

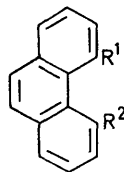
## Reductive Silylation of Aromatic Acids: an Anomalous Product

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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.<sup>1</sup>



(I)  $R^1 = R^2 = \text{Me}$ , (II)  $R^1 = \text{CHO}$ ;  $R^2 = \text{CO}_2\text{H}$ , (III)  $R^1 = R^2 = -\text{CH}_2\text{SiCl}_3$ , (IV)  $R^1, R^2 = -\text{CH}_2\text{OCH}_2-$ , (V)  $R^1 = R^2 = \text{CO}_2\text{H}$ .

Although (I) is a well-characterized compound,<sup>2</sup> existing routes to it are multistep. We envisaged a simple preparation of (I) from readily available<sup>3</sup> (II) by reductive silylation

with trichlorosilane-tertiary amine<sup>1a</sup> followed by basic hydrolysis of the expected benzylic silane (III) to give (I). The analogous reaction sequence performed on phthalic acid is reported<sup>1c</sup> to afford *o*-xylene in 64% yield and, while subtle factors seem to control the product distribution when aldehydes are the substrates,<sup>1a</sup> 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.,<sup>2</sup> 77–78°),  $\delta$  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;<sup>4</sup> (b) acids seem generally<sup>1c</sup> 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.

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<sup>2</sup> G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 1950, 2326.

<sup>3</sup> R. J. Dessy and M. S. Newman, *Org. Synth. Coll. Vol.* **4**, 484.

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

<sup>5</sup> C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, pp. 143–146.