Reductive Silylation of Aromatic Acids: an Anomalous Product

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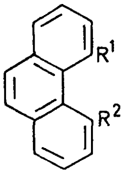
Summary 5-Formyl-4-phenanthroic and phenanthrene-4,5-dicarboxylic acids yield a cyclic ether rather than the expected 4,5-dimethylphenanthrene, upon reductive silylation followed by hydrolysis.

WE report the anomalous production of a cyclic ether in an attempted preparation of 4,5-dimethylphenanthrene (I) from 5-formyl-4-phenanthroic acid (II) by reductive silylation followed by basic hydrolysis.[1]



(I) $R^1 = R^2 = Me$, (II) $R^1 = CHO$; $R^2 = CO_2H$, (III) $R^1 = R^2 = -CH_2SiCl_3$, (IV) R^1, $R^2 = -CH_2OCH_2-$, (V) $R^1 = R^2 = CO_2H$.

Although (I) is a well-characterized compound,[2] existing routes to it are multistep. We envisaged a simple preparation of (I) from readily available[3] (II) by reductive silylation with trichlorosilane–tertiary amine[1a] followed by basic hydrolysis of the expected benzylic silane (III) to give (I). The analogous reaction sequence performed on phthalic acid is reported[1c] to afford *o*-xylene in 64% yield and, while subtle factors seem to control the product distribution when aldehydes are the substrates,[1a] the shortness of the procedure was still appealing.

Application of this reductive silylation–hydrolysis sequence to (II) or (V) affords (IV) (30%) m.p. 74—76° (lit.,[2] 77—78°), δ 7·6 (m, 8H) and 4·77 (s, 4H), p.p.m., *m/e* 220.

Several points may be raised with regard to the mechanism: (a) cyclisations between functional groups in the 4- and 5-positions on phenanthrene are not uncommon;[4] (b) acids seem generally[1c] to proceed to alkylbenzenes *via* anhydrides under silylating conditions; (c) there seems to be no precedent for nucleophilic attack of hydroxide on carbon, displacing silicon, although the converse is well-precedented.

We thank the National Research Council of Canada for supporting this work.

(*Received*, 26*th October* 1972; *Com.* 1816.)

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[1] (a) R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, 1969, **91**, 1556; (b) R. A. Benkeser and J. M. Gaul, *ibid.*, 1970, **92**, 720; (c) R. A. Benkeser and W. E. Smith, *ibid.*, p. 3232.

[2] G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 1950, 2326.

[3] R. J. Dessy and M. S. Newman, *Org. Synth.* Coll. Vol. **4**, 484.

[4] See, *e.g.*, D. H. R. Barton, P. G. Sammes, and G. G. Weingarten, *J. Chem. Soc.* (*C*), 1971, 729.

[5] C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, pp. 143—146.