A BASE-CATALYZED REARRANGEMENT OF DIBENZOTROPONE OXIDE

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Dibenzo- and benzotropone oxides (1, mp 132°C; 2, mp 124.5°C; 3, mp 122.5°C), among which dibenzo- tropones oxide (1), in contrast to 2 and 3, exhibited interesting chemical reactivities.

When dibenzo- tropones oxide (1) was heated with sodium hydrox-
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-d₆) 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), mp 89.5°C [δ (CDCl₃) 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 \( \alpha \)-position of \( \alpha,\beta \)-epoxy ketones under the action of the base and the subsequent formation of \( \alpha \)-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%; \( \nu \) (KBr) 1740 cm\(^{-1}\); \( \delta \) (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-0 bond followed by the 1,2 shift of the carbon as shown by Scheme 2.

**Scheme 1**

![Scheme 1 diagram](image-url)
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REFERENCES
1 Cordially dedicated to Professor Tetsuo Nozoe on the occasion of his 77th birthday.

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Scheme 2

\[
\begin{align*}
1 & \quad 220^\circ C \\
\begin{array}{c}
\text{O} \\
\text{Me}
\end{array} & \quad \rightarrow & \quad \begin{array}{c}
\text{O} \\
\text{H-C} = \text{O}
\end{array}
\end{align*}
\]

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