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THE PHOTOLYSIS OF BICYCLO[5.2.1] DECAN-10-ONE

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It has been reported by Gutsche and Armbruster[1] that bicyclo[5.2.1]-decan-10-one (I) undergoes photolysis to yield a mixture of bicyclo-[5.2.0]nonane (II) and octamethyleneketene (III). In an extension of this work to related systems, however, results so much at variance with those reported for I were obtained that a reinvestigation of the earlier work was launched. Emerging from this study is the fact that a part of the earlier communication is in error.

Following the previously-described conditions, a sample of bicyclo-[5.2.1]decan-10-one (I) in n-pentane solution (cyclopentane used in the earlier work) was photolyzed with a 100 watt Hanovia mercury vapor lamp for 80 hrs. The solvent was removed by careful distillation through a glass helix packed column, and the residue was chromatographed on alumina with n-pentane as the eluant. The first fractions contained the hydrocarbons; and the later fractions contained starting material and cyclononanone. The hydrocarbon fraction was separated into two components by passage through a 1/4" x 16' vapor phase chromatographic column packed with neopentyl sebacate (15% by weight) on 40-50 mesh type ABS Anakrom. The more volatile component possessed an analysis compatible with a C_9H_{16} formula (Calcd: C, 87.02; H, 12.98. Found: C, 86.80; H, 13.03) and, contrary

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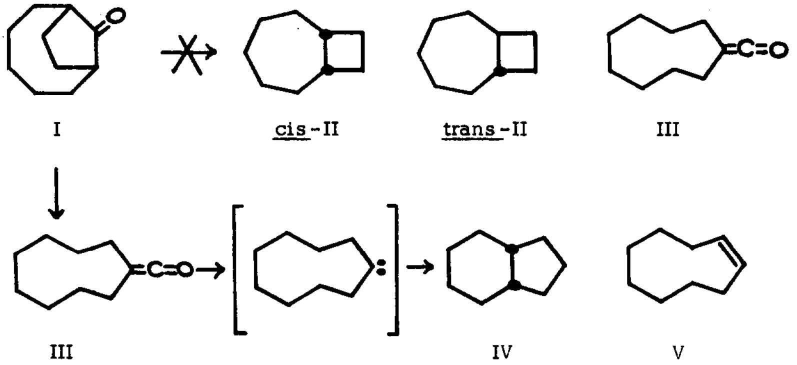
[1] C. D. Gutsche and C. W. Armbruster, Tetrahedron Letters No. 26, 1297 (1962).

to the earlier report[1], possessed a vpc retention time, an infrared spectrum, and an nmr spectrum identical in every detail with the vpc retention time, infrared spectrum, and nmr spectrum of an authentic sample of *cis*-bicyclo[4.3.0]nonane (IV). Thus, the more volatile component is not the *cis* isomer of bicyclo[5.2.0]nonane (II) but is the *cis* isomer of bicyclo[4.3.0]nonane (IV). The less volatile component possessed an analysis compatible with a C_9H_{16} formula (Calcd: C, 87.02; H, 12.98. Found: C, 86.85; H, 13.23) and, contrary to the earlier report, rapidly decolorized bromine and permanganate solutions. It had an infrared spectrum identical with that reported for *cis*- cyclononene[2] and an nmr spectrum completely in accord with this structure (a multiplet at δ= 5.0 - 5.5 corresponding to 2 vinyl protons). Thus, the less volatile component is not the *trans* isomer of bicyclo[5.2.0]nonane but is the *cis* isomer of cyclononene (V).



As an additional check on the identity of the saturated hydrocarbon product, an authentic synthesis of bicyclo[5.2.0]nonane (II) was carried out. Bicyclo[5.2.0]nonene-9(1)-carboxamide (VI) was synthesized by the method of Fleming and Harley-Mason[3] from cycloheptanone enamine and

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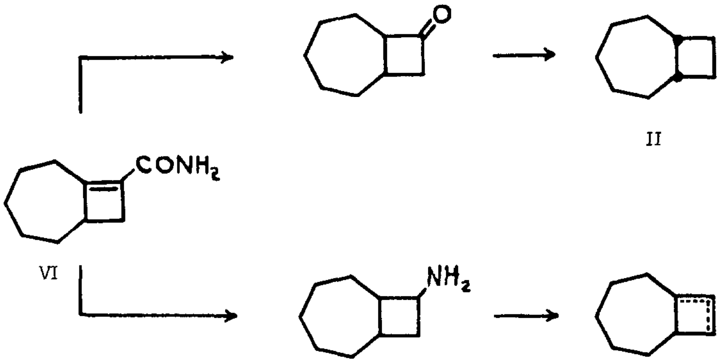
[2] A. T. Blomquist, L. H. Lui, and J. C. Bohrer, *J. Amer. Chem. Soc.*, **74**, 3642 (1952).

[3] I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 2165 (1964).

acrylonitrile followed by deamination and hydrolysis. A Hoffmann rearrangement of VI yielded bicyclo[5.2.0]nonan-9-one which, upon Wolff-Kischner reduction, gave *cis*-II. Alternatively, the unsaturated amide VI was hydrogenated to the saturated analog and a Hoffmann rearrangement carried out to yield 8-aminobicyclo[5.2.0]nonane. Conversion of the amine to the quaternary ammonium hydroxide followed by a Hoffmann elimination yielded a mixture of olefins (presumably the $\Delta^{1,9}$ and $\Delta^{8,9}$ isomers) from which *cis*-II was obtained on catalytic hydrogenation. Although *cis*-II could not be resolved from *cis*-IV on any of the vpc columns used[4], its infrared spectrum was convincingly different from that of *cis*-IV.



In the light of these data, the course of the photolysis of bicyclo[5.2.1]-decan-10-one (I) must be reinterpreted. That the ketene is one of the primary products was established in the earlier work[1]. That it is probably the *only* primary product is suggested now by the formation, in almost quantitative yield, of N-cyclohexyl cyclononanecarboxamide, m.p. 154-154.5°

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[4] Included among these was a column packed with tricresyl phosphate on firebrick which effects a separation of *cis*-II from *trans*-II (N. Allinger, M. Nakazaki, and . Zalkow, *J. Amer. Chem. Soc.*, **81**, 4074 (1959).

(Calcd: C, 76.44; H, 11.63. Found: C, 76.37; H, 11.84) from a photolysis carried out in the presence of cyclohexylamine. The hydrocarbons, therefore, appear to be secondary products from the photolysis of octamethyleneketene (III). Assays of the product at various times during the photolysis support this contention; i.e. the ratio of hydrocarbon products to ketene increases with increasing time. Thus, it is postulated that photolysis of the octamethyleneketene yields carbon monoxide and octamethylenecarbene, the carbene undergoing intramolecular 1,2 and 1,5 shifts to yield IV and V, respectively. This same reaction has been studied by Friedman and Shechter[5] who generated the carbene by pyrolysis of diazocyclononane and observed IV, V, and bicyclo[7.1.0]nonane in 66%, 22%, and 10% yields, respectively. The different mode of carbene generation, diazoalkane pyrolysis vs. ketene photolysis, may explain the different ratios observed in the present case, and this point is currently under investigation.

Contrary to the earlier allegation that bicyclo[5.2.1]decan-10-one decomposes along two pathways to yield octamethyleneketene and bicyclo[5.2.0]nonanes[1], it is now clear that only the first of these pathways is followed. This photolysis is not an example of the once rare but now well-documented[6] carbon monoxide extrusion reaction occuring in the condensed phase. Rather, it is but another example of the even better-documented formation of ketenes from cyclic ketones[7]. The discrepancies in the earlier work are difficult to account for and must probably be charged to the fallibility of the junior author and the gullibility of the senior author.

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[5] L. Friedman and H. Shechter, J. Amer. Chem. Soc., **83**, 3159 (1961)

[6] See N. J. Turro, G. W. Byers, and P. A. Leermakers, J. Amer. Chem. Soc., **86**, 955 (1964) for a compilation of references.

[7] See G. Quinkert, Angew. Chem., International Ed., **4**, 211 (1965) for a comprehensive review of this reaction.