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TROPONE OXIDES

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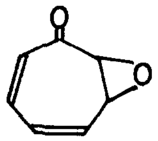
Homoconjugation has recently been the subject of extensive investigations, and homoaromaticity in homotropones[1-4] as well as in homotropylium ions[5-7] has been documented. Tropone oxides (1 and 2) are the oxygen analogs of homotropones and the extent to which the oxido group participates in the homoconjugation in these oxides would be an interesting problem to study. Furthermore, they may also be of interest in view of the chemistry of arene oxides[8] as well as of oxiranes[9-11]. We wish to report the first synthesis and thermal reactivities of tropone-2,3-oxide (1) and-4,5-oxide (2).

Tropone oxides 1, b.p. 70°C /0.7mmHg, and 2, b.p. 60°C /0.7mmHg[12] were prepared by treating tropone epidioxide (3)[13] which in turn was obtained from tropone and singlet oxygen, with one mole equivalent of triphenylphosphine in 25 and 4% yields respectively.

The structure of 1 was assigned on the basis of the following evidence: $\lambda_{max}^{cyclohexane}$ (log ε) 252 sh.(3.44), 260 (3.53), 283 (3.64), 332 sh.(2.56) mμ; λ_{max}^{EtOH} (log ε) 285 (3.68), 343 (2.3) mμ; ν (neat) 3000, 1665 (C=O), 1436, 1197, 1067, 822, 810 and 720 cm^{-1}; m/e 122 (M^+), 94 (M-CO), 66 and 65; nmr ($\delta_{100\ Mc}^{C_6D_6}$) 2.96 ($H_3$; t.d., $J_{3,4}$=4.5, $J_{3,5}$=1.5 Hz), 3.76 (H_2; d.d., $J_{2,3}$=4.3, $J_{2,7}$=1.4 Hz), 5.53 (H_5; m., $J_{5,6}$=5.1 Hz), 5.72 (H_4; q.d., $J_{4,5}$=11.8 Hz), 5.89 (H_6 and H_7; m.). The ultraviolet spectrum of 1 showed a similarity to 2,3-homotropone[1-3]. The carbonyl absorption in the infrared spectrum of 1 is lower by approximately



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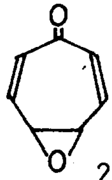

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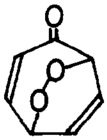

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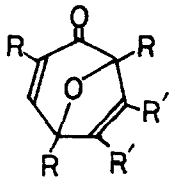
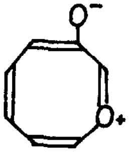


4a: R = R' = H
4b: R = R' = ph
4c: R = ph; R' = CO_2Me



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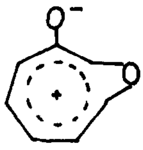

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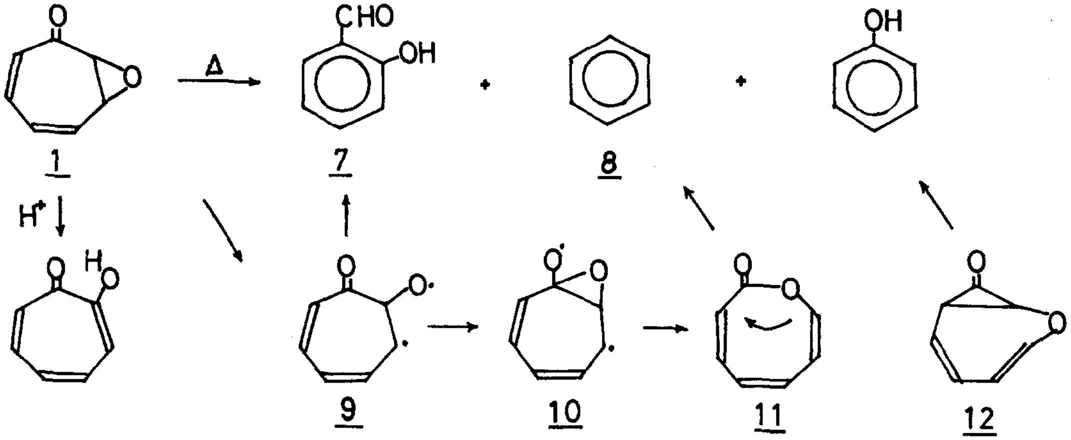

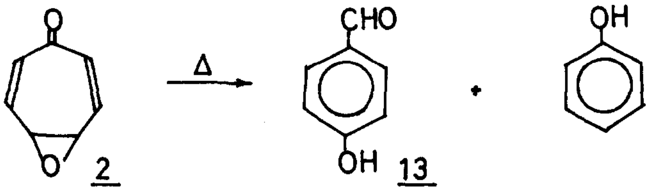

25 cm^{-1} than that of 3 or of oxabicycloheptadienone (4b)[14], eliminating alternate structure 4a. Coupling constants in the nmr spectrum of 1 are in good correspondence with those of 8-carboethoxybicyclo[4.1.0]octa-3,5-diene-2-one[4a]. Tropone oxide (1) is sensitive to acid; treatment of 1 with weak aqueous acids resulted in the formation of tropolone in quantitative yield. The oxide 1 afforded tropone by the action of triphenylphosphine in 36% yield.

The structural assignment of 2 was based on the following evidence: λ_{max}^{EtOH} (log ε) 229 sh.(3.62) and 272 (3.78) mμ; $\nu_{co}(CHCl_3)$ 1660 cm^{-1}; m/e 122 (M^+), 121, 94, 66 and 65; nmr ($\delta_{60\ Mc}^{CDCl_3}$) 6.94 (H_3 and H_6; d.d., $J_{3,4}$=4.1 Hz), 6.32 (H_2 and H_7; d. with small splittings, $J_{2,3}$=12.5 Hz), 3.91 (H_4 and H_5; d. with small splettings). The ultraviolet spectrum and the coupling constant of the olefinic protons in the nmr spectrum of 2 are in good correspondence with those of 4,5-homotropone[2].

Since tropone oxides are the oxygen analogs of homotropones, it is interesting to examine whether or not the oxido group contributes to the homoconjugation, by which, for example, zwitterionic species such as 5 or 6 would be expected to arise from 1. The similarity of the spectral data of 1 and 2 with those of the corresponding homotropones indicates that there is no interaction of the oxido group with the conjugated system in 1 and 2 under usual spectroscopic conditions. Due to the instability of 1 and 2 toward acids, spectroscopic studies under strong acidic conditions could not been carried out.

In connection with the homoconjugation, the thermal reactivities of these oxides were examined. Heating 1 in dry acetone at 175° in a sealed tube afforded salicylaldehyde (7), benzene (8) and phenol in 25, 24 and 3% yields respectively. The oxide 2 afforded by heating at 220° 4-hydroxybenzaldehyde (13)(45 %) and phenol (6 %). All of 7, 8, and 13 are products of the cleavage of the C-O bond in these oxides, and the formation of 7 and 8 from 1 may be accounted for as being derived from intermediate species 9 and 11 which is formed by the oxygen migration via 10, respectively. The formation of 7 and 8 may be in analogy to the formation of cyclohexa-1,3-diene-6-aldehyde from 1,2-epoxytropilidene[15] and to that of dimethyl 3,4,6-triphenylphthalate from 4c[15], respectively. Phenol, a minor product, is assumed to arise from the intermediates formed by the Cope rearrangement[3], such as 12 (for 1). As summary, it is evident that the cleavage of the C-O bond is the main reaction pattern in 1 and 2, and we conclude that the contribution of the oxido group to the homoconjugation which, for example, may lead to the formation of 5 or 6 from 1, is not attained in these oxides.

Further chemistry of tropone oxides will appear in our forthcoming paper.

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