

1,6-Diacetylnaphthalene

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Acetylation of naphthalene with acetyl chloride and aluminium chloride in carbon disulphide at 80 °C affords 1,6- and 1,5-diacetylnaphthalene in the ratio 4:1.

ACETYLATION of naphthalene with acetyl chloride and aluminium chloride in carbon disulphide at 50 °C affords a diacetylated fraction which appears to consist largely of 1,5-diacetylnaphthalene.¹ We have found that when the reaction is carried out at about 80 °C the main product is not the 1,5- but the 1,6-diacetyl compound. G.l.c. analysis of the diacetylated fraction obtained at 80 °C showed that it consisted almost entirely of the 1,6- and 1,5-isomers in the ratio of about 4:1; when the reaction was effected at 70 °C the proportion of the two isomers was 3:2. 1,6-Diacetylnaphthalene was readily isolated by chromatography on alumina, and was identified by oxidation to naphthalene-1,6-dicarboxylic acid and comparison of the dimethyl ester with an authentic specimen. Reduction of the diester with lithium aluminium hydride gave the 1,6-bishydroxymethyl derivative; the derived tosylate was similarly reduced to give 1,6-dimethylnaphthalene.

1,6-Diacetylnaphthalene is reported² to be formed by acetylation of 2-acetylnaphthalene with acetyl chloride and aluminium chloride at 80 °C, and this may be its mode of formation in the present case. It apparently does not arise by isomerisation of the 1,5-diacetyl compound, which was unchanged by treatment with 1 mol. equiv. of aluminium chloride under the conditions of the acetylation experiment.

¹ G. Lock, *Monatsh.*, 1950, **81**, 850; R. Stephan, *Chem. Ber.*, 1957, **90**, 296; see also W. Carruthers, N. Evans, and R. Pooranamoorthy, *J.C.S. Perkin I*, 1973, 44.

EXPERIMENTAL

U.v. spectra were measured with a Unicam SP 800 spectrometer and refer to solutions in 95% ethanol. Mass spectra were recorded with a Hitachi RMU 60 instrument and ¹H n.m.r. spectra with a Perkin-Elmer 60 MHz instrument for solutions in deuteriochloroform. G.l.c. analyses were run at 160 °C on a Pye 104 instrument with a glass column (1.5 m × 6 mm) packed with 3% silicone SE 30 on 80–100 mesh Chromosorb W.

1,6-Diacetylnaphthalene.—The reaction was carried out as previously described¹ except that the naphthalene (16 g) was added to the mixture of aluminium chloride (75 g) and acetyl chloride (25 ml) in carbon disulphide (250 ml) at 80 °C (bath temperature). Distillation of the product afforded a diacetylated fraction (11.8 g) at 180–195° and 0.5 mmHg shown by g.l.c. to consist of two products in the ratio 4:1. The minor product, 1,5-diacetylnaphthalene, was isolated by fractional crystallisation from ethanol as plates, m.p. 132 °C (lit.,² 132.8 °C). The 1,6-isomer was most conveniently obtained from the ethanol-soluble fraction (2.3 g) by chromatography on alumina (64 g). Elution with light petroleum (b.p. 60–80 °C) containing gradually increasing proportions of benzene afforded first mixtures and then 1,6-diacetylnaphthalene (1.6 g) as needles, m.p. 79–80 °C (from light petroleum) (lit.,² 82–84 °C) (Found: C, 79.3; H, 5.8%; *M*⁺, 212. Calc. for C₁₄H₁₂O₂: C, 79.2; H, 5.7%; *M*, 212); λ_{max} 227sh, 235, 260sh, 267, 291, and 343sh nm (log ε 4.46, 4.47, 4.38, 4.42, 3.72, and 3.1).

² D. E. Pearson and C. R. McIntosh, *J. Chem. Eng. Data*, 1964, **9**, 245.

Oxidation of the 1,6-diacetyl compound with sodium hypochlorite at reflux for 12 h gave naphthalene-1,6-dicarboxylic acid, m.p. 304—307 °C (decomp.), converted by diazomethane into the dimethyl ester, needles (from light petroleum), m.p. and mixed m.p. 99—100 °C.

Reduction of the dimethyl ester (2 g) with lithium aluminium hydride (720 mg) in ether for 12 h gave 1,6-bishydroxymethylnaphthalene (1.4 g) as needles (from benzene-methanol), m.p. 180 °C (Found: C, 76.4; H, 6.3%; M^+ , 188. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%; M , 188. This diol (1.3 g) was converted into the tosylate by reaction with toluene-*p*-sulphonyl chloride (2.1 g) in

pyridine overnight, and the crude product (2.1 g) was reduced with lithium aluminium hydride (700 mg) in ether (20 ml) at reflux for 12 h. Chromatography on alumina and elution with light petroleum gave 1,6-dimethyl naphthalene (0.87 g), b.p. 60—63 °C at 0.1 mmHg; the mass and n.m.r. spectra were identical with those of an authentic specimen. The picrate formed orange needles in ethanol, m.p. and mixed m.p. 114—115 °C.

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