

and for current support by the National Science Foundation (Grant GP-5662).

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 Received February 8, 1967

Photosensitized Decarbonylation of Furans

Sir:

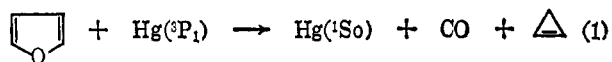
The photochemistry of furans appears to have attracted very little attention. We wish to report that the photosensitized decomposition of furan and two substituted furans in the vapor phase leads to decarbonylation as the principal process.

Irradiation of a mixture of furan (5–150 mm) and mercury vapor at room temperature with the mercury resonance radiation at 2537 Å gave rise to carbon monoxide and a C_3H_4 (mol wt, 40 (mass spectrometry)) fraction. By means of infrared analysis, it was observed that this fraction contained very little propyne (3429, 2150, and 1260 cm^{-1}) or allene (1980 cm^{-1})¹ but was made up principally of a third compound with an absorption at 1645 cm^{-1} and an intense band at 998 cm^{-1} . The nmr spectrum of this material (CCl_4 solution at room temperature; $SiMe_4$ as internal reference) showed a triplet at τ 9.04 ($J \sim 1.5$ cps) and another triplet of equal intensity at τ 3.05. The material polymerized readily at room temperature. These data agree well with those reported for cyclopropene by Wiberg and co-workers.^{2,3} A vapor sample of this material when condensed with a vapor sample of 1,3-cyclopentadiene was observed to give a product whose infrared spectrum agreed with the spectrum that has been reported for the adduct of cyclopropene and 1,3-cyclopentadiene.³

Similarly, the decomposition of 2-methylfuran in the vapor phase by mercury (3P_1) atoms gave carbon monoxide and a C_4H_6 fraction, which was found to consist of a mixture of 1,3-butadiene (45 parts) and 3-methylcyclopropene (55 parts). The latter had an infrared absorption at 1630 cm^{-1} and nmr absorptions at τ 9.04, 8.58, and 3.05 whose intensities were in the ratio of 3:1:2. These data agree with the properties of 3-methylcyclopropene that have been reported by Closs, *et al.*⁴

Mercury-photosensitized decomposition of 2,3-benzofuran in the gas phase also gave carbon monoxide. The only other product that was observed was a polymer.

In quantitative studies, it was found that the yield of carbon monoxide was nearly equal to the amount of furan that disappeared. The yield of cyclopropene was even at best only one-half of this value, which is not surprising in view of the instability of this compound at room temperature. The principal photochemical reaction appears to be



(1) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp 337, 339.

(2) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

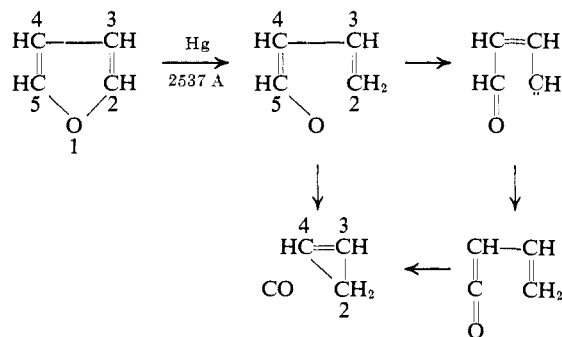
(3) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

(4) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3797 (1963).

It is possible to write two equations similar to (1) for the formation of allene and propyne. However, it should be noted that reaction 1 requires the migration of only one proton from one carbon to another, whereas the formation of allene or propyne will require the migration of two protons.⁵

The quantum yields for the formation of CO (in the sensitized reaction) from furan (5–15 mm), 2-methylfuran (12 mm), and benzofuran (2 mm) were 0.41, 0.29, and 0.03, respectively. The dependence of the quantum yield on the pressure was studied in the case of furan. Over a 20-fold increase in pressure, the quantum yield decreased by less than a factor of 2. In view of the ready availability of furan and the high quantum yield of reaction 1, the use of this method for the synthesis of cyclopropene is being investigated.⁶

With the data that are available, it is not possible to suggest a unique mechanism for the decarbonylation process. However, certain possibilities can be ruled out. An initial valence tautomerization of furan seems unlikely since irradiation of furan in the condensed phase gave neither carbon monoxide nor an isomer of furan.⁷ The most likely pathways are those that follow the initial break of a C–O bond.



It is undoubtedly the C_3 - C_4 bond that ends as the double bond in cyclopropene, as 2-methylfuran gives 3-methylcyclopropene rather than 1-methylcyclopropene. The initial break in 2-methylfuran is not likely to be between oxygen and C_2 because a stable acetyl group would then be formed. The elimination of CO from 2,3-benzofuran would also suggest an initial break at the substituted side of the furan ring.

The timing of the initial rupture of the C–O bond cannot be established at present. A concerted mechanism as well as a mechanism which involves a transient vinylketene intermediate are two distinct possibilities. Experiments to distinguish between these two are currently being undertaken.

Acknowledgment. The author wishes to thank Mr. Hershel W. Amburn and Miss Marianne J. Carlson for the nmr spectra, and Dr. Harold Shechter for many helpful discussions.

(5) Propyne is reported to be a product of the pyrolysis of cyclopropene,³ but allene was not reported to be formed.

(6) The principal requirement seems to be the use of a fast flow system to sweep the cyclopropene from the irradiation zone as quickly as it is formed.

(7) We assume that, if a valence tautomer is formed, it is likely to be stable enough to be detected only in the condensed phase.

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Received January 3, 1967