refluxed for 8 hr. Filtration and removal of acetone left an oil which was washed with dilute sodium hydroxide and extracted with ether. Evaporation of ether gave the dimethyl ether as a yellow oil (3.9 g.).

The potassium carbonate residue was treated with water and then with dilute potassium

<sup>1</sup> Baker, Brown, and Scott, *J.*, 1939, 1923.

<sup>2</sup> Rajagopalan, Seshadri, and Varadrajana, *Proc. Ind. Acad. Sci.*, 1949, **30**, A, 270.

<sup>3</sup> Shah and Laiwalla, *J.*, 1938, 1828.

hydroxide and filtered. The insoluble residue was separated and acidified to give 2-hydroxy-6-methoxy-3-methoxycarbonylbenzaldehyde, which formed thin flakes (3.1 g.), m. p. 121° (from rectified spirit). The alkaline filtrate gave starting material (4.5 g.).

**3-Carboxy-2-hydroxy-6-methoxybenzaldehyde.** 2-Hydroxy-6-methoxy-3-methoxycarbonylbenzaldehyde (5.0 g.) was hydrolysed with hot sodium hydroxide (100 c.c.; 10%) for 1 hr. The clear solution after acidification gave the *acid* which formed thin brown needles (4.0 g.), m. p. 225° (decomp.) (from alcohol). (Found: C, 55.1; H, 4.2.  $C_9H_8O_5$  requires C, 55.1; H, 4.1%). It gives a red colour with alcoholic ferric chloride.

**3-Carboxy-2:5-dihydroxy-6-methoxybenzaldehyde.** Potassium persulphate (5.2 g.) in water (140 c.c.) was added dropwise with stirring to a cooled solution of the above acid (4.0 g.) in sodium hydroxide (80 c.c.; 10%), and the mixture left overnight at room temperature. It was then just acidified and unchanged material removed. More concentrated hydrochloric acid (25 c.c.) was added and the mixture heated on the steam-bath for 1 hr. Extraction with ether afforded a pale yellow product which formed needles (2.1 g.), m. p. 196°, from acetic acid (Found: C, 51.1; H, 3.7.  $C_9H_8O_6$  requires C, 50.9; H, 3.8%). It gives a brownish green colour with alcoholic ferric chloride.

**3:6-Dihydroxy-2-methoxybenzaldehyde.** The above *acid* (1.0 g.) and water (30 c.c.) were heated at 135–140° for 8 hr. A large amount of charred material was filtered off and the filtrate extracted with ether. The yellow *product* crystallised from chloroform–light petroleum in thin pale yellow needles (0.25 g.), m. p. 85–86° (Found: C, 57.0, 56.9; H, 4.9, 4.8.  $C_8H_8O_4$  requires C, 57.1; H, 4.8%). It gives a deep green colour with alcoholic ferric chloride.

**2:3:6-Trimethoxybenzaldehyde.** This was obtained as an oil on methylation of the decarboxylated product with dimethyl sulphate and anhydrous potassium carbonate in acetone. It formed a 2:4-dinitrophenylhydrazone, thin crimson red needles, m. p. 221° (from acetic acid) (Found: N, 14.5.  $C_{16}H_{16}O_7N_4$  requires N, 14.9%).

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[Received, May 10th, 1957.]

## 825. The Structure of Sodium Stannate.

By R. L. WILLIAMS and R. J. PACE.

THE chemical analysis of sodium stannate corresponds to the composition,  $Na_2SnO_3 \cdot 3H_2O$ . However, the water is not removed by prolonged desiccation and can only be removed at 140° *in vacuo*, during which process the nature of the substance is fundamentally altered. This suggests<sup>1</sup> that the 3 water molecules form part of an ion  $[Sn(OH)_6]^{2-}$ , a deduction supported by Wyckoff's X-ray evidence that the lattice of potassium stannate was similar to that of potassium chloroplatinate with six groups arranged octahedrally around the central atom.

Since it is frequently possible to distinguish spectroscopically between water of crystallization and hydroxyl groups, we have measured the infrared spectrum of sodium stannate over the range 2–15  $\mu$ . Only two absorption bands were found. The first was a relatively sharp, strong band at  $3597 \pm 10$   $cm^{-1}$  with an apparent half-width of 70  $cm^{-1}$ . This band had a weak shoulder at 3493  $cm^{-1}$  which decreased to zero intensity at 3250  $cm^{-1}$ . The second band absorbed at  $898 \pm 5$   $cm^{-1}$  and was of medium strength with an apparent half-width of 130  $cm^{-1}$ .

The spectrum of water under a range of conditions, such as different concentrations and solvents, has been studied by Mecke and his co-workers,<sup>3</sup> who found two principal absorptions, *viz.*, a strong band at about 1630  $cm^{-1}$  and two very strong bands around 3500  $cm^{-1}$ , which merged together and shifted towards lower frequencies under conditions of strong hydrogen bonding. When the spectra of hydrated inorganic salts are examined, it is found that these two absorptions are almost always present. Thus, in the sixty-five hydrated salts examined by Miller and Wilkins,<sup>4</sup> the only possible exceptions are ammonium sulphite and manganese phosphate, all the others showing bands around 1630 and 3500  $cm^{-1}$ .

<sup>1</sup> Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1949, Vol. I., p. 602.

<sup>2</sup> Wyckoff, *Amer. J. Sci.*, 1928, **15**, 297.

<sup>3</sup> Greinacher, Lüttke, and Mecke, *Z. Elektrochem.*, 1955, **59**, 23.

<sup>4</sup> Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

In the spectrum of sodium stannate, even though the band at  $3597\text{ cm.}^{-1}$  is very strong, there is no trace of absorption around  $1630\text{ cm.}^{-1}$  so that the presence of water of crystallisation is most unlikely. On the other hand, the frequency of  $3597\text{ cm.}^{-1}$  is consistent with those of the hydroxyl-stretching vibration in covalent molecules and in the hydroxyl ion. For the former a range  $3650\text{--}3590\text{ cm.}^{-1}$  is recorded,<sup>5</sup> while similar values are found for the latter, *e.g.*, the frequencies for potassium, sodium, and lithium hydroxides are  $3597$ ,  $3637$ , and  $3678\text{ cm.}^{-1}$ , respectively.<sup>6,7</sup>

The value of  $3637\text{ cm.}^{-1}$  for sodium hydroxide has been confirmed for a Nujol mull in this work, but an extra band was found at  $3572\text{ cm.}^{-1}$ . However, both bands differ from the sodium stannate frequency by considerably more than the experimental error, so that the stannate band did not originate in sodium hydroxide as impurity.

The  $898\text{-cm.}^{-1}$  band of sodium stannate, can be assigned to the deformation vibration of the hydroxyl groups. Similar vibrations in primary alcohols<sup>5</sup> lie near  $1050\text{ cm.}^{-1}$ , but if the Sn-OH link possesses some ionic character then the frequency of the corresponding vibration in sodium stannate would be reduced.

The spectrum of sodium stannate therefore shows no evidence of water of crystallization but is completely consistent with the structure  $\text{Na}_2[\text{Sn}(\text{OH})_6]$ .

*Experimental.*—Sodium stannate was precipitated from an aqueous solution of the commercial product by adding a carbonate-free sodium hydroxide solution until the concentration of the latter in the stannate solution reached 5N. The precipitate was filtered off, and washed with 5N-sodium hydroxide, alcohol, and finally ether (Found: Na, 17.3; Sn, 44.1. Calc. for  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ : Na, 17.2; Sn, 44.5. Loss in weight at  $630^\circ$ . Found: 19.6. Calc., 20.3%). The spectra were measured as Nujol or perfluorocarbon mulls with either a Grubb-Parsons S.3.A. double-beam spectrometer, fitted with a rock-salt prism, or a Grubb-Parsons G.S.2. grating spectrometer, equipped with a 2400 line/inch grating.

We thank Mr. W. R. Cox for preparing and analysing the sodium stannate

MINISTRY OF SUPPLY, EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT,  
WALTHAM ABBEY, ESSEX. [Received, May 15th, 1957.]

<sup>5</sup> Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 83.

<sup>6</sup> Jones, *J. Chem. Phys.*, 1954, **22**, 217.

<sup>7</sup> Busing, *ibid.*, 1955, **23**, 933.

## 826. *An Example of Correlation Between Taft's $\sigma^*$ Parameters and Infrared Spectral Frequencies.*

By D. G. O'SULLIVAN and P. W. SADLER.

Molecular-orbital calculations by Jaffé<sup>1</sup> added cogency to the general supposition that the  $\sigma$  values, obtained originally by Hammett<sup>2</sup> from ionization constants of *meta*- and *para*-substituted benzoic acids, are related to the changes in electron density produced by inductive and resonance effects of substituents. Taft<sup>3</sup> has split these  $\sigma$  values into inductive and resonance contributions,  $\sigma = \sigma_I + \sigma_R$ . The recent demonstration<sup>4</sup> of precise correlations between nuclear magnetic shielding parameters for *meta*- and *para*-substituted fluorobenzenes<sup>5</sup> and  $\sigma_I$  and  $\sigma_R$  values respectively has provided further compelling evidence for the total dependence of  $\sigma$  values on polar effects of substituents. Substituent constants have also been constructed for *ortho*-groups and for general and aliphatic radicals.<sup>6</sup> These are defined for the group R, compared with the methyl group, by  $\sigma^* = [\log (k/k_0)_B - \log (k/k_0)_A]/2.48$ , where  $k$  and  $k_0$  are the rate constants for hydrolysis of  $\text{R}\cdot\text{CO}_2\text{Et}$  and  $\text{Me}\cdot\text{CO}_2\text{Et}$  respectively, and subscripts *B* and *A* refer to

<sup>1</sup> Jaffé, *J. Chem. Phys.*, 1952, **20**, 279, 778, 1554.

<sup>2</sup> Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188; Jaffé, *Chem. Rev.*, 1953, **53**, 191.

<sup>3</sup> Taft, "Steric Effects in Organic Chemistry," (Editor: M. S. Newman), John Wiley, New York, 1956, pp. 578, 594; Roberts and Moreland, *J. Amer. Chem. Soc.*, 1953, **75**, 2167.

<sup>4</sup> Taft, *ibid.*, 1957, **79**, 1045.

<sup>5</sup> Gutowsky, McCall, McGarvey, and Meyer, *ibid.*, 1952, **74**, 4809; Meyer and Gutowsky, *J. Phys. Chem.*, 1953, **57**, 481.

<sup>6</sup> Taft, *J. Amer. Chem. Soc.*, 1953, **75**, 4231; 1952, **74**, 2729, 3126.

alkaline- and acid-catalysed hydrolysis under otherwise identical conditions.<sup>7</sup> Rate and equilibrium constants for reactants RY, in a wide variety of reaction types involving the Y group, obey the linear free-energy relation  $\log k/k_0$  (or  $K/K_0$ ) =  $\sigma^*\rho^*$ , where  $\sigma^*$  is the Taft substituent constant for the R group.<sup>6</sup> Evidence that  $\sigma^*$  values are direct measures of polar effects of the Mulliken intrinsic electronegativity type,<sup>8</sup> although not yet as strong as for Hammett's  $\sigma$ -values, has sufficed for Taft to suggest that  $\sigma^*$ -values could be used to define polar effects.<sup>6</sup> In chemical reactions generally, the nature of group R imposes other effects, classified as steric effects, on velocities and equilibria.

The polar effect of R can sometimes modify the force constant of a bond in group Y and consequently influence its vibrational frequency. Thus the infrared spectral frequencies of many groups,<sup>9</sup> e.g., CO, NH<sub>2</sub>, OH, NO<sub>2</sub>, attached to a benzene ring are linearly related to the Hammett  $\sigma$  value of a further substituent present in the *meta*- or *para*-position. Interesting frequency regularities also exist for *ortho*-substituted benzenoid compounds,<sup>10</sup> and it has been stated that the OH stretching frequencies of carboxylic acids<sup>11</sup> are linearly related to Taft constants.<sup>12</sup> Frequency correlation studies in a variety of compounds has led Bellamy *et al.*<sup>13</sup> to suggest that additional field effects frequently outweigh any direct polarization influence. However, when variation in group R produces proportional variation in the frequencies of corresponding bonds in the sets of compounds RY' and RY'', it is reasonable to suppose that the frequency shifts are primarily dependent on the polar effect of R. This is confirmed by non-proportionality in cases where large field effects are expected. Bellamy and Williams<sup>14</sup> have shown the existence of linear relations between the CO and NO frequencies in R·COMe and R·NO, for both the vapour and condensed phase, for a wide range of R groups. The main exception (R = CF<sub>3</sub>) could readily be explained on the basis of different steric effects for rotational isomers.<sup>14</sup> Infra- $\sigma^*$  Values of group R, carbonyl frequencies (cm.<sup>-1</sup>) of compounds R·COMe, and nitrosyl frequencies (cm.<sup>-1</sup>) of compounds R·NO.

R .....	$\sigma^*$	Vapour phase		Condensed phase or solution	
		$\nu(\text{R}\cdot\text{COMe})$	$\nu(\text{R}\cdot\text{NO})$	$\nu(\text{R}\cdot\text{COMe})$	$\nu(\text{R}\cdot\text{NO})$
F .....	3.08	1872	1844	—	—
Cl .....	2.94	1822	1799	1806	1813
Br .....	2.80	1827	1801	1814	1807
Ac .....	1.65	—	—	1718 <sup>a</sup>	—
HO .....	1.55	1785	1696	—	—
MeO .....	1.46 <sup>b</sup>	1774	1682	1742 <sup>a</sup>	—
EtO .....	1.35 <sup>c</sup>	1765	1676	1745	1653
Ph .....	0.60	1707	1520	1682	1513

<sup>a</sup> Data quoted by Jones and Sandorfy (West, "Chemical Applications of Spectroscopy," Interscience Publ., London, 1956, pp. 472, 483), remaining infrared data are quoted by Bellamy and Williams.<sup>14</sup> <sup>b</sup> Value obtained from the Taft value <sup>6</sup> for the MeO·CH<sub>2</sub>· group by use of  $\sigma^*(\text{MeO}) = 2.8\sigma^*(\text{MeO}\cdot\text{CH}_2\cdot)$ .<sup>7</sup> <sup>c</sup> Value inferred from Taft's data <sup>6</sup> by use of the relations  $\sigma^*(\text{EtO}) = \sigma^*(\text{MeO})[\sigma^*(\text{MeO}\cdot\text{CH}_2\cdot)/\sigma^*(\text{HO}\cdot\text{CH}_2\cdot)] = 2.8[\sigma^*(\text{Me}\cdot\text{O}\cdot\text{CH}_2\cdot)]^2/\sigma^*(\text{HO}\cdot\text{CH}_2\cdot)$ .

red frequencies and  $\sigma^*$  values, listed in the annexed Table, are linearly related with good approximation. The equations of the regression lines for the frequencies are

$$\begin{aligned} \nu &= 1690 + 52.56\sigma^*(\text{R}\cdot\text{COMe, vapour phase}) \\ \nu &= 1500 + 110.1\sigma^*(\text{R}\cdot\text{NO, vapour phase}) \\ \nu &= 1655 + 53.71\sigma^*(\text{R}\cdot\text{COMe, condensed phase or solution}) \\ \nu &= 1458 + 124.3\sigma^*(\text{R}\cdot\text{NO, condensed phase or solution}) \end{aligned}$$

<sup>7</sup> Taft, *J. Chem. Phys.*, 1957, **26**, 93.

<sup>8</sup> Mulliken, *ibid.*, 1934, **2**, 782; 1935, **3**, 573; *J. Phys. Chem.*, 1937, **41**, 318; Moffitt, *Proc. Roy. Soc.*, 1950, **A**, **202**, 548.

<sup>9</sup> Flett, *Trans. Faraday Soc.*, 1948, **44**, 767; Ingraham, Corse, Bailey, and Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297; Fuson, Josien, and Shelton, *ibid.*, 1954, **76**, 2526; Kross and Fassel, *ibid.*, 1956, **78**, 4225; Davison, *J.*, 1951, 2456; O'Sullivan and Sadler, *J.*, 1956, 2202; *J. Org. Chem.*, 1956, **21**, 1179; Kellie, O'Sullivan, and Sadler, *J.*, 1956, 3309; *J. Org. Chem.*, 1957, **22**, 29.

<sup>10</sup> O'Sullivan and Sadler, *J.*, 1957, 2839.

<sup>11</sup> Goulden, *Spectrochim. Acta*, 1954, **6**, 129.

<sup>12</sup> Bellamy, *J.*, 1955, 4221.

<sup>13</sup> Bellamy, Thomas, and Williams, *J.*, 1956, 3704; Bellamy and Williams, *J.*, 1957, 861.

<sup>14</sup> *Ibid.*, *J.*, 1957, 863.

and the respective correlation coefficients are 0.955, 0.967, 0.953, and 0.989. It must be stressed that no general correlation between  $\sigma^*$  and  $\nu$  values can be expected, as the shifts in the latter can depend on factors other than the electronegativity of the R group. However, the existence of this correlation for the compounds listed provides mutual support for the views of Bellamy<sup>14</sup> and of Taft,<sup>6</sup> and adds to the mounting evidence supporting the general validity of  $\sigma^*$  constants.

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[Received, May 16th, 1957.]

### 827. Some Compounds from 5-Methoxy-8-methyl- and 5-Methoxy-6 : 8-dimethyl-1-tetralones.

By WESLEY COCKER, B. E. CROSS, and W. R. N. WILLIAMSON.

DURING a wider investigation these tetralones were prepared and their properties examined.

2-Ethoxycarbonyl-5-methoxy-8-methyl- and 2-ethoxycarbonyl-5-methoxy-6 : 8-dimethyl-1-tetralones were obtained from the corresponding methoxymethyl- and methoxydimethyl-tetralones.<sup>1</sup> *via* the glyoxylates by Bachmann's method.<sup>2</sup> They did not react with ethyl  $\alpha$ -bromopropionate in the presence of sodium ethoxide (cf. Cocker and Lipman<sup>3</sup>).

Bromination of 5-methoxy-8-methyltetralone in ether gave the 2-bromo-compound which was dehydrobrominated to 5-methoxy-8-methyl-1-naphthol by boiling dimethyl-aniline. Refluxing the bromo-tetralone in diethyl methylmalonate-pyridine gave a bromo-pyridinium salt, which failed to react with the ester.

Both parent tetralones behaved normally as active methylene compounds.

*Experimental.*—Light-absorption measurements were determined in 95% ethanol, a Beckman D.U. spectrophotometer being used.

*Ethyl 5-methoxy-8-methyl-1-oxo-2-tetralylglyoxylate.* A solution of 5-methoxy-8-methyl-1-tetralone<sup>1</sup> (5.1 g.) in diethyl oxalate (3.5 g.) was added to cooled solid sodium ethoxide [from sodium (0.57 g.)] at 5–7°. The mixture was left overnight, then decomposed by ice-water, followed by hydrochloric acid. The resulting oil was refluxed in benzene with charcoal and extracted with 2% sodium hydroxide solution. Acidification afforded the *glyoxylate* (3.1 g.), yellow needles, m. p. 70–70.5° [from light petroleum (b. p. 60–80°)] (Found: C, 65.4; H, 6.3. C<sub>16</sub>H<sub>18</sub>O<sub>5</sub> requires C, 66.2; H, 6.2%). It gave an intense red-violet colour with ferric chloride in ethanol.<sup>2</sup>

*2-Ethoxycarbonyl-5-methoxy-8-methyl-1-tetralone.* The glyoxylate (1.22 g.) was heated with powdered soft glass (1.22 g.) at 175–180° for 1.5 hr. The oil (1.05 g.) so produced was collected in ether, from which by removal of solvent and addition of light petroleum (b. p. 40–60°) a solid was obtained. Recrystallisation from light petroleum (b. p. 60–80°) and finally from ethanol gave the *ethoxycarbonyl-tetralone*, very pale yellow needles, m. p. 76.5–77.5° ( $\lambda_{\max}$ , 229, 257, 325 m $\mu$ ; log  $\epsilon$  4.38, 3.98, 3.56, respectively) (Found: C, 69.0; H, 6.8. C<sub>15</sub>H<sub>18</sub>O<sub>4</sub> requires C, 68.7; H, 6.9%). It gave a green ferric chloride reaction in ethanol.<sup>2</sup>

*2-Ethoxycarbonyl-5-methoxy-6 : 8-dimethyl-1-tetralone.* Dry sodium ethoxide [from sodium (6.02 g.)] was suspended in benzene (100 ml.), cooled to 0°, and a cooled solution of 5-methoxy-6 : 8-dimethyl-1-tetralone<sup>1</sup> (26.72 g.) in benzene (50 ml.)–diethyl oxalate (38.24 g.) was added with stirring. After being kept overnight the mixture was processed as before to give a brown oil which would not solidify. It gave a purple-red ferric chloride reaction in alcohol. The oil was heated with powdered soft glass (36 g.) at 150–170° for 6.5 hr. (*i.e.* until the ferric chloride reaction changed to a green-blue). Leaching from the glass with hot ethanol gave the *ethoxycarbonyl-tetralone* (21.8 g.) as pale yellow diamond-shaped plates, m. p. 84.5–85.5°, having a green ferric chloride reaction in ethanol<sup>2</sup> ( $\lambda_{\max}$ , <215, 262, 307 m $\mu$ ; log  $\epsilon$  >4.25, 4.1, 3.4, respectively) (Found: C, 69.9; H, 7.4. C<sub>16</sub>H<sub>20</sub>O<sub>4</sub> requires C, 69.6; H, 7.2%).

*2-Bromo-5-methoxy-8-methyl-1-tetralone.* To a stirred, cooled solution of 5-methoxy-8-methyl-1-tetralone (5 g.) in anhydrous ether (60 ml.) dry bromine (1.3 ml.) in ether (10 ml.) was

<sup>1</sup> Cocker, Lipman, and Whyte, *Chem. and Ind.*, 1950, 237; *J.*, 1950, 1519; Hayes, Ph.D. Thesis, Dublin Univ., 1952.

<sup>2</sup> Bachmann, *J. Amer. Chem. Soc.*, 1940, **62**, 824, 2222.

<sup>3</sup> Cocker and Lipman, *J.*, 1947, 537.



added at such a rate that the temperature was kept at 10°, each drop of bromine solution being decolorised before addition of the next (cf. ref. 3). After a further hour's stirring and removal of the ether a solid (6.3 g.) was obtained. Crystallisation from light petroleum (b. p. 60—80°) gave *2-bromo-5-methoxy-8-methyl-1:2:3:4-tetrahydro-1-oxonaphthalene* as needles (3.5 g.), m. p. 75—76° (Found: C, 53.3; H, 4.7.  $C_{12}H_{13}O_2Br$  requires C, 53.5; H, 4.8%). It was strongly lachrymatory. When heated in ethanol with 25% sodium hydroxide solution (hydrolysis to an ene-diol) for a minute and then cooled rapidly it gave a purple colour with aqueous *o*-dinitrobenzene.<sup>4</sup>

*5-Methoxy-8-methyl-1-naphthol*.—The 2-bromo-tetralone (10 g.) was refluxed for 0.5 hr. in dimethylaniline (43.5 ml.). The solution was then poured into dilute sulphuric acid and steam-distilled. The *naphthol* (1.63 g.), from the distillate, crystallised from light petroleum (b. p. 60—80°) as white needles, m. p. 72—72.5° ( $\lambda_{max}$ . 229, 255, 301, 320, 332  $\mu$ ;  $\log \epsilon$  4.6, 3.7, 3.75, 3.76, 4.05, respectively) (Found: C, 76.4; H, 7.1.  $C_{12}H_{12}O_2$  requires C, 76.6; H, 6.4%). The *picrate* crystallised from benzene as red needles, m. p. 154—156° (Found: C, 52.0; H, 3.5.  $C_{18}H_{15}O_9N_3$  requires C, 51.8; H, 3.6%). The *carbanilate* formed plates, m. p. 176—178°, from ligroin (b. p. 100—130°) (Found: C, 73.6; H, 5.6.  $C_{19}H_{17}O_3N$  requires C, 74.3; H, 5.5%).

*(5-Methoxy-8-methyl-1-oxo-2-tetralyl)pyridinium bromide*.—The above bromo-tetralone (1 g.) in diethyl methylmalonate (3.92 g.) and pyridine (1 ml.) was refluxed for 0.5 hr. The solid (0.9 g.) was filtered off and washed with light petroleum (b. p. 40—60°), giving the *pyridinium bromide* as brownish plates, m. p. 258° (decomp.) (Found: Br, 22.7.  $C_{17}H_{18}O_2NBr$  requires Br, 23.0%). It was highly insoluble in the usual organic solvents, but was soluble in water: the solution gave pyridine on being heated with sodium hydroxide and could be titrated with silver nitrate solution.

*2-Benzylidene-5-methoxy-8-methyl-1-tetralone*. The corresponding methoxymethyltetralone (1 g.), benzaldehyde (1.1 g.), and 5*N*-sodium hydroxide solution (0.5 ml.) were mixed in methylated spirits (10 ml.) and left overnight. Water was added and the mixture was set aside at 0° for 7 days. The *benzylidene derivative* (0.42 g.) crystallised as yellow needles, m. p. 80.5—90.5°, from methylated spirits (Found: C, 81.9; H, 6.3.  $C_{19}H_{18}O_2$  requires C, 82.0; H, 6.5%).

*2-Ethylidene-5-methoxy-6:8-dimethyl-1-tetralone*. The corresponding methoxydimethyltetralone (5 g.) in acetaldehyde (4.4 g.) was saturated at 0° with dry hydrogen chloride and set aside at room temperature.<sup>5</sup> After treatment in ether with sodium hydrogen carbonate solution the ethylidene compound was obtained as an oil (after three distillations), b. p. 165°/4 mm. (Found: C, 77.2; H, 7.9. Calc. for  $C_{15}H_{18}O_2$ : C, 78.2; H, 7.9. Calc. for  $C_{13}H_{16}O_2$ : C, 76.4; H, 7.9%) [ $\lambda_{max}$ . <215, 284, 320 (shoulder);  $\log \epsilon$  >4.2, 4.22, 3.65 respectively]. It rapidly reduced potassium permanganate in acetone.

One of us (W. R. N. W.) thanks the Government of the Irish Republic for a Maintenance Grant.

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<sup>4</sup> Fearon and Kawerau, *Biochem. J.*, 1943, **37**, 326.

<sup>5</sup> Ramart and Hoch, *Bull. Soc. chim. France*, 1938, **5**, 848.

## 828. *Combretum verticillatum* Gum.

By R. J. McILROY.

THE genus *Combretum*, comprising over three hundred species of woody plants, is widely distributed in the tropics and sub-tropics and is well represented in Africa. Several species yield gum which is pale and of good solubility, but the best *Combretum* gums so far examined have proved inferior to *Acacia* gums.

*Combretum verticillatum* gum consists of soluble and insoluble fractions in the ratio of 9 : 1. The crude gum swells in cold water to a clear colourless gel, most of which dissolves readily in dilute alkali from which it is precipitated by acidified ethanol. The isolated soluble fraction is precipitated from aqueous solution by acetone as a pale, straw-coloured powder which dries to a hard solid.

The aqueous solution was dextrorotatory and did not reduce Fehling's solution.

Paper chromatography of the products of hydrolysis, by N- or 2N-sulphuric acid, of the water-soluble fraction indicated arabinose, galactose, and glucuronic acid. The last two components were further identified by their oxidation products. The water-soluble gum is thus a galactoaraban similar in composition to the gums isolated from mesquite,<sup>1,2</sup> *Anogeissus schimperi*,<sup>3</sup> lemon, and grapefruit.<sup>4</sup>

*Experimental.*—Paper chromatography was carried out by the descending method<sup>5</sup> on Whatman No. 1 filter paper, the solvent system being butan-1-ol-acetic acid-water (4 : 1 : 5) (top layer). The solvent front was permitted to advance 30 cm. from the starting line at 28°. The positions of the sugars were revealed by spraying with aniline hydrogen phthalate in butan-1-ol and development at 100°. Where a sugar was indicated by the  $R_F$  value the identity was established by running further chromatograms with reference sugar spots.

*Isolation of the gum.* The crude gum dissolved incompletely in 4% aqueous sodium hydroxide. From 100 g. of crude gum three main fractions were obtained: (A) 40.9 g., precipitated from solution in cold 4% sodium hydroxide by acid ethanol (2 vols.); (B) 5.4 g., precipitated from solution in hot 4% sodium hydroxide by acid ethanol (2 vols.); and (C) 5.0 g., insoluble in 4% sodium hydroxide. The insoluble fraction thus comprises about 10% of the gum.

*Purification (soluble fractions).* Fraction A and B after re-solution in sodium hydroxide and precipitation by acid ethanol (3 times) became soluble in water and were further purified by precipitation from this solvent, acidified with hydrochloric acid, by addition of acetone. Precipitated as a straw-coloured powder, the gum dried to a brittle solid [Found: Ash (A, B), 10.5%].

The soluble portion did not reduce Fehling's solution, gave a negative Millon's test for protein, and positive tests for carbohydrate (Molisch) and uronic acid (naphtharesorcin); it had  $[\alpha]_D^{25} + 53^\circ$  (c 0.90 in H<sub>2</sub>O).

*Graded hydrolysis.* (a) Fraction (B) (2.03 g.) was heated with N-sulphuric acid (200 ml.) for 7½ hr. in a boiling-water bath;  $[\alpha]_D^{25}$  changed from +53° to +100° (const.) in 90 min. The neutralised (barium carbonate), filtered hydrolysate was evaporated under reduced pressure and the residue (2.29 g.) extracted with boiling methanol (4 × 50 ml.). Evaporation of the extracts gave a syrup (1.00 g.) which was examined by paper chromatography. Two spots,  $R_F$  0.08 and 0.16, were revealed identical with galactose and arabinose on the same paper. The former was confirmed by oxidation to mucic acid, m. p. 213°.

(b) The methanol-insoluble barium salt (1.29 g.) (Found: Ba, 20%) was taken up in 2N-sulphuric acid (150 ml.), the mixture filtered, and the filtrate heated in a boiling-water bath for 10 hr.;  $[\alpha]_D^{25}$  changed from +46.5° to +34.8° (const.) in 7½ hr. The neutralised (barium carbonate), filtered hydrolysate was evaporated under reduced pressure and the residue extracted with boiling methanol. Evaporation of the extracts gave a residue (67 mg.) which reduced Fehling's solution and gave a positive Molisch test but in which no sugars could be detected by paper chromatography. It is suggested that the sugar moiety was degraded by the prolonged hydrolysis.

The methanol-insoluble barium salt (0.75 g.) (Found: Ba, 30%), taken up in water, was passed through Amberlite IR-120 resin, and the effluent examined chromatographically. No sugars were detected but a tailing spot near the origin indicated glucuronic acid. The spot did not correspond to D-galacturonic acid on the same paper. Identity of the uronic acid with glucuronic acid was confirmed by oxidation to potassium hydrogen saccharate and by the basic lead acetate test which gave a cream-coloured precipitate changing to yellow-brown when heated.

*Estimation of sugars.* Oxidation of the soluble fraction of the gum by nitric acid yielded mucic acid corresponding to 15.0% of anhydrogalactose.<sup>6</sup> 20.4% of furfuraldehyde was produced on distillation with 12% hydrochloric acid.<sup>7</sup> This corresponds to 38.0% of anhydroarabinose.

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[Received, May 20th, 1957.]

<sup>1</sup> Anderson and Sands, *Ind. Eng. Chem.*, 1925, **17**, 1257; *J. Amer. Chem. Soc.*, 1926, **48**, 3172.

<sup>2</sup> Anderson and Otis, *ibid.*, 1930, **52**, 4461.

<sup>3</sup> McIlroy, *J.*, 1952, 1918.

<sup>4</sup> Connell, Hainsworth, Hirst, and Jones, *J.*, 1950, 1696.

<sup>5</sup> Partridge, *Biochem. J.*, 1948, **42**, 238.

<sup>6</sup> Assoc. Offic. Agric. Chemists, *Methods*, 7th Edn., 1950.

<sup>7</sup> Norris and Resch, *Biochem. J.*, 1935, **29**, 1590.

**829. Stannic Iodohypophosphite.**

By D. A. EVEREST.

STANNIC IODOHYPOPHOSPHITE  $\text{Sn}(\text{H}_2\text{PO}_2)_4, \text{SnI}_4$  was obtained as a pale yellow solid by action of hypophosphorous acid on an alcoholic solution of stannic iodide. The solid darkens at *ca.* 100° and melts at 319°, decomposing immediately above this temperature with evolution of phosphine. Stannic iodohypophosphite was insoluble in most solvents including alcohol, but it was dissolved by hot hydrochloric acid, concentrated hypophosphorous acid, and alkali. It was readily attacked by concentrated oxidising acids with evolution of phosphine and iodine.

Oxidising a solution of stannous bromide with hydrogen peroxide followed by addition of hypophosphorous acid, gave a product similar in character to stannic iodohypophosphite and to stannic chlorohypophosphite,<sup>1</sup> but which analysis showed to be impure. It is noteworthy that although three stannic halogenohypophosphites appear to exist, all attempts to prepare the corresponding germanium compounds have failed, probably partly because of the greater tendency for quadrivalent germanium compounds to be hydrolysed (*e.g.*, compare the behaviour of germanium and tin tetrachlorides in aqueous solutions<sup>2,3</sup>), and partly because of the lesser tendency to form complexes with hypophosphorous acid. For example, stannic oxide is extremely soluble in hypophosphorous acid and, in absence of halide ions, no reduction occurs.<sup>1</sup> Quadrivalent germanium compounds, however, are reduced by hypophosphorous acid even in absence of halide ions,<sup>4</sup> although the bivalent state of germanium is much less stable than the bivalent state of tin.

Attempts to prepare halogenophosphites of stannic tin and of bivalent germanium and tin analogous to the well-characterised halogenohypophosphites have failed.<sup>1,4,5</sup> There appears to be a fundamental difference in the ability of hypophosphorous and phosphorous acids to form complexes of this kind.

*Experimental.*—*Stannic iodohypophosphite.* To a saturated solution of stannic iodide in alcohol (20 ml.) was added 20% hypophosphorous acid (5 ml.); crystals slowly separated [Found: Sn, 23.8; I, 49.8.  $\text{Sn}(\text{H}_2\text{PO}_2)_4, \text{SnI}_4$  requires Sn, 23.6; I, 50.5%]. Tin and iodide were determined as previously described.<sup>1,5</sup>

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[Received, May 27th, 1957.]

<sup>1</sup> Everest, *J.*, 1951, 2903.<sup>2</sup> Everest and Harrison, *J.*, 1957, 1820.<sup>3</sup> *Idem*, *J.*, 1957, 1439.<sup>4</sup> Everest, *J.*, 1952, 1670; 1953, 4117.<sup>5</sup> *Idem*, *J.*, 1954, 4698.**830. Absorption Spectra of Ketones in the 200—220  $m\mu$  Region.**

By C. W. BIRD, J. K. NORZYMBERSKI, and GILBERT F. WOODS.

THE intense absorption of ultraviolet light by olefins ( $\lambda_{\text{max}}$  180—195  $m\mu$ )<sup>1</sup> extends into a region (200—220  $m\mu$ ) accessible to examination with a quartz spectrophotometer.<sup>2</sup> Bladon, Henbest, and Wood<sup>3</sup> showed that, at least in the steroid series, measurement of such end-absorptions provides valuable information concerning the presence and position of isolated double bonds. The present investigation was intended to establish the extent to which the high-intensity absorption bands of ketones<sup>4</sup> extend into the same spectral region.

The measurements were performed on 50 compounds, all steroids except two, in ethanol, two spectrophotometers of identical design being used (Unicam S.P. 500). In 0.2 cm. cells apparent maximal absorptions<sup>5</sup> were recorded at  $201 \pm 2 m\mu$ , in 1 cm. cells at  $205 \pm 2 m\mu$ . The results presented in the Table require little comment. (i) The relatively

<sup>1</sup> Stark, Steubing, Enklaar, and Lipp, *Jahrb. Radioakt. Elektronik*, 1913, **10**, 139.<sup>2</sup> Bateman and Koch, *J.*, 1944, 600.<sup>3</sup> Bladon, Henbest, and Wood, *J.*, 1952, 2737.<sup>4</sup> Mohler and Sorge, *Helv. Chim. Acta*, 1940, **23**, 100; Platt and Klevens, *Rev. Mod. Phys.*, 1944, **16**, 182; Holdsworth and Duncan, *Chem. Rev.*, 1947, **41**, 311.<sup>5</sup> Sidel, Goldfarb, and Kalt, *Science*, 1951, **113**, 683; Vandenbelt, Henrich, and Bash, *ibid.*, 1951, **114**, 576; ref. 3.

strong absorptions of methyl 3 $\beta$ -acetoxy-11-oxocholanate (12) and of methyl 3 $\alpha$ -acetoxy-12-oxocholanate (13) suggest either appreciable end-absorption of the methoxycarbonyl group superimposed on that of the carbonyl group or interaction between the two groups. (ii) The absorption intensities of the 3 : 17-dione (18) and the 3 : 20-dione (20) are much lower than those expected from the summation of the intensities of the appropriate monoketones. Since in either instance interaction between the two carbonyl groups is improbable, the anomaly is attributed to the inaccuracy of measurement and/or slight impurities in the reference compounds. In contrast, the extinctions found for the 11 : 20-dione (12), the 3 : 11 : 17-trione (19), and the 3 : 11 : 20-trione (22) are reasonably close to expectation. (iii) Introduction of halogen in the  $\alpha$ -position to an oxo-group resulted in greatly increased absorption. With one exception (17; cf. 42),  $\alpha$ -hydroxyl groups and, to a smaller extent,  $\alpha$ -acetoxy groups similarly enhanced the absorption intensities of the parent ketones.

In view of the limitations inherent in the use of a quartz spectrophotometer for the measurement of end-absorptions in the 200—220  $m\mu$  region (deviation from Beer's law, sensitivity to changes of experimental design, inability to distinguish between bathochromic and hyperchromic effects) further discussion of the present results seems

	Light path (mm.)	$\epsilon_{205}$	$\epsilon_{210}$
<i>Non-ketonic Compounds</i>			
1. Cholestan-3 $\beta$ -ol .....	10	45	35
	5 or 1	200	150 <sup>3</sup>
2. Cholestan-3 $\beta$ -yl acetate .....	5 or 1	200	150 <sup>3</sup>
3. Cholestan-3 $\alpha$ -yl bromide .....	2	340	300
4. Cholesterol .....	10	3300	2020
	5 or 1		1600 <sup>3</sup>
5. Cholesteryl acetate .....	10	3540	2100
	5 or 1		1500 <sup>3</sup>
<i>Monoketones</i>			
6. Camphor .....	2	200	80
7. Cholestan-3-one .....	2	530	250
	10	260	150
	5 or 1	350	200 <sup>3</sup>
8. 17 $\beta$ -Hydroxyandrostan-3-one .....	10	230	130
9. 3 $\beta$ -Hydroxycholestan-6-one .....	10	680	460
10. 3 $\beta$ -Acetoxyergostan-11-one .....	10	410	290
11. 3 $\beta$ -Acetoxy-9 $\beta$ -ergostan-11-one .....	10	420	290
12. Methyl 3 $\beta$ -acetoxy-11-oxocholanate .....	2	880	610
13. Methyl 3 $\alpha$ -acetoxy-12-oxocholanate .....	2	1280	700
14. 3 $\alpha$ -Hydroxyandrostan-17-one .....	10	140	70
15. 3 $\alpha$ : 11 $\beta$ -Dihydroxy-5 $\beta$ -androstan-17-one .....	10	200	100
16. 5 $\alpha$ -Pregnan-20-one .....	10	560	310
17. 3 $\beta$ -Hydroxy-5 $\alpha$ -pregnan-20-one .....	10	490	260
<i>Di- and tri-ketones</i>			
18. Androstane-3 : 17-dione .....	10	240	130
19. 5 $\beta$ -Androstane-3 : 11 : 17-trione .....	10	830	660
20. Pregnane-3 : 20-dione .....	10	460	220
21. 3 $\beta$ -Acetoxy-5 $\alpha$ -pregnane-11 : 20-dione .....	10	1120	840
22. 5 $\alpha$ -Pregnane-3 : 11 : 20-trione .....	10	1300	970
<i><math>\alpha</math>-Halogenoketones</i>			
23. 3 $\alpha$ -Bromocamphor .....	2	1590	1150
$\Delta$ 3 $\alpha$ -Br (vs. 6) * .....		1390	1070
24. 3 $\alpha$ -Chlorocholestan-2-one .....	2	1910	1240
25. 3 $\alpha$ -Bromocholestan-2-one .....	2	2010	1610
26. 2 $\beta$ -Chlorocholestan-3-one .....	2	1310	840
$\Delta$ 2 $\beta$ -Cl (vs. 7) .....		780	590
27. 2 $\alpha$ -Chlorocholestan-3-one .....	2	990	520
$\Delta$ 2 $\alpha$ -Cl (vs. 7) .....		460	270
28. 2 $\beta$ -Bromocholestan-3-one .....	2	1260	990
$\Delta$ 2 $\beta$ -Br (vs. 7) .....		730	740
29. 2 $\alpha$ -Bromocholestan-3-one .....	2	2700	1930
$\Delta$ 2 $\alpha$ -Br (vs. 7) .....		2170	1680
30. 3 $\beta$ : 5 $\alpha$ -Diacetoxy-7 $\alpha$ -bromocholestan-6-one .....	2	2920	2350
$\Delta$ 7 $\alpha$ -Br (vs. 34) .....		1920	1600
31. 3 $\beta$ : 5 $\alpha$ -Diacetoxy-7 $\beta$ -bromocholestan-6-one .....	2	3460	2370
$\Delta$ 7 $\beta$ -Br (vs. 34) .....		2460	1620

<i>α-Hydroxy- and α-Acetoxy-ketones</i>		Light path (mm.)	$\epsilon_{205}$	$\epsilon_{210}$
32.	$3\beta : 5\alpha$ -Dihydroxycholestan-6-one .....	10	1220	930
	$\Delta 5\alpha$ -OH ( <i>vs.</i> 9) .....		<i>540</i>	<i>470</i>
33.	$3\beta$ -Acetoxy-5 $\alpha$ -hydroxycholestan-6-one .....	10	1660	1310
34.	$3\beta : 5\alpha$ -Diacetoxycholestan-6-one .....	10	1000	750
35.	Methyl 3 $\alpha$ -acetoxy-12 $\beta$ -hydroxy-11-oxocholanate .....	2	1890	1400
	$\Delta 12\beta$ -OH ( <i>vs.</i> 12) .....		<i>1210</i>	<i>940</i>
36.	Methyl 3 $\alpha : 12\beta$ -diacetoxy-11-oxocholanate .....	2	1190	720
	$\Delta 12\beta$ -OAc ( <i>vs.</i> 12) .....		<i>310</i>	<i>110</i>
37.	Methyl 3 $\alpha$ -acetoxy-11 $\beta$ -hydroxy-12-oxocholanate .....	2	2970	1730
	$\Delta 11\beta$ -OH ( <i>vs.</i> 13) .....		<i>1690</i>	<i>1030</i>
38.	3 $\alpha : 17\alpha$ -Dihydroxypregnan-20-one .....	10	1100	890
	$\Delta 17\alpha$ -OH ( <i>vs.</i> 17) .....		<i>610</i>	<i>630</i>
39.	3 $\alpha : 17\alpha$ -Dihydroxypregnane-11 : 20-dione .....	10	1580	1370
40.	3 $\beta : 17\alpha$ -Dihydroxy-5 $\alpha$ -pregnane-11 : 20-dione .....	10	1770	1520
41.	3 $\beta : 17\alpha$ -Diacetoxy-5 $\alpha$ -pregnane-11 : 20-dione .....	10	1330	980
	$\Delta 17\alpha$ -OAc ( <i>vs.</i> 21) .....		<i>210</i>	<i>140</i>
42.	3 $\alpha : 21$ -Dihydroxypregnan-20-one .....	10	270	230
	$\Delta 21$ -OH ( <i>vs.</i> 17) .....		<i>-220</i>	<i>-30</i>
43.	3 $\alpha : 21$ -Dihydroxypregnane-11 : 20-dione .....	10	1200	980
44.	3 $\alpha : 21$ -Diacetoxypregnane-11 : 20-dione .....	10	1440	1200
	$\Delta 21$ -OAc ( <i>vs.</i> 21) .....		<i>320</i>	<i>360</i>
45.	3 $\alpha : 17\alpha : 21$ -Trihydroxypregnane-11 : 20-dione .....	10	2200	1960
	$\Delta 17\alpha$ -OH ( <i>vs.</i> 43) .....		<i>1000</i>	<i>980</i>
	$\Delta 21$ -OH ( <i>vs.</i> 39) .....		<i>620</i>	<i>590</i>
46.	21-Acetoxy-3 $\beta : 17\alpha$ -dihydroxy-5 $\alpha$ -pregnane-11 : 20-dione .....	10	2570	2270
	$\Delta 21$ -OAc ( <i>vs.</i> 40) .....		<i>800</i>	<i>750</i>
47.	3 $\beta : 21$ -Diacetoxy-17 $\alpha$ -hydroxy-5 $\alpha$ -pregnane-11 : 20-dione .....	10	2150	1970
48.	3 $\alpha : 21$ -Diacetoxy-17 $\alpha$ -hydroxypregnane-11 : 20-dione .....	10	2070	1940
	$\Delta 17\alpha$ -OH ( <i>vs.</i> 44) .....		<i>630</i>	<i>740</i>
49.	3 $\alpha : 17\alpha : 21$ -Triacetoxypregnane-11 : 20-dione .....	10	1580	1350
	$\Delta 17\alpha$ -OAc ( <i>vs.</i> 44) .....		<i>140</i>	<i>150</i>
50.	3 $\beta : 17\alpha : 21$ -Triacetoxy-5 $\alpha$ -pregnane-11 : 20-dione .....	10	1670	1430
	$\Delta 21$ -OAc ( <i>vs.</i> 41) .....		<i>340</i>	<i>450</i>

\* Entries thus designated show the differences (in italics) caused by the substitution concerned.

unprofitable. The outstanding and unequivocal fact here established is that, depending on the structural environment of the carbonyl group, the end-absorption intensities of ketones vary within a wide range ( $\epsilon_{205}$  200—3500;  $\epsilon_{210}$  80—2400) which overlaps that found for olefins ("  $\epsilon_{\max.}$ " 600—10,600;  $\epsilon_{210}$  200—10,500).<sup>3</sup>

*Experimental.*—Measurements were made with two Unicam S.P. 500 spectrophotometers, using ethanolic (Burrough's Analytical Grade) solutions in 1.0 or 0.2 cm. cells, at concentrations so adjusted as to give maximal optical density values of 0.3—0.5. Except for 2 $\beta$ -bromocholestan-3-one (see below), the compounds listed in the Table were fully described elsewhere. The physical constants (m. p.s and, in most instances, rotations) of the specimens here used were in agreement with those reported in the literature.

2 $\beta$ -Bromocholestan-3-one. 2 $\beta$ -Bromocholestan-3 $\alpha$ -ol<sup>6</sup> (98 mg.) in acetic acid (10 ml.) was treated with chromium trioxide (18 mg.) in a few drops of water overnight at room temperature. Addition of water gave a precipitate which on crystallisation from cold ether-methanol afforded 2 $\beta$ -bromocholestan-3-one, m. p. 95°,  $[\alpha]_D +142^\circ$  (*c* 0.85, in CHCl<sub>3</sub>),  $\lambda_{\max.}$  310 m $\mu$  ( $\epsilon$  97 in EtOH),  $\nu_{\max.}$  1720 cm.<sup>-1</sup> (in CHCl<sub>3</sub>) (Found: C, 69.4; H, 9.75. C<sub>27</sub>H<sub>45</sub>OBr requires C, 69.65; H, 9.75%).

A solution of the above compound in benzene was filtered through a column of alumina. Evaporation to dryness followed by crystallisation from ether-methanol furnished 2 $\alpha$ -bromocholestan-3-one, m. p. and mixed m. p. 169—170°,  $[\alpha]_D +42^\circ$  (*c* 1.25 in CHCl<sub>3</sub>).

Numerous compounds were obtained from the Medical Research Council Steroid Reference Collection; these included compounds given to the Collection by Messrs. Parke Davis, Roussel, Syntex, and Upjohn. We are indebted to Dr. W. Klyne for this facility, and for some other compounds to Dr. C. Tamm (Basle). Financial assistance from the Empire Rheumatism Council (to J. K. N.) and from the Ford (Dagenham) Trust (to C. W. B.) is gratefully acknowledged.

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[Received, May 30th, 1957.]

<sup>6</sup> Alt and Barton, *J.*, 1954, 4284.

### 831. *The Preparation of Potassium [<sup>15</sup>N]Nitrite and [<sup>15</sup>NO]Dimethylnitrosamine.*

By D. F. HEATH.

THE following modification of Milbauer and Vogel's method<sup>1</sup> for the reduction of potassium nitrate to nitrite affords a simple way of making [<sup>15</sup>N]nitrite in 80—90% yield (determined by permanganate titration or conversion into dimethylnitrosamine) on starting from 0.6 g. of labelled potassium nitrate.

*Experimental.*—*Potassium nitrite.* Potassium nitrate (0.6 g.) was mixed with coarsely powdered lead (1.6 g.; 60—80 mesh to the inch) in a small hard-glass test-tube (8—10 mm. × 60 mm.). The nitrate was gently fused over a naked flame, and the tube then rapped sharply a few times against an asbestos board to make the lead sink. The tube was then transferred immediately to a heating block, at 440—460° for 3 hr., during which a slow stream of nitrogen, freed from traces of oxygen by passage through alkaline pyrogallol, was passed over the melt. The tube was allowed to cool, and the contents (broken up when necessary) extracted with several small quantities of boiling water and filtered. The final volume was adjusted to 10 ml. for analysis or conversion into dimethylnitrosamine. In five runs with unlabelled nitrate, yields ranged from 80.3 to 87.3%, as estimated by titration with permanganate.

The mesh of lead is critical. Fine lead powder is floated by bubbles formed in the reaction, and is largely rendered ineffective. Granulated lead does not pack under the surface of the molten nitrate, and tends to fuse into large globules of low surface area. Both give yields of only 40—60%. It is also important to fuse the nitrate outside the heating block and to tap the lead down. Bubble formation is most rapid at the beginning of the reaction, and will float even 60—80 mesh lead unless this is done.

*Dimethylnitrosamine.* The crude nitrite solution, prepared as above, was poured into dimethylammonium chloride (5—6 g.), glacial acetic acid (10 ml.) was added, and the mixture held at 24—26° for 1 hr. The product was diluted to about 70 ml., the pH adjusted to 4.5—5 with sodium hydroxide solution, and the mixture two-thirds distilled off, the distillate being collected in an iced receiver. This gave a reasonable separation from dimethylamine. The distillate was made about 3N with respect to sodium hydroxide and half-distilled.<sup>2,3</sup> In trial runs the dimethylnitrosamine was determined in the distillate at this stage by a polarographic method.<sup>3</sup> Yields, based on nitrite, were 82—83%, and were markedly reduced by carrying out the reaction at 37°.

In the preparations of labelled dimethylnitrosamine the product, prepared as above, was further distilled from saturated salt solution adjusted to pH 3—4 with sulphuric acid and then from sodium hydroxide as before. The yield on potassium nitrate containing 64 atom-% of <sup>15</sup>N was 71%; the product was obtained as a neutral aqueous solution containing 18.7 mg./ml.

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[Received, May 30th, 1957.]

<sup>1</sup> Milbauer and Vogel, *Chem. Listy*, 1926, **20**, 390.

<sup>2</sup> Dutton and Heath, *J.*, 1956, 1892.

<sup>3</sup> Heath and Jarvis, *Analyst*, 1955, **80**, 613.

### 832. *Some Properties of Tetramethylhydrazine.*

By B. J. AYLETT.

TETRAMETHYLHYDRAZINE was first prepared by Class, Aston, and Oakwood;<sup>1</sup> it has since been synthesised by Beltrami and Bissell,<sup>2a</sup> and by Watson<sup>2b</sup> and some of its physical properties have been reported. In order to compare it with the corresponding silicon compound,<sup>3</sup> measurements of its vapour pressure, melting point, and infrared absorption have been made.

The boiling point, 72.9°, agrees well with that found by Class *et al.* (73°), and, as expected, the Trouton's constant of 21.5 indicates that the liquid is not associated. The

<sup>1</sup> Class, Aston, and Oakwood, *J. Amer. Chem. Soc.*, 1953, **75**, 2937.

<sup>2</sup> (a) Beltrami and Bissell, *ibid.*, 1956, **78**, 2467; (b) Watson, *J.*, 1956, 3677.

<sup>3</sup> Aylett, *J. Inorg. Nuclear Chem.*, 1956, **2**, 325.

melting point of tetramethylhydrazine was found to be  $-104^\circ$ , some  $14^\circ$  higher than the value given by Class *et al.*; a glass-like solid phase was often formed, similar to that given by trimethylamine, and the slightest trace of amines caused the solid to melt irreproducibly over a wide temperature range. Analysis of the compound by normal combustion techniques was very unreliable. On some occasions the compound exploded, as has been reported for 1:2-diethyl-1:2-dimethylhydrazine,<sup>4</sup> and on other occasions a liquid of extremely low volatility was deposited in the weighing train, evidently having been formed by pyrolysis and incomplete oxidation of the tetramethylhydrazine. It is suggested that tensiometric homogeneity is a more satisfactory criterion of purity.

As it is possible to remove primary and secondary amines from a tertiary amine by treatment with a compound containing a carbonyl group,<sup>5</sup> one sample suspected of containing 1:2-dimethylhydrazine was treated with acetic anhydride, and a purification effected. This should be contrasted with the observation<sup>4</sup> that 1:1-dimethylhydrazine will not react with methyl benzoate.

*Experimental.—Technique.* Most of the work was carried out in a conventional high-vacuum apparatus. Low temperatures were at first measured with a pentane-filled thermometer, standardised at regular intervals against vapour-pressure thermometers containing carbon dioxide or ethylene. Later, a cryostat—a simplified version of that described by Scott and Brickwedde<sup>6</sup>—was used; temperatures in the range  $+20^\circ$  to  $-140^\circ$  were measured by means of copper-constantan thermocouples, calibrated in the usual way.<sup>7</sup>

*Preparation of tetramethylhydrazine.* The method of Class *et al.* was used. (On one occasion, after the reduction with lithium aluminium hydride, there was an explosion during the removal of the ether. The whole reaction mixture inflamed, and much product was lost.) The compound was then purified by distillation at low pressure (b. p.  $-16^\circ/12.5$  mm.) in an atmosphere of dry oxygen-free nitrogen; a small column was used, packed with 4-mm. Fenske helices, and immersed in a low-temperature bath. Repeated fractional condensation at  $-84^\circ$  *in vacuo* removed traces of amines, apparently formed during the treatment with calcium hydride. The resulting sample was shown to be homogeneous by dividing it into twelve portions; the vapour pressure at  $0^\circ$  of each was identical [Found: C, 54.3; H, 14.2; N, 31.4%; *M* (vapour),  $87 \pm 1$ . Calc. for  $C_4H_{12}N_2$ : C, 54.5; H, 13.7; N, 31.8%; *M*, 88].

(a) *Vapour pressure at low temperatures.* A sensitive type of spoon gauge was used, giving the following results:

Temp. ....	$-64^\circ$	$-56^\circ$	$-49^\circ$	$-41^\circ$	$-36^\circ$	$-29^\circ$	$-24^\circ$	$-18^\circ$
V.p., mm. ....	0.33	0.65	1.16	2.24	3.38	5.40	7.80	11.5
Temp. ....	$-13^\circ$	$-8^\circ$	$-4^\circ$	$0^\circ$	$4^\circ$	$8^\circ$	$12^\circ$	$16^\circ$
V.p., mm. ....	14.9	21.6	27.5	35.3	44.6	55.2	67.1	82.1

(b) *Vapour pressure above room temperature.* An all-glass tensiometer was used; it was immersed in a water-bath fitted with a thermostat.

Temp. ....	$17.2^\circ$	$21.3^\circ$	$24.8^\circ$	$32.7^\circ$	$35.1^\circ$	$38.8^\circ$	$43.0^\circ$	$47.6^\circ$
V.p., mm. ....	90	108	128	179.5	198	229	268.5	326.5
Temp. ....	$51.2^\circ$	$54.8^\circ$	$59.0^\circ$	$63.4^\circ$	$67.8^\circ$	$69.5^\circ$	$71.9^\circ$	$73.0^\circ$
V.p., mm. ....	374.5	427	490	555	650.5	688.5	739.5	760

From these values, the vapour pressure of tetramethylhydrazine is given by the equation:  $\log_{10} p(\text{mm.}) = -2426.0/T - 5.311 \log_{10} T + 23.378$ . Hence the calculated b. p. is  $72.9^\circ$ , the latent heat of vaporisation is 7460 cal./mole, and Trouton's constant is 21.5.

*Melting point.* The apparatus was similar to that described by Stock.<sup>8</sup> The mean of nineteen determinations was  $-104^\circ \pm 1^\circ$ .

*Infrared spectrum.* Gas-phase measurements, with a Hilger model H800 spectrometer used as a double-beam instrument, gave the following band centres (in  $\text{cm.}^{-1}$ ): 3000 vs, 2960 vs, 2830 vs, 2780 vs, 1450 vs, 1231 s, 1201 w, 1151 vs, 1089 s, 1026 vs, 969 w, 899 vs, 712 s, 508 s, and 435 w.

<sup>4</sup> Hinman, *J. Amer. Chem. Soc.*, 1956, **78**, 1645.

<sup>5</sup> "Chemistry of Carbon Compounds," Ed. Rodd, Elsevier Publ. Co., Amsterdam, 1951, p. 389.

<sup>6</sup> Scott and Brickwedde, *J. Res. Nat. Bur. Stand.*, 1931, **6**, 481.

<sup>7</sup> American Institute of Physics, "Temperature, its Measurement and Control in Science and Industry," Reinhold Publishing Corp., New York, 1941.

<sup>8</sup> Stock, *Ber.*, 1917, **50**, 156.

*Reaction of crude tetramethylhydrazine with acetic anhydride.* A sample (1.1 g.; *M*, 80; v. p. 33.6 mm./0°), suspected of containing 1 : 2-dimethylhydrazine as a result of incomplete methylation, was mixed *in vacuo* with acetic anhydride (2 ml.). Subsequent treatment with calcium hydride and repeated fractional distillation gave a product (*M*, 88; v. p. 35.3 mm./0°) whose infrared spectrum was identical with that of a pure sample of tetramethylhydrazine.

The author thanks Dr. D. C. McKean for assistance with the infrared measurements and also Dr. R. A. Chalmers and Miss D. A. Thomson, who performed the microanalyses.

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[Received, June 3rd, 1957.]

### 833. *The Preparation and Decomposition of Diethyl 2-Diethylaminoethylphosphonate.*

By J. I. G. CADOGAN.

IN connection with another investigation diethyl 2-diethylaminoethylphosphonate was required. Its preparation from diethyl 2-bromoethylphosphonate has been described<sup>1,2</sup> but, more conveniently, it may be obtained by a Michaelis reaction of sodium diethyl phosphite and 2-diethylaminoethyl chloride in boiling xylene. An Arbuzov reaction between triethyl phosphite and the same halide failed, dimerisation to give 1 : 1 : 4 : 4-tetraethylpiperazinium dichloride resulting.

Diethyl 2-diethylaminoethylphosphonate is stable under ordinary conditions of storage but, after 34 hr. at 150°, extensive decomposition had occurred to give triethylamine, diethyl vinylphosphonate, and an involatile residue which appeared (infrared spectrum) to be a complex mixture of phosphorus oxyacids.

The presence of the base can be explained on the basis of a self-alkylation involving nucleophilic attack by the basic group in the diethylaminoethylphosphonate on an ester  $\alpha$ -carbon atom, followed by thermal decomposition of the quaternary salt so formed. For intramolecular reaction this salt could be formulated as (I). Decomposition followed by loss of a proton would give diethyl vinylphosphonate.



This alkylation resembles that of tertiary amines by phosphate esters,<sup>3</sup> and the thermal decomposition of some organophosphorus amidates.<sup>4</sup>

*Experimental.*—*Diethyl 2-diethylaminoethylphosphonate.* Sodium (4.6 g.) was added to diethyl hydrogen phosphite (27.6 g.) in xylene (dried over sodium; 400 ml.), and the mixture was boiled under reflux until salt formation was complete. To the boiling solution was added freshly distilled 2-diethylaminoethyl chloride (27.0 g.), and boiling was continued for a total of 1.5 hr. Filtration, followed by removal of the xylene, left an oil (b. p. 168°/40 mm.) which was redistilled, the fraction, b. p. 125—130°/12 mm.,  $n_D^{25}$  1.4378 (18 g.), being retained for analysis (Found: C, 50.4; H, 9.9.  $\text{C}_{10}\text{H}_{24}\text{O}_3\text{NP}$  requires C, 50.6; H, 10.1%). Kosolapoff<sup>1</sup> records  $n_D^{25}$  1.4380.

An attempt to prepare this compound from 2-diethylaminoethyl chloride and triethyl phosphite by Arbuzov's method resulted in dimerisation of the halide to 1 : 1 : 4 : 4-tetraethylpiperazinium dichloride. The reaction was then attempted with 2-diethylaminoethyl chloride hydrochloride and triethyl phosphite in butanol. Again the reaction was unsuccessful, transesterification of triethyl phosphite with the solvent occurring.

Diethyl 2-bromoethylphosphonate (b. p. 106°/1 mm.;  $n_D^{25}$  1.4566), prepared by Ford-Moore and Williams's method,<sup>2</sup> was treated with anhydrous triethylamine to give diethyl vinylphosphonate (b. p. 99°/16 mm.;  $n_D^{25}$  1.4268).

*Decomposition of diethyl 2-diethylaminoethylphosphonate.* The phosphonate (11.7 g.) was kept at 150° (thermostat) for 34 hr. Distillation gave a low-boiling base (b. p. 50—90°; 2.4 g.) and an oil (b. p. 120°/40 mm.;  $n_D^{25}$  1.4255; 3.3 g.), leaving a gum which appeared (infrared

<sup>1</sup> Kosolapoff, *J. Amer. Chem. Soc.*, 1948, **70**, 1971.

<sup>2</sup> Ford-Moore and Williams, *J.*, 1947, 1465.

<sup>3</sup> Clark and Todd, *J.*, 1950, 2023.

<sup>4</sup> Cadogan, *J.*, 1957, 1079.



spectrum) to be a complex mixture of phosphorus oxyacids. The low-boiling fraction was redistilled to give triethylamine (methiodide, m. p. and mixed m. p. 294—295°). The higher-boiling oil was dissolved in hydrochloric acid and extracted with chloroform. The extracts gave an oil (b. p. 200°/760 mm.;  $n_D^{25}$  1.4270; 1.9 g.) which, after redistillation had an infrared spectrum identical with that of diethyl vinylphosphonate, prepared as described above.

A replicate experiment gave the same results.

The microanalyses were by Mr. F. E. Charlton and the infrared data are due to Mr. L. C. Thomas and Mr. M. J. Rumens, to all of whom thanks are accorded. This investigation was carried out during the tenure of a Civil Service Senior Research Fellowship.

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[Received, June 11th, 1957.]

### 834. *The Dimethyldiphenyls.*

By E. A. JOHNSON.

DURING investigations (with G. H. Beaven) into the effects of alkyl substitution on the ultraviolet absorption spectra of diphenyls, and their behaviour in gas-liquid chromatography,<sup>1</sup> the preparation of the series of dimethyldiphenyls was completed. In this way it was hoped to resolve the questions posed by the unexpectedly low intensity of the ultraviolet absorption bands of 2:3'- and 3:4'-dimethyldiphenyl as given by Woods, Van Artsdale, and Reed<sup>2</sup> and also obtain more data on the effects of competitive conjugation and of vicinal substitution. At least nine of the twelve compounds are mentioned in the literature, but many references give boiling point as the only characteristic. They are not all quoted here.

Some physical properties are given in Table I. Purities were estimated by gas-liquid

TABLE I.

Dimethyldiphenyl *	Purity, %	B. p./mm.	M. p.	$n_D^{20}$	$d_4^{20}$	Rel. retn. vol. ‡
2:2'- <i>a, b</i> .....	99.8	—	19.5—20.2°	1.5752	0.9906	1.005
3:3'- <i>a, c, d</i> .....	>99.8	150°/18	9.0—9.5	1.5946	0.9993	2.40
4:4'- <i>a, e</i> .....	>99.8	—	120.7—121.5	—	—	2.69
2:3'- <i>c</i> .....	99.5	135/13.5	—	1.5810	0.9933	1.43
2:4'- .....	99.5	137/12.5	—	1.5826	0.9924	1.55
3:4'- <i>c, e</i> .....	>99.8	153/15	14.5—14.8	1.5968	0.9978	2.54
2:3- .....	>99.8	141/14	41.8—42.3	—	—	1.67
2:4- .....	99.3	—	—	1.5844	0.9947	1.55
2:5- .....	>99.5	140/14.5	—	1.5819	0.9931	1.49
2:6- .....	99.5	132/16.5	—5	1.5745	0.9907	1.09
3:4- .....	>99.8	—	29.2—29.7	1.6036 †	1.0087 †	2.86
3:5- .....	>99.8	—	22.3—22.8	1.5952 †	0.9990 †	2.36

\* For previous work see: <sup>a</sup> Ullmann and Meyer, *Annalen*, 1904, **332**, 39. <sup>b</sup> Hall, Leslie, and Turner, *J.*, 1950, 711. <sup>c</sup> Woods, Van Artsdale, and Reed, ref. 2. <sup>d</sup> Mills, *Nature*, 1951, **167**, 726. <sup>e</sup> Kruber, *Ber.*, 1932, **65**, 1382. † Supercooled liquid. ‡ Ref. 1.

chromatography. The boiling-point data are incomplete, but in any case are not of especial accuracy. Attempts to determine boiling points at atmospheric pressure by García's micro-method<sup>3</sup> were not successful. The Abbé refractometer used for the refractive-index measurements was checked with a glass standard and also with pure hydrocarbon samples including alkyldiphenyls prepared at the Lewis laboratory of the U.S. National Advisory Committee for Aeronautics. The maximum refractive index error is  $\pm 0.0002$ . Densities were determined with a pycnometer of 0.120 ml. capacity; error  $\pm 0.0005$ . The gas-liquid chromatographic retention volumes were determined

<sup>1</sup> Beaven, James, and Johnson, *Nature*, 1957, **179**, 490.

<sup>2</sup> Woods, Van Artsdale, and Reed, *J. Amer. Chem. Soc.*, 1950, **72**, 3221.

<sup>3</sup> García, *Ind. Eng. Chem. Anal.*, 1943, **15**, 648.

TABLE 2.\*

Dimethyldiphenyl †	Short-wave band	Minimum	Conjugation band	Long-wave features
2 : 2'- <sup>a</sup> .....	(206) (36,000)	—	(227) (6,100)	S
3 : 3'- <sup>b,c</sup> .....	207.5 (49,000)	227.5 (5,600)	250.5 (16,100)	—
		[227.5 (5,750)]	[251 (15,800)]	
4 : 4'- <sup>b</sup> .....	203 (43,500)	226 (4,500)	254.5 (21,000)	—
2 : 3'- <sup>c</sup> .....	205 (44,000)	225.5 (7,050)	238 (9,600)	(W)
		[225.5 (6,000)]	[237.5 (7,750)]	
2 : 4'- .....	202.5 (41,000)	224.5 (7,900)	239.5 (11,700)	(V.W.)
3 : 4'- <sup>c</sup> .....	206.5 (45,500)	227.5 (5,300)	253 (18,500)	—
		[228.5 (3,600)]	[253.5 (12,600)]	
2 : 3- .....	203.5 (41,500)	227.5 (8,250)	237 (9,850)	(V.W.)
2 : 4- .....	203 (42,500)	226 (7,800)	241 (11,800)	(V.W.)
2 : 5- .....	202.5 (42,000)	230.5 (8,400)	239 (9,500)	(M)
2 : 6- .....	(202.5) (39,500)	—	(231) (5,600)	(M)
3 : 4- .....	205 (42,500)	227.5 (5,300)	253.5 (18,400)	—
3 : 5- .....	205.5 (43,000)	231 (6,850)	251.5 (16,100)	—

\* Solvent, light petroleum (b. p. 100—120°); wavelengths in  $\mu$  followed by  $\epsilon_{\max}$ . or  $\epsilon_{\min}$ . (in parentheses); wavelengths and long-wave features in parentheses indicate inflections.

† For previous work see: <sup>a</sup> Beaven, Hall, Leslie, Turner, and Bird, *J.*, 1954, 131. <sup>b</sup> Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, New York, 1951. <sup>c</sup> Woods, Van Artsdale, and Reed, ref. 2; for each compound their values are given in [square] brackets.

relative to diphenyl by using a stationary phase of Apiezon M on alkali-washed kieselguhr at 197°, and nitrogen as carrier gas.<sup>1</sup>

The ultraviolet absorption data summarised in Table 2 are consistent with previous work on the effects of alkyl substitution in diphenyls (cf. Everitt, Hall, and Turner,<sup>4</sup> and references quoted therein). Those given by Woods, Van Artsdale, and Reed have proved to be significantly in error. The "long-wave features" are bands or inflections resulting from benzenoid transitions appearing in significant strength only in the hindered 2-substituted diphenyls; only a qualitative indication of their strength is given here. These spectra will be considered in relation to those of other diphenyls elsewhere, and it is also hoped to publish the infrared absorption spectra.

*Experimental.*—All compounds, with the exception of the specimen of 2 : 2'-dimethyldiphenyl kindly provided by Dr. D. M. Hall of Bedford College, London University, were prepared by conventional methods. The principal method was the condensation of an aryl-lithium with the appropriate cyclohexanone, followed by dehydration and dehydrogenation of the resulting carbinol. The Ullmann method and that of Gomberg and Pernert<sup>5</sup> were also used for the 3 : 3'- and 4 : 4'-, and for the 3 : 4-dimethyl compounds, respectively. The halides and substituted cyclohexanones were prepared from intermediates purified until free from isomers. I am indebted to Dr. S. F. Birch of the British Petroleum Co. Ltd. for a generous gift of pure 1 : 3 : 5-xylylidine.

The dehydrogenations were carried out initially either with sulphur or with a palladium-on-charcoal catalyst, but a chance observation showed that the seemingly illogical mixture of the two resulted in a much smoother and more rapid reaction at a rather lower temperature, 190—200°. It is possible that active carbon alone would be as effective as palladised carbon.

The resulting crude diphenyls were subjected to prolonged treatment with sodium and wherever possible purified by repeated crystallisation from ethanol at suitable temperatures down to -50°. The four compounds which could not be induced to crystallise were purified by vacuum fractionation in a small spinning-band column. Dehydrogenation, crystallisation, and distillation were all controlled by gas-liquid chromatographic analysis, without which work on this scale (<10 g.) would scarcely have been possible. Analyses for carbon and hydrogen are not quoted individually, but were all within  $\pm 0.2\%$  of the values required for C<sub>14</sub>H<sub>14</sub> (C, 92.3; H, 7.7%).

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[Received, June 21st, 1957.]

<sup>4</sup> Everitt, Hall, and Turner, *J.*, 1956, 2286.

<sup>5</sup> Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, 48, 1372.