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THE Hg SENSITIZED VAPOR PHASE PHOTOLYSIS OF CYCLIC ANHYDRIDES

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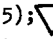
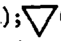
We have reported the mercury sensitized vapor phase photolysis of cyclic lactones and butenolides leading to the extrusion of carbon dioxide and formation of cyclic hydrocarbons.[1] The course of this reaction is formally analogous to the well studied extrusion of carbon monoxide from cyclic ketones.[2] This study has now been extended to cyclic anhydrides, where both decarbonylation and decarboxylation occur.[3,4]

Table

Anhydride	Percent Conversion	Products (Percent Yields)*
succinic	33.0	$CH_2{=}CH_2$ (15.4); $HC{\equiv}CH$ (38.2)
glutaric	44.0	$CH_2{=}CH_2$ (4.7); $HC{\equiv}CH$ (23.5);  (53.8);  (0.4); $CH_2{=}C{=}O$ (Trace)
adipic	30.0	$CH_2{=}CH_2$ (23.3); $HC{\equiv}CH$ (54.3);  (Trace);  (1.9);  (5.0); $CH_2{=}C{=}O$ (Trace)
cis-cyclobutane-dicarboxylic	20.0	$CH_2{=}CH_2$ (7.5); $HC{\equiv}CH$ (30.0);  (3.8);  (7.5)
maleic	20.0	$HC{\equiv}CH$ (83.1)
dimethylmaleic	26.0	$CH_3C{\equiv}CCH_3$ (33.0); $CH_2{=}CH_2$ (1.7); $HC{\equiv}CH$ (1.1); $CH_3C{\equiv}CH$ (0.7);  (0.6); $HC{\equiv}CCH_2CH_3$ (0.6); $CH_2{=}C{=}CHCH_3$ (0.6)

*Some polymer formed on the walls of the irradiation vessel in all cases.

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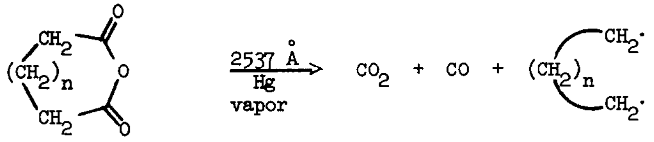
The results are summarized in the Table. All photolyses were carried out on a one gram scale; however, the apparatus and flow technique are such that larger amounts of the anhydride could easily have been used. The starting materials were available commercially, and were purified by recrystallization or column chromatography when necessary. Gaseous photoproducts were identified by standard analytical procedures and compared with authentic materials. Percent yields were determined by nmr utilizing an internal standard.

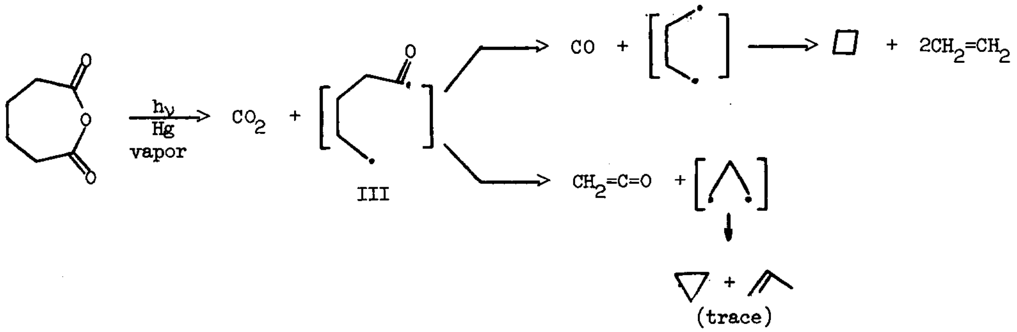
The major hydrocarbon products can be accounted for by the extrusion of carbon dioxide and carbon monoxide with formation of the diradical II, followed by bonding, fragmentation, or hydrogen migration.[5] Compounds resulting from secondary reactions of the



I II

initial products are also formed. Secondary reaction may occur either before vibrational deactivation, or upon further photolysis (e.g., acetylene from succinic anhydride; 1,3-butadiene from <u>cis</u>-cyclobutanedicarboxylic anhydride).

The formation of ketene from glutaric and adipic anhydrides was unexpected, since it cannot be accounted for by the above mechanism. Additional proof for its presence in addition to the ir, was formation of acetanilide (ir, mass spectrum, mp) upon addition of aniline to the gaseous photoproducts. One possible mechanism for the formation of ketene is fragmentation of the acyl diradical (III), which would result from initial acyl-oxygen cleavage.[6] This fragmentation is believed to occur with the 1,4-acyl alkyl diradical formed as an intermediate in the photolysis of cyclobutanone.[7-9] However, diradical III is a proposed



intermediate in the vapor phase photolysis of cyclopentanone,[2,10,11] where ketene has not been observed among the products.

Attempts at characterizing products which might have arisen via a stepwise extrusion process have not been successful.[12] This is not unexpected, however, since decarbonylation, decarboxylation, or cleavage of the intermediate acyl or acyloxy diradical should be rapid relative to closure.[3,13-15]

The mercury sensitized vapor phase photolysis of cyclic anhydrides provides a novel example of extrusion reactions. The simplicity of the apparatus and technique, and the ready availability of anhydrides, make this a promising synthetic method for cyclic hydrocarbons.

References

(1) I. S. Krull and D. R. Arnold, Tetrahedron Letters, 1247 (1969).

(2) R. Srinivasan in "Advances in Photochemistry," W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Editors, Vol. 1, W. J. Wiley and Sons, Inc., New York, N. Y., 1963, pp 83-113.

(3) P. Ausloos, Can J. Chem., **34**, 1709 (1956). The direct vapor phase photolysis of acyclic anhydrides has been shown to involve two primary processes: a) cleavage to an acyloxy and acyl radical; and b) fragmentation to a ketene and an acid via a cyclic six-membered transition state. The latter pathway is sterically prohibited in the cyclic anhydrides reported here.

(4) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," J. Wiley and Sons, Inc., New York, N. Y., 1966, pp 433-434.

(5) For a general review of this area, see: B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, London, England, 1967, Chaps. 1-4.

(6) The greater stability of the acetyl over acetoxy radical when generated at low temperatures by the vapor phase photolysis of acetic anhydride is consistent with formation of III.[3]

(7) H. O. Denschlag and E. K. C. Lee, J. Am. Chem. Soc., **89**, 4795 (1967).

(8) E. W. Schlag, et al., ibid., **89**, 5098 (1967).

(9) T. H. McGee, J. Phys. Chem., **72**, 1621 (1968).

(10) H. M. Frey, Chem. and Ind., 1367 (1961).

(11) H. M. Frey, ibid., 947 (1966).

(12) Trace amounts of γ-butyrolactone (glutaric anhydride) and cyclopentanone (adipic anhydride) were detected by vpc, however, they were not isolated or characterized further.

(13) B. Rickborn, et al., Chem. and Ind., 1951 (1964).

(14) B. Rickborn, et al., J. Phys. Chem., **69**, 3225 (1965), and references therein. The rearrangement of trans 2,6-dimethylcyclohexanone to the cis-isomer is a minor pathway (< 5%) under vapor phase photolytic conditions.

(15) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," J. Wiley and Sons, Inc., New York, N. Y., 1966, pp 389ff.