A BASE-CATALYZED REARRANGEMENT OF DIBENZOTROPONE OXIDE[1]

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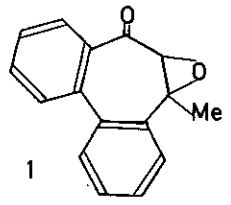
Dibenzotropone oxide (1) rearranges to dihydrophenanthrene derivative (4) in reaction catalyzed by a base, while 1 gives methylphenanthrol (6) by thermal reaction. Mechanistic paths of these reactions are discussed.

Base-catalyzed rearrangements of troponoid to benzenoid compounds have been studied extensively.[2] We now wish to report a novel base-catalyzed rearrangement of dibenzotropone oxide (1).

In the course of studies of the tropone oxide,[3] we prepared dibenzo- and benzotropone oxides (1, mp 132°C; 2, mp 124.5°C; 3, mp 122.5°C),[3] among which dibenzotropone oxide (1), in contrast to 2 and 3, exhibited interesting chemical reactivities.

When dibenzotropone oxide (1) was heated with sodium hydrox-



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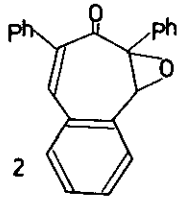

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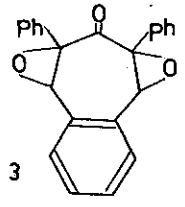

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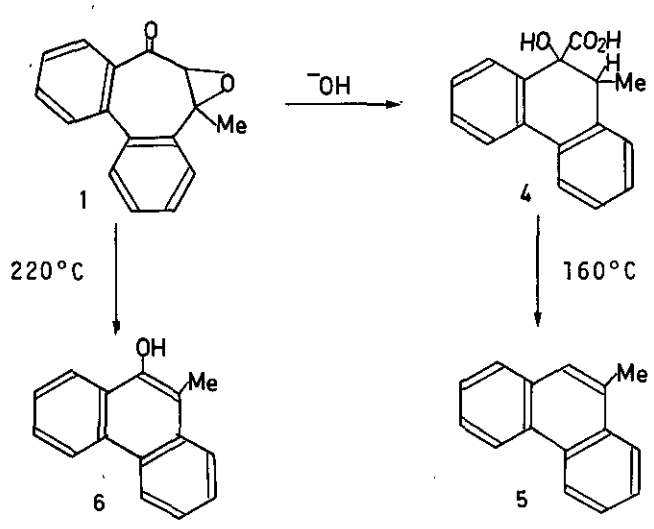


ide in aqueous ethanol under reflux for 24 hours, an acidic compound (4), mp 142°C (dec.) was formed in 55% yield. The structure of 4 was assigned on the basis of the following spectroscopic and chemical data.

4, Anal. Found: C, 75.72; H, 5.53%; ν (KBr) 3400, 1720, 1220, and 1120 cm^{-1}; δ (acetone-d_6) 1.23 (3H, d, J = 7.0 Hz), 3.43 (1H, q, J = 7.0 Hz), 6.53 (OH), and 7.23 - 8.03 (8H, m); m/e 254 (M^+), 192, and 165. The compound 4, upon heating at 160°C, afforded methylphenanthrene (5),[4] mp 89.5°C [δ ($CDCl_3$) 2.80 (3H, s) and 7.5 - 8.9 (9H, m); m/e 192 (M^+) and 165] in 84% yield.

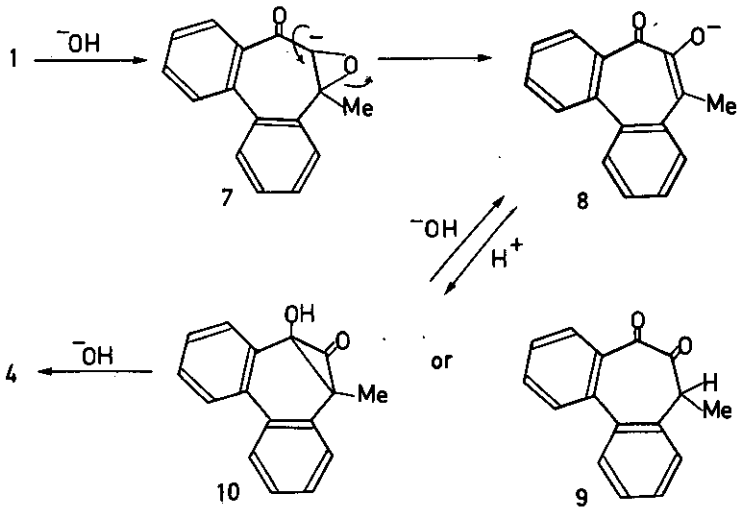
The rearrangement of 1 to 4 *may* be accounted for by a mechanistic path shown by Scheme 1. The base abstracts a proton from the α-position of the ketone of 1 *to give a carbanion* (7) isomerizing to dibenzotropolonate anion (8), from which 4 may arise by the benzilic acid or the Favorski rearrangement via 9 or 10

respectively. The formation of a carbanion at the α-position of α,β-epoxy ketones under the action of the base and the subsequent formation of α-diketones are known.[5]

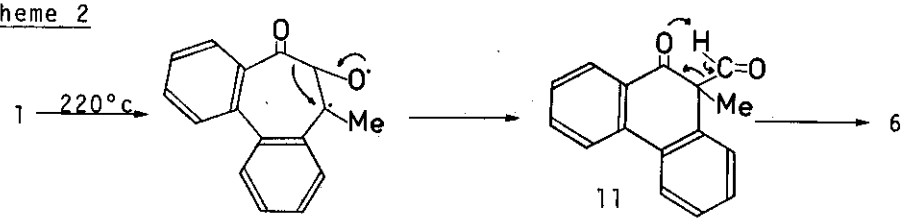
On the other hand, when dibenzotropone oxide (1) was heated at 220°C, methylphenanthrol (6)[3,6] (mp 126°C) [acetate, mp 148°C; Anal. Found: C, 81.55; H, 5.60%; ν (KBr) 1740 cm^{-1}; δ ($CDCl_3$) 2.43 (3H, s), 2.47 (3H, s), 8.07 (6H, m), and 8.40 - 8.67 (2H, m)] was formed in quantitative yield by the loss of a CO moiety.

In the thermal reaction methylphenanthrol (6) may arise via keto-aldehyde (11) which is derived from 1 by the cleavage of the oxide C-O bond followed by the 1,2 shift of the carbon as shown by Scheme 2.

Scheme 1



Scheme 2



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