

NOTES.

The Supposed Mandeloisnitrile. By WILSON BAKER and RANDAL
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WOOD and LILLEY (J., 1925, **127**, 95) have described the spontaneous transformation of mandelonitrile to a "yellow solid," m. p. 196° (corr.), stated to be mandeloisnitrile. They claim to have confirmed the isonitrile structure by determinations of the molecular weight and of the percentage of nitrogen, by reduction to the base CHPh(OH)·NH·CH_3 (I) (yellowish-grey solid, m. p. 180° decomp.), and also by acid hydrolysis giving benzaldehyde, formic acid, tarry matter and mandelic acid. It is very unlikely that the change nitrile \rightarrow isonitrile should occur, and the high melting points of Wood and Lilley's products are not consistent with the structures given. Further the base (I) spontaneously loses water, giving the Schiff's base CHPh·N·CH_3 (Zaunschirm, *Annalen*, 1888, **245**, 281). We have found that the pure substance, crystallised twice from alcohol and twice from benzene, melts at 198° and has the formula $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_2$ (Found : C, 77.7; H, 5.1; N, 7.6; *M*, by Rast's method, 372. Calc. : C, 78.0; H, 5.1; N, 7.9%; *M*, 354), and that it is rapidly and completely hydrolysed by dilute acids, giving

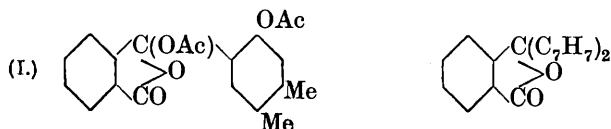
benzaldehyde (1 mol.), mandelic acid (2 mols.), and ammonia (2 mols.).

Examination of the literature showed that this substance, $C_{23}H_{18}O_2N_2$, was first obtained from bitter-almond oil and described by Laurent in 1835 under the name "benzimide" (*Ann. Chim. Phys.*, [2], **59**, 398; see also Laurent, *ibid.*, 1835, [2], **60**, 218; *Annalen*, 1836, **17**, 89; *Ann. Chim. Phys.*, 1837, [2], **66**, 194; *Berzelius' Jahresber.*, 1837, **16**, 246). Zinin in 1840 (*Annalen*, **34**, 188; see also *Berzelius' Jahresber.*, 1842, **21**, 356) and Gregory in 1845 (*Annalen*, **54**, 372) prepared it from bitter-almond oil and potassium cyanide, and both assigned to it the correct molecular formula. It is clear that Gregory prepared it as early as 1834, but did not examine it till later. Laurent and Gerhardt (*Jahresber.*, 1850, 488) realised the identity of "benzimide" with Zinin and Gregory's product. Later Zinin showed (*J. Russ. Chem. Soc.*, 1869, **1**, 213; see *Ber.*, 1869, **2**, 509, 552) that the substance could be hydrolysed by acid to benzaldehyde, mandelic acid, and ammonia. The compound was first recognised as the acetal of benzaldehyde and mandelonitrile — di-(α -cyanobenzyloxy)phenylmethane, $CHPh[O-CH(CN)Ph]_2$ —by Schiff in 1870 (*Annalen*, **154**, 346). The same conclusion was reached as the result of careful work and rational syntheses by Stollé (*Ber.*, 1902, **35**, 1590) and later by Savelsberg (*J. pr. Chem.*, 1916, **93**, 271), the latter having acknowledged Stollé's priority (*ibid.*, 1917, **96**, 186). A correction of Wood and Lilley's work (Stollé, *Ber.*, 1925, **58**, 975) appears to have been overlooked (see, for example, "Organic Syntheses," Vol. **6**, 60) and we desire to record our complete agreement with the work of Stollé and Savelsberg.—THE DYSON PERRINS LABORATORY, OXFORD. [Received, April 5th, 1930.]

Syntheses of 1-Methylantraquinones. By ARTHUR FAIRBOURNE
and GRAHAM EDWARD FOSTER.

IN an attempt to obtain a sample of 1:2-dimethylantraquinone, by a process which should ensure its being free from the difficultly separable 2:3-isomeride (J., 1921, **119**, 1573), 4-hydroxy-1:2-dimethylantraquinone was prepared (J., 1923, **123**, 1137). The intermediate 2-*o*-hydroxyxyloylbenzoic acid, with acetic anhydride and sodium acetate, has yielded colourless plates, m. p. 195° (Found: C, 67.5; H, 5.1; *M*, 360. $C_{20}H_{18}O_6$ requires C, 67.8; H, 5.1%; *M*, 354). Since it was stable towards hot water, this *diacetate* presumably has the structure (I) (compare Gleason and Dougherty, *J. Amer. Chem. Soc.*, 1929, **51**, 310). The *hydroxyantraquinone* has similarly been acetylated to yield 4-*acetoxy*-1:2-dimethylantraquinone, yellow

needles from alcohol, m. p. 154° (Found : C, 73.5; H, 4.9. $C_{18}H_{14}O_4$ requires C, 73.5; H, 4.8%), but could not successfully be reduced in either acid or alkaline media (compare Elbs, *J. pr. Chem.*, 1890, **41**, 1; Braun and Bayer, *Ber.*, 1926, **59**, 914); distillation over zinc dust produced a colourless crystalline sublimate, m. p. 200°, which cannot have been the unknown 1:2-dimethylantracene since it was oxidisable to a product melting at 280° (compare Birukoff, *Ber.*, 1887, **20**, 2068; Fischer and Sapper, *J. pr. Chem.*, 1911, **83**, 201).



The proposed method of Pickles and Weizmann (P., 1904, **20**, 201) for synthesising anthraquinones of proved structures from the corresponding Grignard reagents and phthalic anhydride is likely to be particularly applicable when 1-methylantraquinones are required, but appears never to have been adopted for that purpose, owing to a fear that simultaneous formation of diarylphthalides (as II) would render it unsuitable. Opportunity for synthesising 1:2-dimethylantraquinone from magnesium *o*-3-xylyl bromide has not occurred, but the method has been tested in the similar case of magnesium *o*-tolyl bromide, under conditions maintaining a continuous excess of the anhydride to minimise further reaction of 2-*o*-toluoylbenzoic acid. The latter crystallised from alcohol in colourless needles, m. p. above 120° (Found: equiv. by titration with *N*/10-baryta, 236. $C_{15}H_{12}O_3$ requires equiv., 240), and was converted into 1-methylantraquinone, m. p. 173°, agreeing with the description of Fischer and Sapper (*loc. cit.*) of a specimen synthesised in a different manner (Found: C, 81.0; H, 4.4. Calc.: C, 81.1; H, 4.5%). The method thus renders possible reaction (c) (J., 1921, **119**, 1574) which could not previously be realised.

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