Revision to the Literature concerning the Friedel–Crafts Acetylation of Tetraphthene

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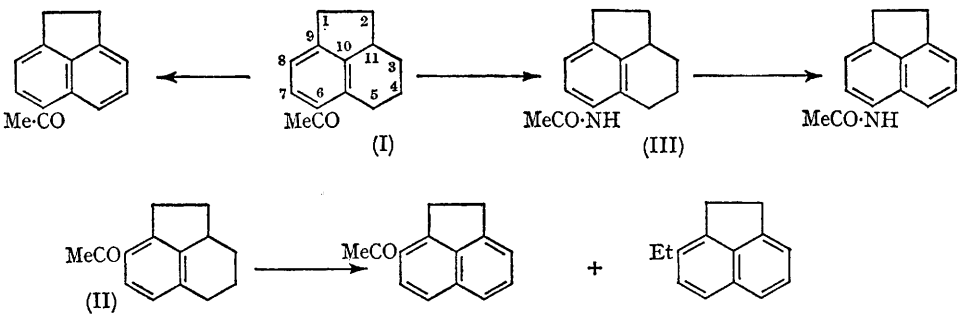
VON BRAUN and co-workers[1,2] reported the aluminium chloride-catalysed Friedel–Crafts acetylation of tetraphthene (3,4,5,11-tetrahydroacenaphthene) with acetyl chloride as giving a single, liquid ketone (oxime, m.p. 148°; semicarbazone, m.p. 240—241°), which they considered to be 6-acetyltetraphthene (I). This, if it were so, would be an example of a remarkably strong difference between the orientating effects of the pentagonal and the hexagonal alicyclic rings on nuclear substitution. In view of its important theoretical implications, von Braun's observation needed confirmation; our investigation has shown it to be incorrect.

Gas-chromatographic fractionation of von Braun's ketone revealed it to be a mixture of *ca.* 53% 6-acetyltetraphthene, b.p. 168—170°/11 mm., $n_D^{23.5}$ 1·5751 (oxime, m.p. 128°; semicarbazone, m.p. 251°) and *ca.* 47% 8-acetyltetraphthene (II), b.p. 168—170°/11 mm., m.p. 47° [oxime, m.p. 158°; semicarbazone, m.p. 268° (decomp. > 230°)]. The same mixture was obtained when light petroleum replaced carbon disulphide as solvent; with methylene chloride, the proportions were 72% of (I) and 28% of (II). The structure of ketone (I) was demonstrated by dehydrogenation over palladised charcoal into 5-acetylacenaphthene (two forms, m.p. 59° and m.p. 69·5°, as reported by



Fieser and Hershberg[3]), and by Beckmann rearrangement of its oxime to 6-acetaminotetraphthene, m.p. 146°, which, on dehydrogenation, gave 5-acetaminoacenaphthene, m.p. 188°; this last compound was identical with a sample prepared from 5-aminoacenaphthene. The structure of ketone (II) was established by dehydrogenation over palladised charcoal into a mixture of 3-acetylacenaphthene, m.p. 104·5° (lit.,[4] 104·7—105·2°), and 3-ethylacenaphthene, picrate m.p. 104·5° (lit.,[5] 104·7—105·1°).

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[4] L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, 1940, **62**, 49.
[5] L. F. Fieser and G. W. Kilmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1354; J. W. Cook, G. A. D. Haslewood, and A. M. Robinson, *J. Chem. Soc.*, 1935, 667.