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ISOMERIZATION OF 2,7-DIPHENYLTROPONE-2,3-OXIDE TO 1,3-DIPHENYL-8-OXABICYCLO[3.3.0]OCTA-3,6-DIENE-2-ONE[1]

Takahiro Tezuka* and Miyoshi Shinba
Department of Chemistry, The University of Tsukuba,
Sakura-mura, Ibaraki 300-31, Japan
Takaharu Abe, Ryoichi Miyamoto, and Toshio Mukai
Department of Chemistry, Faculty of Science,
Tohoku University, Sendai, Japan

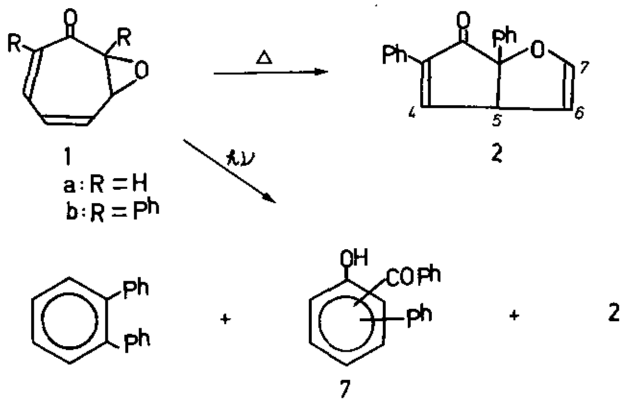
2,7-Diphenyltropone-2,3-oxide (1b) isomerizes thermally to its bicyclic isomer (2) probably via ionic intermediate species such as 3, while benzo- and dibenzotropone oxides (8 and 9) are converted to aromatic compounds by thermal reaction. Photochemical reaction of 1b is also reported.

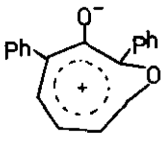
A recent publication by Prinzbach et al.[2] on the cis-trans isomerization of 2,3:6,7-dioxa-bis-σ-homotropone in which delocalized ylide intermediate is proposed, prompts us to report our preliminary studies on isomerization of 2,7-diphenyltropone-2,3-oxide (1b) and benzo- and dibenzotropone oxides (8 and 9), which may provide some insight into such an ionic intermediate species.

We have reported previously that tropone-2,3-oxide (1a) is converted to salicylaldehyde and benzene by thermal or photochemical reaction,[3] in which the opening of the C_2-C_3 oxide bond is not implicated. We have found in this study that the diphenyl analog (1b), in contrast to 1a, isomerizes thermally to its bicyclic isomer (2) by the ionic opening of the C_2-C_3 oxide bond.

When the tropone oxide 1b[4] is heated in benzene, xylene, ethanol, or acetonitrile under reflux, the bicyclic isomer 2, mp 102°[5], is formed in quantitative yield. The structural assignment of this isomer is based on the following spectral and chemical data: ν (KBr) 1710, 1145, and 1065 cm^{-1}; δ (100 Mc in $CDCl_3$) 3.98 (H_5, ddd, $J_{5,4}$= 3.2, $J_{5,6}$= 2.8, $J_{5,7}$= 2.0 Hz), 5.05 (H_6, dd, $J_{6,7}$= 3.0 Hz), 6.43 (H_7, dd), 7.92 (H_4, d), and 7.1 (phenyl); m/e 274 (M^+, 18%), 246 (100%), 204 (2%), 203 (8%, $M^*_{obs.}$= 166 - 169), 202 (17%), 144 (50%), and 115 (63%).

The coupling pattern and chemical shifts of H_4 and H_5 in the nmr spectrum of 2 are consistent with those observed for the corresponding protons of 1,3-diphenylbicyclo[3.2.0]hepta-3,6-diene-2-one.[6] The chemical shifts of H_6 and H_7 of 2 are comparable with those of the olefinic protons (H_2 and H_3) of dihydrofuran derivative.[7] The appearance of the fragment ions m/e 204 and 202 which are equivalent to diphenylcyclobutadiene and benzobiphenylene respectively, also supports the assigned structure. On catalytic hydrogenation over platinum oxide,





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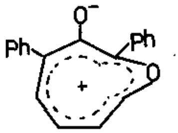

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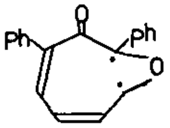

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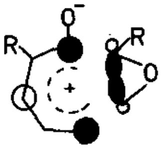

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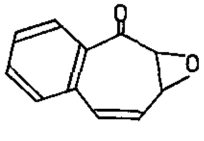
2 affords a tetrahydro derivatives, mp 158°; ν(KBr) 1755 cm^{-1}; m/e 278 (M^{+}), 145, and 105.

The thermal isomerization of 1b to 2 is of significance from a mechanistic point of view. The isomerization may be interpreted either by an ionic reaction path proceeding through an intermediate species such as 3 (or 4) or a radical path involving 5. It is also explicable in terms of vinylcyclopropane rearrangement mechanism. Although trapping of such species as 3 or 4 by use of dipolarophiles such as dimethyl acethylenedicarboxylate and tolan has not been successuful, the kinetic solvent effect for this reaction supports an ionic reaction path. It has been found that the reaction is of first order and the rate of the isomerization is faster in methanol ($k^{70°} = 1.1 \times 10^{-3}$ sec^{-1}) than in benzene ($k^{70°} = 3.6 \times 10^{-5}$ sec^{-1}).[8] In addition, a rough measurement indicated that the reaction is complete in 15, 14, 1, or 0.5 hours when 1b is heated in benzene, acetonitrile, ethanol, or acidic ethanol under reflux, respectively. In protic solvents the conversion is accelerated. The proton may exert a stabilizing influence on the developing oxide anion of such species as 3.

The oxide C-C bond opening of 1b leading to 3 may be a consequence of the perturbational LUMO-HOMO interaction between a pentadienyl cation part formed by the polarization of the carbonyl group and the C-C σ-bond of the oxide as shown by a simple MO model in 6. This is a thermally allowed mode for such an interaction. From this point of view the comparison with photochemical reaction is interesting. Photolysis of 1b in benzene, acetone, or ethanol with 3500 Å light affords o-terphenyl (18 - 24%) and hydroxybenzophenone derivatives (7), mp 101° (13 - 34%) and mp 157° (15 - 21%), as the major products. They may arise from 1b by the cleavage of the oxide C-O bond. The bicyclic isomer 2, in this case, is formed as a minor product (15 - 19%).

In the hope of obtaining a stable oxahomotropylium oxide (or delocalized ylide), benzo- and dibenzotropone oxides (8, bp 75°/0.04 mm, and 9, mp 132°)[5] were prepared and their thermal reactions were studied. It has been found, however, that these tropone oxides give products arising solely by the oxide C-O



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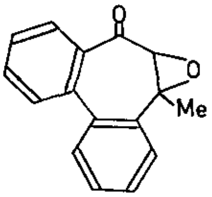

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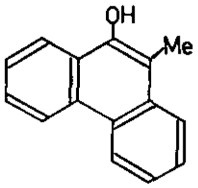

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bond cleavage. Upon heating 8 in acetone in a sealed tube at 160°C, naphthalene is formed in 11% yield together with the recovery (26%). Upon heating 9 at 220°C, the phenanthrol derivative 10, mp 126° (acetate, mp 148°),[5,9] is formed in quantitative yield.

The evidence cited seems to indicate that both the phenyl substituent[10] at C_2 and the delocalized dienone part[11] at C_4-C_7-C_1 (see 6) are requisite for the opening of the C-C oxide bond of the tropone-2,3-oxide. The kinetic data support the ionic reaction path for the isomerization of 1b to 2, in which the homoaromatic species 3 rather than the delocalized ylide 4, antiaromatic ground state,[12] is invoked as an intermediate.

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REFERENCES AND NOTES

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