Photolysis of Tropone in the Vapor Phase1)

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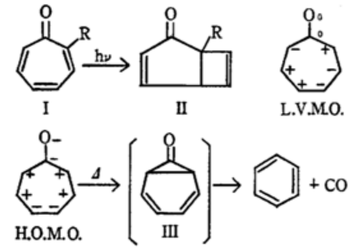
In solution, most tropone derivatives (I), upon irradiation, afford their valence isomer, II2). On the other hand, the thermolysis of the troponoids gives benzenoids in a very good yield.3) The kinetic study of the thermoylsis has suggested that the decarbonylation proceeds *via* norcardadienones.3) The good contrast between the photochemical behavior and the thermal behavior of the troponoid can be supported by the molecular orbital symmetry theory.4) The disrotatory process of the lowest vacant molecular orbital can lead to II while the highest occupied molecular orbital leads to III. However, the photoreaction of tropone (I, R=H) is an exceptional case: dimers5) and benzene2) were obtained instead of II (R=H). Although the yield was very poor, the photochemical formation of benzene may be assumed to arise from the use of III as an intermediate.2) However, this assumption is contrary to the molecular orbital symmetry theory described above.



We have studied the photolysis of tropone *in the vapor phase* in order to clarify the mechanism for the decarbonylation of tropone. The photolysis was carried out in a Pyrex vessel (170 m*l*) at 100±5°, under completely degassed conditions, by external irradiation using Toshiba H 400-P lamp.6) The results obtained are shown in the table, although all of them are only preliminary.

The yield of the decarbonylation (runs 1 and 2) increased to about 30% compared with the photolysis in solution, where the yield was 1%. In addition, when an inert gas such as carbon dioxide was added to the reaction system, a decrease in the yield for the decarbonylation was observed (run 3).

These facts suggest that the excited molecule of tropone converts isoenergetically to the vibrationally-excited molecule, which then gives benzene and carbon monoxide through the intermediate III. Although the photo-excited state of tropone cannot be assigned on the basis of the results of the present experiment, it seems unlikely that the triplet state is involved, considering that the estimated triplet energy of tropone (42—53 kcal/mol)5d) is rather less than the activation energy of the thermal decarbonyl process of tropone (54.1 kcal/mol).3) The interpretation of the quenching effect of oxygen (run 4) is left for future investigation.

TABLE 1

Run	Tropone μ mol (mmHg)	Gas added (mmHg)	Irr. time hr	CO (μ mol)	Benzene (μ mol)
1	32.1(4.30)	—	1.0	12.2	10.0
2	26.0(3.53)	—	0.5	7.96	5.1
3	41.5(5.63)	CO_2(15)	0.5	0.42	not detect
4	38.5(5.22)	O_2(21)	0.5	0.27	not detect

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6) Control reaction indicated that, under the same condition, heating of tropone underwent no decarbonylation.