The Anomalous Acetylation of 2,6-Dimethylnaphthalene†

By P. H. GORE* and M. YUSUF

(*Department of Chemistry, Brunel University, Woodlands Avenue, London, W.3*)

Summary Friedel–Crafts acetylation of 2,6-dimethylnaphthalene affords mainly 1-acetyl-3,7-dimethylnaphthalene, or, with an excess of the reagents, mainly 1,5-diacetyl-3,7-dimethylnaphthalene.

BY analogy with the proven nitration[1] or Friedel–Crafts benzoylation[2] of 2,6-dimethylnaphthalene, which give 1-substituted derivatives, Dziewonski, Stec, and Zagala[3] claimed that the product of a Friedel–Crafts acetylation was 1-acetyl-2,6-dimethylnaphthalene, m.p. 71°. This orientation has since been accepted also for some twelve derived compounds.[4]

We have found that acetylations of 2,6-dimethylnaphthalene generally give good yields of a mixture of ketones, the major component (65—96%) of which is 1-acetyl-3,7-dimethylnaphthalene, m.p. 70° [ν_{max} in $CHCl_3$: 1664 cm^{-1} (C=O)]. Its orientation follows from its (a) non-identity with authentic 1-acetyl-2,6-dimethylnaphthalene, a liquid [ν_{max} in $CHCl_3$: 1689 cm^{-1} (C=O)], and (b) ^{1}H n.m.r. spectrum [resonances at τ 7·58 (s, 7-CH_3), 7·53 (s, 3-CH_3), 7·44 (s, COCH_3), 2·84 (d, 6-H), 2·52 (d, 5-H), 2·47 (s, 2-H), 2·47 (s, 8-H), 1·59 (s, 4-H); $J_{5,6}$ 8·5, $J_{6,8}$ 1·6 Hz]. Acetylation under more vigorous conditions affords mixtures of diketones, the major component being 1,5-diacetyl-3,7-dimethylnaphthalene, m.p. 167° {^{1}H n.m.r. spectrum: τ 7·50 [s, 3(7)-CH_3], 7·32 [s, 1(5)-COCH_3], 2·34 [d, 2(6)-H], 1·46 [d, 4(8)-H]; $J_{2,4}$ 1·2 Hz}.

This anomalous substitution behaviour (*meta*-orientation with respect to Me-groups) in these acylations is similar to those of other β-methyl-substituted naphthalenes,[5] and reflects the larger steric requirements of the acylation species[6] in the acetylation reaction when compared with the benzoylation reaction.

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† For previous paper in this series, see: P. H. Gore, C. K. Thadani, and S. Thorburn, *J. Chem. Soc.* (*C*), 1968, 2502.

[1] F. Mayer and E. Alken, *Ber.*, 1922, **55**, 2278; A. Davies and K. D. Warren, *J. Chem. Soc.* (*B*), 1969, 873.

[2] J. W. Cook, *J. Chem. Soc.*, 1932, 456.

[3] K. Dziewonski, K. Stec, and P. Zagala, *Bul. Acad. polon. Sci.*, *Ser. Sci. chim.*, *geol.*, *geog.*, 1938, A, 324.

[4] "Elsevier's Encyclopaedia of Organic Chemistry," ed. F. Radt, Elsevier, New York, 1950, vol. 12B.

[5] K. Dziewonski and M. Brand, *Roczniki Chem.*, 1932, **12**, 693; G. A. R. Kon and W. T. Weller, *J. Chem. Soc.*, 1939, 792; P. H. Gore, C. K. Thadani, and S. Thorburn, *J. Chem. Soc.* (*C*), 1968, 2502.

[6] H. C. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, 1959, **81**, 3310; P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), 1966, 1729; R. B. Girdler, P. H. Gore, and C. K. Thadani, *J. Chem. Soc.* (*C*), 1967, 2619.