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Troponoid-Benzenoid Rearrangement by Pyrolytic Process

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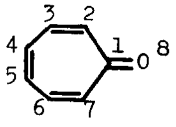
Photochemistry of troponoid derivatives has been investigated extensively, and it was found that most derivatives afforded valence bond isomers having $\Delta^{3,6}$ bicyclo[3.2.0]heptadienone system.[1] However, no pyrolytic reaction of troponoid system has been reported except for suggestion that tropone formed as intermediate in the pyrolysis of methoxytropilidene yielded benzene.[2] Recently molecular orbital symmetry theory provided a clear-cut explanation of differences between photochemical and thermal valence isomerizations of polyolefines.[3] Consideration of differences in the coefficients of the highest occupied and lowest vacant molecular orbital of tropone as depicted as below,[4] suggests that tropone and its derivatives may show different type of reaction via different valence isomerization induced by light and heat.



No. of atom. orb.	1	2	3	4	5	6	7	8
H.O.M.O.	-	+	+	-	-	+	+	-
L.V.M.O.	0	+	-	-	+	+	-	0

From this point of view, the pyrolytic reaction of the troponoid system was extensively investigated for comparison with the photochemical reaction of the same system. Pyrolyses were carried out under nitrogen atmosphere (flow rate: 40 cc./min.) by passing the neat troponoids or their benzene solutions through a quartz column (12 mm x 12 cm) containing quartz tips (8-12 mesh) preheated at desired temperature. Under this condition most troponoid derivatives rearrange to benzenoid derivatives with decarbonylation,[5] and the results obtained are shown in Table 1. Since the pyrolytic decarbonylation of tropone is peculiar

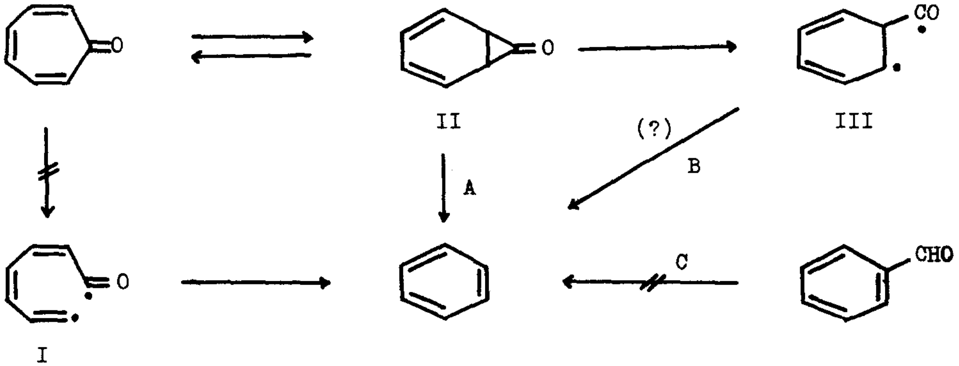
Table 1. Pyrolytic Reaction of Troponoid Derivatives

No.	Compound	Temperature	Product (yield %)
1	Tropone[a]	400°	recov (100)[b]
2	Tropone[a]	500°	recov (90) Benzene (10)[b]
3	Tropone[a]	600° and 700°	Benzene (100)[b]
4	Tropone[a]	800°	Benzene (50) Biphenyl (50)[b]
5	Tropone[a]	900°	Benzene (25) Biphenyl (75)
6	Tropolone	700°	Phenol (70)
7	Tropolone Methyl Ether	500°	Anisole (80)
8	Tropolone Methyl Ether	700°	Phenol (60)
9	2-Aminotropone	700°	Aniline (60)
10	2-Phenyltropone	700°	Biphenyl (65)
11	2,6-Diphenyltropone	600°	m-Terphenyl (50)
12	2,7-Diphenyltropone	600°	o-Terphenyl (60)
13	4-Isopropyltropolone	600°	3-Isopropylphenol (39) recov (55)
14	5-Isopropyltropolone	600°	4-Isopropylphenol (33) recov (54)
15	4-Isopropyltropolone Methyl Ether	500°	3-Isopropylanisole (90)
16	5-Isopropyltropolone Methyl Ether	500°	4-Isopropylanisole (59)
17	2-Phenyl-4-methoxytropone	600°	3-Methoxybiphenyl (16)
18	3-Phenyl-4-methoxytropone	600°	2-Methoxybiphenyl (20)
19	3,4-Benzotropolone	500°	α-Naphthol (14) recov (69)
20	3,4-Benzotropolone	600°	α-Naphthol (83) Naphthalene (trace)
21	2-Methyl-4,5-benzotropone	700°	recov (95)
22	2-Methyl-4,5-benzotropone	800°	β-Methylnaphthalene (38) recov (28)

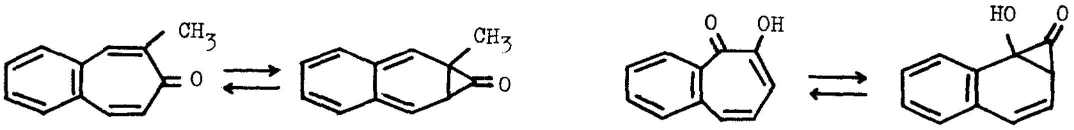
a) Pyrolysis of neat liquid; in other cases in benzene.

b) Yield was estimated by V.P.C.; in other cases it was estimated by isolated products.

reaction (Nos. 2 and 3), the kinetic study was also investigated by a conventional flow method using other apparatus in which a toluene solution of tropone was pyrolyzed in a stream of helium at temperature ranging from 420° to 490°.[6] The reaction was found to be unimolecular and the value of Ea, ΔH^{*} and ΔS^{*} were 52.7 Kcal/mol, 51.2 Kcal/mol and 1.2 e.u.. As the first step of the pyrolysis of tropone, α-cleavage of the ring giving biradical I or the formation of norcaradienone (II) are possible. The latter pathway may be preferable to the former one, because of relatively lower Ea value compared with C_1-C_2 bond fission energy of tropone,[7,8] and of relatively small ΔS^{*} value of this pyrolysis. Furthermore, the formation of II is not imcompatible with the molecular orbital symmetry theory, although it may not be sure to apply the calculated result to such a high-temperature reaction. Subsequent decarbonylation from II would proceed by a concerted process (path A) or a stepwise one via biradical III (path B) or benzaldehyde (path C). Of these paths, path C can be discarded, because pyrolysis of benzaldehyde under the same conditions did not yield benzene. The fact that no bibenzyl could be detected in the kinetic study using toluene as solvent suggests that path A seems to be preferable to B. However, path B could not be ruled out completely, if the decarbonylation from III occurred very rapidly.



The formation of biphenyl from tropone at higher temperature (Nos. 4,5) was probably resulted from a different pathway. Pyrolysis of tropolone (No. 6), its methyl ether (Nos. 7,8) and 2-aminotropone (No. 9) afforded the corresponding benzenoid derivatives with decarbonylation. From their pyrolytic temperature, it may be concluded that the ease of rearrangement decreases in the order, tropolone methyl ether > tropone > tropolone > 2-aminotropone. The pyrolytic reaction was also applicable to aryltropones (Nos. 10-12), alkyltropolone and their methyl ethers (Nos. 13-16) and 4-methoxytropone derivatives (Nos. 17,18). The condensed troponoids were pyrolyzed to yield the expected rearrangement products (Nos. 19-22). It is noted, however, that the decarbonylation of 2-methyl-4,5-benzotropone (IV) occurred with more difficulty than 3,4-benzotropolone (V). The reason is likely that compound V can isomerize to an intermediate VII having a benzenoid structure, whereas compound IV has to isomerize to a valence isomer with quinonoid structure VI, which is not profitable for resonance stabilization.



IV VI V VII

These pyrolytic reactions represent a novel type of troponoid-benzenoid rearrangement and provide a useful tool for structural elucidation of troponoid derivatives, because of simplicity of the method. Pyrolyses of 2,7-diphenyltropone (No. 12) and of two methyl ethers (Nos. 17,18) derived from 2-phenyl-4-hydroxytropone are good examples for the case.[9] It should be noted that the pyrolytic decarbonylation of troponoids is analogous to their decomposition occurring by electron impact.[10] The kinetic study of the pyrolytic reactions of tropolone, its methyl ether and 2-aminotropone is in progress.[6]

Acknowledgement. The authors are indebted to Dr. A. Amano for the kinetic study and Mr. A. Takeshita and K. Okayama for help in experiments. Financial support from the Sankyo Co. is also acknowledged.

REFERENCES AND FOOTNOTES

1. O. L. Chapman, Advances in Photochemistry, 1, 323 (1963). It is known as an exception that irradiation of tropone afforded benzene via norcaradienone intermediate, although the yield was very poor.

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3. R. B. Woodward, R. Hoffmann, ibid., **87**, 395 (1965); R. Hoffmann, R. B. Woodward ibid., **87**, 2046 (1965); H. C. Longuet-Higgins, E. W. Abrahamson, ibid., **87**, 2045 (1965); K. Fukui, Tetrahedron Letters, **24**, 2009 (1965).
4. Y. Amako, H. Yamaguchi and H. Azumi, Tetrahedron, in press.
5. Upon pyrolysis, some troponoids such as 2-halotropone and 2-phenoxytropone afforded rearrangement products without decarbonylation in addition to the decarbonylated products. Details will be reported soon.
6. Details will be reported by A. Amano, T. Nakazawa, K. Okayama, T. Yamada and T. Mukai.
7. K. N. Klump and J. P. Chesick, J. Am. Chem. Soc., **85**, 130 (1963); W. G. Woods, J. Org. Chem., **23**, 110 (1958).
8. Since the C_1-C_2 bond of tropone has double bond character, the α-clevage dissociation energy is thought to be more than the bond dissociation energy of acetone 71 Kcal. cf. J. R. Majer, C. R. Patrick and J. C. Robb, Trans. Farad. Soc., **57**, 14 (1961).
9. The common reactions applicable to troponoid system can not be applied to 2,7-diphenyltropone for elucidation of its structure. cf. T. Mukai, Bull. Chem. Soc. Japan, **31**, 852 (1958).
10. H. Budzikiewicz, C. Djerassi and D. H. Williams, Interpretation of Mass Spectra of Organic Compounds, Holden-Day, Inc., San Francisco, Calif., 1964, p 241.