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THE PHOTOLYSIS OF 10-KETOBICYCLO[5.2.1]DECANE AND RELATED COMPOUNDS

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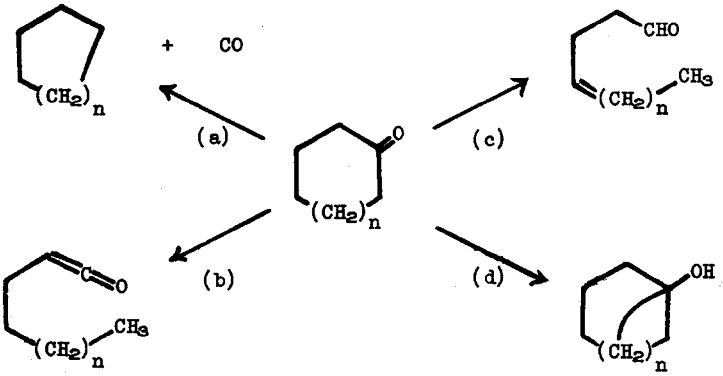
THE photolysis of cyclic ketones has been studied in a number of cases, and the reaction proceeds along one or more of the following pathways[1]:



This communication describes the photolysis of a cyclic ketone which proceeds simultaneously along pathways a and b, a hitherto unrecognized circumstance with respect both to this particular combination of pathways and to the occurrence of pathway a in solution.

A 5.0 g. sample of 10-ketobicyclo[5.2.1]decane (I)[2] in 150 ml. of

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[1] P. De Mayo and S. T. Reid, Quart. Rev. 15, 393 (1961).

[2] C. D. Gutsche and T. D. Smith, J. Amer. Chem. Soc. 82, 4067 (1960).

cyclopentane (spectral grade) was placed in an apparatus which allowed the introduction of an inert gas and the withdrawal of aliquots during the course of the reaction and which carried a quartz well in which was immersed a 100 watt Hanovia mercury vapor lamp. The vessel was evacuated and filled with nitrogen, and the photolysis was carried on for periods up to 264 hrs. Careful removal of the solvent through an efficient distillation column left a residue comprised of ca. 80% of volatile material and 20% of non-volatile material. Passage of the volatile fraction through a vapor phase fractometer (1/4" x 16' column packed with 0.5% Dow-Corning Silicone oil no. 710 on glass beads) indicated five materials, designated in their sequence of appearance from the column as α, β, γ, δ, and ε, to be present in the approximate ratio of 32:33:5:6:24 in addition to ca. 20% of unreacted starting material. Components α and β, collected together by passage of the volatile fraction through an alumina column, possessed an analysis compatible with that for a C_9H_{16} hydrocarbon (Calcd: C, 87.02; H, 12.98. Found: C, 86.99; H, 13.16.). Since the α,β mixture showed no reactivity toward bromine or potassium permanganate, olefinic structures are excluded and bicyclic structures are demanded.

By a comparison of the vpc characteristics and the infrared spectrum of the α,β mixture with an authentic sample of cis-bicyclo[5.2.0]nonane[3] it is concluded that the α-component corresponds to this compound (II). An authentic sample of trans-bicyclo[5.2.0]nonane has not yet been obtained, but it is probable that the β-component corresponds to this isomer (III). This contention is based on the similarity of the infrared spectra and vpc retention times of the α and β components and on the basis of com-

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[3] N. Allinger, M. Nakazaki, and V. Zalkow, J. Amer. Chem. Soc. 81, 4074 (1959). We are indebted to Professor Allinger for a sample of cis-4-ketobicyclo[5.2.0]nonane which facilitated our synthesis of the cis hydrocarbon.

parisons with other bicyclo[x.y.0]nonanes. Thus, bicyclo[6.1.0]nonane[4], trans-bicyclo[4.3.0]nonane[4], and cis-bicyclo[4.3.0]nonane[4] all have retention times different from those of the α and β components. The γ and δ components, present in very small amount, have not been studied except to note that the retention time in the vpc of the γ component is identical with that of bicyclo[6.1.0]nonane. The ϵ component was readily purified either by alumina column chromatography or by preparative vpc and was obtained as a colorless oil possessing an analysis compatible with a $C_9H_{16}O$ compound. Its identity with cyclononanone (V) was shown by a comparison with an authentic sample through infrared spectral measurements and derivative preparations (semicarbazone m.p. 184-185° with no depression in m.p. upon admixture; 2,4-dinitrophenylhydrazone m.p. 145-146° with no depression in m.p. upon admixture).

The transformation of a $C_{10}H_{16}O$ ketone to a $C_9H_{16}O$ ketone, at first glance puzzling, can be rationalized in terms of the intermediate formation of a ketene (IV) which undergoes subsequent oxidation. One of the characteristic chemical properties of monomeric dialkylketenes is the formation, upon exposure to air, of a peroxide which is unstable and decomposes to a ketone and carbon dioxide[5]. That a ketene is present in the photolysis mixture before it is exposed to air is indicated by the following observations. A characteristic physical property of monomeric dialkylketenes is a yellow color and, indeed, the photolysis mixture becomes progressively more yellow as the reaction proceeds, this color persisting until air is admitted to the sample. An infrared spectrum of the reaction mixture before exposure to air included moderately strong

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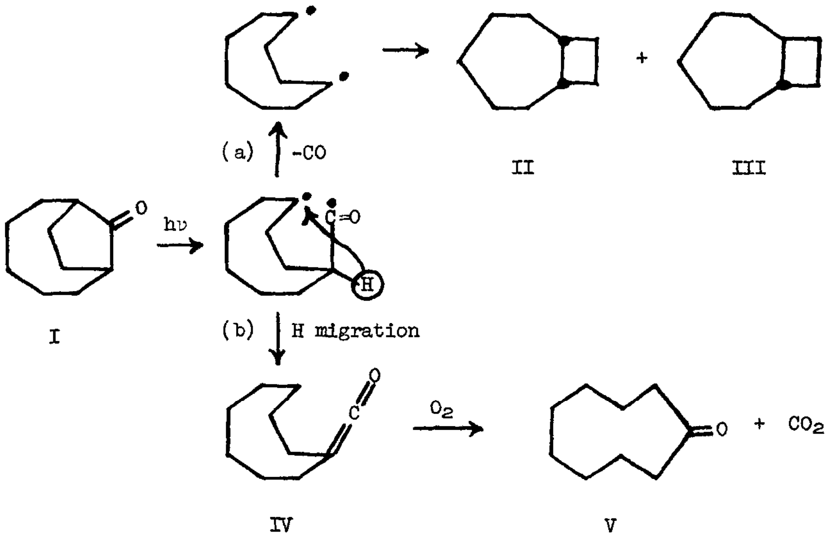
[4] We are indebted to Professor Lester Friedman for his generosity in supplying us with a pure sample of authentic material.

[5] H. Staudinger, K. Dyckerhoff, H. W. Klever, and L. Ruzicka, Chem. Ber. **58**, 1079 (1925).

bands at 2142 and 1133 cm^{-1}, characteristic of ketenes[6]. Upon exposure of the sample to air these disappeared and a new band at 1700 cm^{-1} (cyclononanone) appeared. Addition of methanol to the yellow photolysis mixture resulted in the disappearance of the color (over a period of 2 hrs.) and the formation of methyl cyclononanecarboxylate, characterized by conversion to the carboxanilide, m.p. 138-140°, which was shown to be cyclononanecarboxanilide (reported m.p. 140-141°[2,7]) by comparison with an authentic sample. Direct evidence for the formation of a ketene as a photolysis product of a cyclic ketone has also been obtained earlier this year by Quinkert and co-workers[8] who employed rather similar methods.



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[6] D. H. Whiffen and H. W. Thompson, J. Chem. Soc., 1005 (1946); L. G. Drayton and H. W. Thompson, J. Chem. Soc., 1416 (1948).

[7] V. Prelog and K. Schenker, Helv. Chim. Acta. 36, 896 (1953).

[8] G. Quinkert, B. Wegemund, and E. Blanke, Tetrahedron Letters No. 6, p. 221 (1962).

Other experiments cognate to the one described above have shown that (a) The ratio of ketene (detected as cyclononanone) to hydrocarbon is sensitive to the oxygen present during the photolysis, the ratio increasing as the oxygen tension descreases; in a scrupulously de-gassed reaction mixture the ketene is the major product (volatile product contains 20% of starting material, 15% hydrocarbon, and 65% cyclononanone). (b) The ratio of ketene to hydrocarbon decreases when α,α'-dideutero-10-ketobicyclo[5.2.1]decane is photolyzed. (c) The photolysis of 9-ketobicyclo[4.2.1]nonane yields cyclooctanone and the photolysis of 8-ketobicyclo[3.2.1]octane yields cycloheptanone, undoubtedly *via* the ketene in both cases. (d) Under the conditions employed in the photolysis of the bridged ring ketones, cyclopentanone, cyclohexanone, α,α'-dimethylcyclohexanone, and cycloheptanone fail to undergo any decomposition, while cyclooctanone[9], cyclononanone; and cyclodecanone[9] yield bicyclic alcohols[9].

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[9] M. Barnard and N. Yang, *Proc. Chem. Soc.*, 302 (1958).