Tetrahedron Letters No. 34, pp. 2975-2978, 1970. Pergamon Press. Printed in Great Britain.

# THERMAL REACTION OF TROPONE ETHYLENE KETAL

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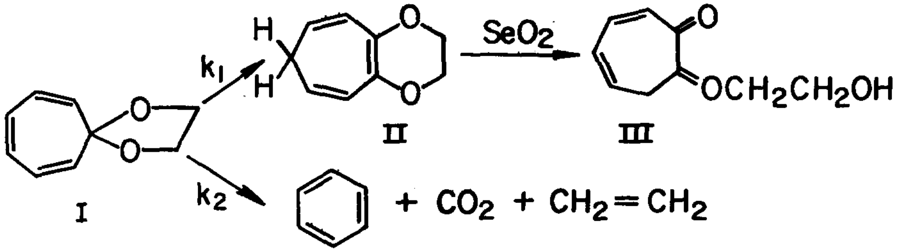
(Received in USA 26 March 1970; received in UK for publication 19 June 1970)

Thermally induced [1, 5] hydrogen shifts in the cycloheptatriene systems have been a subject of considerable interest (2) but other than hydrogen only [1, 5] nitrile migration has been observed (3). Recently a [1, 7] methoxy migration process was considered in the thermal rearrangement of 7,7-dimethoxycycloheptatriene (4). The system is also known (2) to undergo thermally induced skeletal rearrangements and aromatization reactions, probably via norcaradiene intermediates. In some special cases (5, 6, 7), the aromatization occurs with loss of the $C_7$ as a carbene to give benzene. The parallel aromatization behavior has been noted in the isomeric norbornadiene system (8), and many reports have appeared as to whether these two systems aromatize via identical or different transition states (6-10).

We found that tropone ethylene ketal (I) (11, 12) upon heating at 110-150° as neat liquid or in solvents such as acetonitrile and cyclohexane in a sealed tube, smoothly and cleanly gives benzene, ethylene, carbon dioxide, and 3,4-dioxyethylenecycloheptatriene (II), $bp_{1.3}$ 69-70°; $n_D^{25}$ 1.5555; UV max in cyclohexane, 210 (sh log ε, 4.09), 280 nm (3.64); pmr (60 Mc, $CCl_4$) τ 7.73 (triplet, 2H, H-7, J = 6.8 Hz), 6.08 (singlet, 4H), 4.87 (doublet of triplets, 2H, H-1 and 6, J = 9.6 and 6.8) and 4.12 (doublet, 2H, H-2 and 5, J = 9.6); m/e 150 (M, 100%), 149, 94, 78, 77, and 66. Treatment of II with selenium dioxide in boiling dioxane afforded III, m.p. 83-84°, in 78% yield.

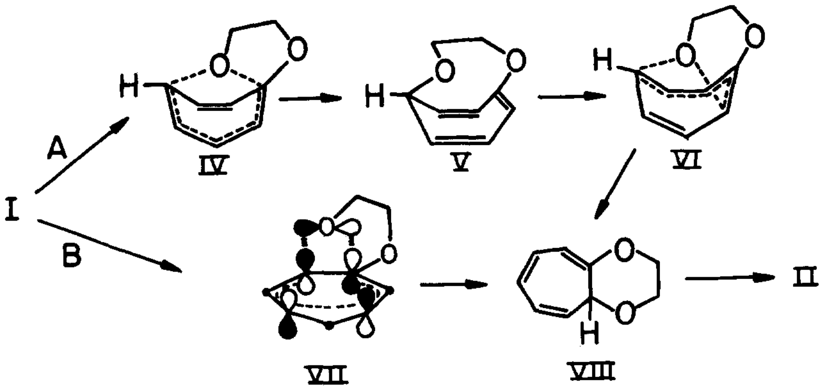


Kinetic study of the thermolysis of I as neat liquid (13) provided the unimolecular rate constants, $k_1$ and $k_2$, and activation parameters, as shown below. The ratio of II to benzene remained constant throughout each run, but a definite trend toward smaller ratios was noted with increasing temperatures.

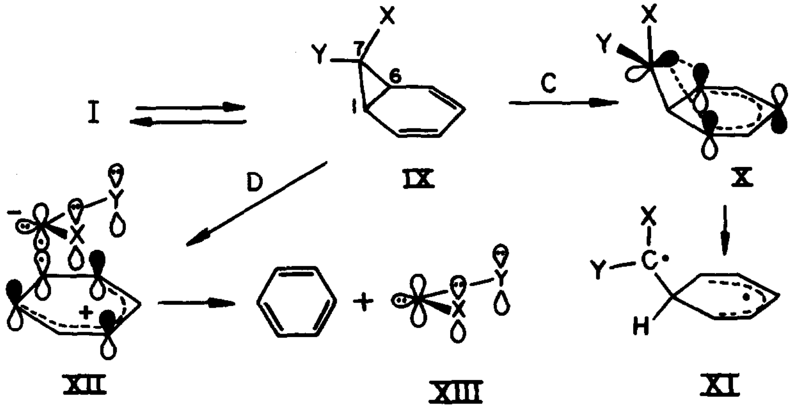
| | $k \times 10^6$ sec$^{-1}$ | | | | $E_a$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|---|---|---|
| | 121° | 124° | 136° | 155.5° | Kcal/mole | Kcal/mole | e.u. |
| I $\longrightarrow$ II | 7.88 | 8.56 | 19.7 | 87.8 | 23.9 | 23.2 | -23 |
| I $\longrightarrow$ $C_6H_6$ | 1.80 | 2.19 | 6.72 | 45.0 | 31.6 | 30.8 | -7.2 |
| $k_1/k_2$ | 4.36 | 3.86 | 2.96 | 1.95 | | | |

Based on the above data the following two paths were considered for the formation of II. Path A involves two consecutive, sigmatropic [1, 5] oxygen shifts and path B a concerted [1, 7] oxygen shift utilizing the antisymmetric $p_y$ (or $p_z$) orbital to give, in both cases, the intermediate VIII, which is expected to undergo a facile hydrogen shift to give II at a rate comparable to that in 7-methoxycycloheptatriene ($2.5 \times 10^{-5}$ sec$^{-1}$ at 121°) (14). In the case of path A the second oxygen shift (V $\longrightarrow$ VIII) may be accelerated by relief of strain and thus proceed more rapidly than the first one, whereas the usually less energetic [1, 5] hydrogen migration becomes infeasible in V because of its rigid bridged structure. The available data, however, do not allow us to decide between the two paths.

In the disintegration reaction ($k_2$) it is assumed that I is in rapid equilibrium with its valence isomer (IX) (2, 3). A concerted decomposition of IX to benzene and ethylenedioxycarbene (or directly to $CO_2$ and ethylene) <u>via</u> a symmetric transition state (linear cheletropic path) is thermally forbidden (15).



Yet the observed activation parameters speak against the path similar to the aromatization of cycloheptatrienes where diradical intermediates have been postulated (16). This process may be visualized to occur (path C) by the initial cleavage of the $C_6$-$C_7$ bond to generate a p-orbital at the $C_7$ ($\pi$ departure) to give a species (X) which closely resembles the transition state of [1, 5] sigmatropic shifts. Further displacement of the p-orbital from the pentadienyl system would give the diradical (XI).



The $\pi$ departure, however, is expected to become less favorable if the $C_7$ substituents bear delocalizable lone pair electrons, since they greatly increase electron repulsions in the interacting $\pi$ system of X. On the other hand, if the cleavage occurs in such a manner as to generate a filled $\sigma$-orbital at the $C_7$ ($\sigma$ departure) as depicted by XII, the lone pairs can favorably interact with the developing cationic pentadienyl system. It is significant that the species (XIII) closely resembles configurationally as well as electronically the transition state proposed for the concerted addition of methylene to olefins (17). Thus, an initial $\sigma$ departure may indeed trigger the concerted disintegration of IX into benzene and a so-called stable carbene (XIII). This mode of decomposition is entirely in concordance with the process designated as non-linear cheletropic reactions. The fact that the disintegration of I occurs more readily than that of the corresponding dimethyl ketal (>110° vs >150°) may be indicative of further stabilization of the transition state from I due to incipient formation of carbon dioxide and ethylene.

In addition to two alkoxy groups in the ketals, two halogen atoms (18) as well as a single dimethylamino group (7) are apparently sufficient to cause non-linear cheletropic decomposition in the cycloheptatriene system. Finally, it should be pointed out that if the reported, similar disintegration of the norbornadienone ketals (8) should occur also by an initial $\sigma$ departure, it must take place in a stepwise and non-concerted manner.

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12. Irradiation of I afforded bicyclo[3.2.0]hepta-3,6-dien-2-one ethylene ketal in 50% yield.
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