The Photolysis of 7-Ketonorbornene[1]

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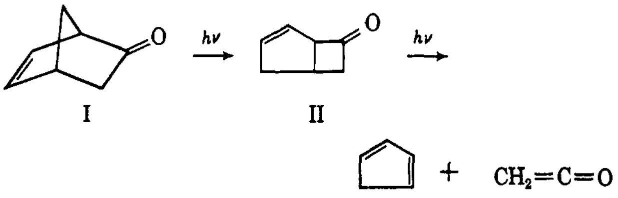
The ultraviolet photolysis of 7-ketonorbornene has been studied in ethyl ether solution. With a Pyrex filter, the photodecomposition is very slow, giving carbon monoxide and 1,3-cyclohexadiene. With Corex or Vycor filters or in the absence of filters, 7-ketonorbornene efficiently gives carbon monoxide, 1,3-cyclohexadiene, and 1,3,5-hexatriene. Control studies of the photolysis of 1,3-cyclohexadiene are described. Some preliminary mechanistic considerations are presented.

In comparison with extensive investigations of the photochemical behavior of cyclic cross-conjugated dienones and α,β-unsaturated ketones,[3] comparatively little attention has been given to studies of the photochemistry of cyclic β,γ-unsaturated ketones. Chapman and his co-workers have reported an unusual reaction on photolysis of 3,5-cycloheptadienone to give carbon monoxide and 1,3,5-hexatriene.[4] While photochemical decarbonylation is a well-known phenomenon in the gas phase,[5] it usually occurs with low efficiency in solution.[6] The reaction reported by Chapman[4] is also intriguing because it is in marked contrast to the interesting set of rearrangements which ensue on photolysis of 2,4-cycloheptadienones.[4,7,8] An entirely different reaction occurs on photolysis of a bicyclic β,γ-unsaturated ketone, dehydronorcamphor (I), which isomerizes to an isomeric ketone (II) and then decomposes to give cyclopentadiene and ketene.[9]



As part of a study on the relationship between the structure and photochemistry of unsaturated ketones, particularly with respect to the geometrical relationship of the carbonyl group and the carbon–carbon double bond(s), it was of interest to study a compound in which the double bond was symmetrically situated with respect to the carbonyl group, a situation which is ideally fulfilled in 7-ketonorbornene (III). In addition, there was the interesting possibility that the photolysis of 7-ketonorbornene would serve as a route to bicyclo[2.2.0]hexene by extrusion of carbon monoxide, a route employed by Srinivasan and others in the synthesis of a number of strained bicyclic compounds.[5]

7-Ketonorbornene (III) was prepared according to the procedure of Gassman and Pape.[10] The ultraviolet spectrum of III [$\lambda_{\max}^{\text{isooctane}}$ 274 mμ (ϵ 31)][10] is in contrast to that of I and other β,γ-unsaturated ketones in which the chromophore is inherently dissymmetric and which show strengthened $n \rightarrow \pi^*$ transitions indicative of interaction between the carbonyl and $>C{=}C<$ groups.[11] Thus, as concluded earlier,[10] little if any interaction of the carbonyl and $>C{=}C<$ groups in III is indicated in both the ground and excited (singlet) states.

The photolysis of III in ethyl ether solution was carried out in a nitrogen atmosphere using a 450-w. Hanovia high-pressure mercury arc in a quartz immersion tube. Experiments were run using Pyrex, Vycor, and Corex filters, as well as in the absence of filters. The reaction was followed by ultraviolet spectra and gas–liquid chromatography (g.l.c.) of aliquots withdrawn during the reaction, and product assignments were made by comparison of spectra and g.l.c. retention times with those of known compounds, and were checked by product isolation using distillation and g.l.c. The extent of reaction was checked by collection of the evolved gas.

With a Pyrex filter, 95% of III could be recovered after 5 hr. and 90% after 26 hr. The product was 1,3-cyclohexadiene, contaminated by some 1,3,5-hexatriene (ratio approximately 40:1). Carbon monoxide was presumably formed, although it was not directly identified. Although evidence for cyclohexadiene was found from the beginning of the reaction, no evidence (ultraviolet) for the presence of 1,3,5-hexatriene was obtained until 2 hr. had passed. Irradiation through Corex or Vycor filters, or in the absence of filters, led to rapid evolution of carbon monoxide and the formation of 1,3-cyclohexadiene and 1,3,5-hexatriene. The reaction was 97% complete after 4.5 hr. Using Corex or Vycor filters, similar mixtures of cyclohexadiene and 1,3,5-hexatriene were formed (ratio 53:47) while in the absence of filters, the product ratio was 1:18. Evidence for the presence of benzene in the product was definitely absent (much less than 1% would have been detectable by g.l.c.), and no evidence for other products, such as bicyclo[2.2.0]hexene, was obtained.

Attempts to sensitize the decarbonylation reaction using a sixfold excess of benzophenone[12] failed. This indicates either that the decarbonylation of 7-ketonorbornene occurs from an excited singlet or that the

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[1] Part IV of a series on the photochemistry of unsaturated ketones. Part III: D. I. Schuster and C. J. Polowczyk, *J. Am. Chem. Soc.*, **86**, 4502 (1964).

[2] Department of Chemistry, The Ohio State University.

[3] For a recent review, see O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

[4] O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

[5] See R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

[6] For a list of references to other reports of photodecarbonylation in solution, see N. J. Turro, G. W. Byers, and P. A. Leermakers, *J. Am. Chem. Soc.*, **86**, 955 (1964).

[7] G. Büchi and E. M. Burgess, *ibid.*, **82**, 4333 (1960).

[8] D. I. Schuster, M. J. Nash, and M. L. Kantor, *Tetrahedron Letters*, **No. 22**, 1375 (1964).

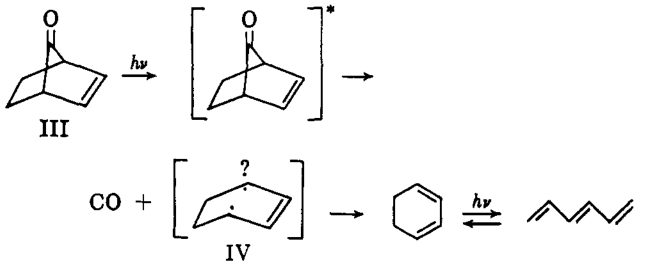
[9] D. I. Schuster, M. Axelrod, and J. Auerbach, *ibid.*, **No. 27**, 1911 (1963).

[10] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

[11] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

triplet excitation energy of III is greater than 68 kcal.[12] The latter is a distinct possibility considering the high energy of the $n \rightarrow \pi^*$ transition (to the excited singlet) and the often observed small multiplet splitting of n–π^* excited states. However, analogy with photodecarbonylation of ketones in the vapor phase, which seem to be best understood as involving excited singlets as reactive intermediates,[5] would argue for the importance of singlet intermediates in the liquid phase photodecarbonylation of III. Clearly, definite assignment must await further experimental data.

The question arises as to whether III decarbonylates directly to a mixture of cyclohexadiene and hexatriene, or whether hexatriene arises from further photolysis of cyclohexadiene. The results in the absence of filters argue for the latter interpretation. The photolysis of 1,3-cyclohexadiene was therefore examined under conditions comparable to those used in the study of III. As expected, there was little reaction of the diene when photolyzed through a Pyrex filter. After 10 hr., the ratio of diene to triene from g.l.c. was 30:1. When this same mixture was irradiated after removal of the filter, the ratio of diene to triene after 5 hr. was 1:6.5 and after 6.5 hr. was 1:8.3, and this ratio did not change appreciably thereafter. Using Corex and Vycor filters, the mixture of diene and triene after several hours had approximately the same composition as that found from photolysis of III (ratio 53:47). These results are most consistently interpreted in terms of initial formation of cyclohexadiene from 7-ketonorbornene and then photoequilibration of the diene and triene in a subsequent step. The latter process has been well studied in the vapor phase,[13] but other products such as hydrogen, benzene, and 1,2,4-hexatriene are formed under those conditions. The absence of benzene in the liquid phase photolyses of III and cyclohexadiene supports the suggestion that benzene formation in the vapor phase photolyses proceeds from a vibrationally excited ground-state molecule,[13] and this reaction would be expected to be totally quenched in solution, as we have found. The photoisomerization of 1,3-cyclohexadiene to 1,3,5-hexatriene is most consistently rationalized on the basis of a pure singlet mechanism.[13,14]



The over-all scheme for the photolysis of 7-ketonorbornene is therefore as given below. At this time, it is not possible to decide between a concerted one-step extrusion of carbon monoxide from the excited state, or a two-step process. It is also not possible to determine if a diradical (IV) is an intermediate in the formation of 1,3-cyclohexadiene, or if the latter is formed directly from the excited state by a geometrical reorganization. Such questions have also not as yet been satisfactorily answered in the much more extensively investigated vapor phase decarbonylations of cyclic and bicyclic ketones.[5]

Experimental

7-Ketonorbornene was prepared according to the procedure of Gassman and Pape.[10] The product, b.p. 63–64° (30 mm.), which was homogeneous by gas–liquid chromatography (g.l.c.) gave two spots on thin layer chromatography (silica gel G) on development with dinitrophenylhydrazine spray. The impurity was removed by column chromatography on Celite with 1:1 ether–pentane.

Photolysis of 7-Ketonorbornene.—Dilute solutions of 7-ketonorbornene in purified anhydrous ether (typical quantities were 0.50 g. in 150 ml. and 0.70 g. in 300 ml.) were flushed with oxygen-free nitrogen (utilizing standard purification trains) for 1 hr. before irradiation commenced. The solutions were kept at room temperature and stirred during photolysis. A Hanovia A-36 450-w. high-pressure mercury vapor lamp encircled by the appropriate filter sleeve in a quartz immersion well was used as the light source. The reactions were followed by periodic withdrawal of aliquots and examination of these by g.l.c. and ultraviolet spectroscopy. In one series of runs (Ohio State) the analytical gas chromatography was performed on an Aerograph Hy-Fi instrument with nitrogen as the carrier gas on a column of Carbowax 20M (20%) on firebrick at 50°. In the other series of runs (New York University) the disappearance of ketone III (retention time 10.4 min.) was followed by g.l.c. on a Perkin-Elmer Model 154 gas chromatograph using column C (silicone oil D.C. 200) at 100°, but under these conditions 1,3-cyclohexadiene and 1,3,5-hexatriene were not separable. The products were separated on a column of Dow 710 silicone oil (25% on Chromosorb P) at 69° at a flow rate of 50 cc./min. The mixture of *cis*- and *trans*-1,3,5-hexatriene appeared as two closely spaced peaks, retention times 4.56 and 5.46 min., well separated from cyclohexadiene at 6.6 min. The ratios of cyclohexadiene and 1,3,5-hexatriene in the various runs were determined by the area ratios of peaks in the gas chromatogram, without correction for difference in thermal conductivities. Runs were carried out without filters, as well as with Pyrex, Corex, and Vycor filters.

The ultraviolet spectra of the aliquots were compared with those of cyclohexadiene (authentic material, $\lambda_{\max}^{\text{ether}}$ 285 mμ) and 1,3,5-hexatriene ($\lambda_{\max}^{\text{isooctane}}$ 245, 255, and 265 mμ).[15] With a Pyrex filter, aliquots taken in the first 2 hr. showed only a single maximum at 258 mμ while the full pattern characteristic of mixtures of *cis*- and *trans*-1,3,5-hexatriene[15] was evident at later times and in runs without filters.

In a typical run using a Pyrex filter, the ratio of cyclohexadiene to hexatriene after a 10-hr. irradiation of III was 258:6.3. In a typical run without any filter, the ratio of diene to triene after a 2-hr. irradiation was 10:180.

In one run, 1.64 g. of III in 300 ml. of ether was irradiated in a nitrogen atmosphere, and a gas buret was connected to the outlet of the apparatus to measure the change in gas volume during photolysis. The total volume change, after correction from a blank run, was taken as a measure of the volume of carbon monoxide evolved. An estimation of the amount of unreacted ketone from this data agreed within 4% of that determined by g.l.c. using an internal standard.

Identification of Products.—After irradiation using Corex and Vycor filters, the ethereal solution was fractionated through an 8-in. glass helix-packed vacuum-jacketed column. Analysis of the crude residue by g.l.c. showed that the product was composed of two unsaturated hydrocarbons with retention times of 10.6 (53%) and 12.0 (47%) min. on the Carbowax column. In these runs, g.l.c. indicated that the product ratio was invariant as a function of time. Comparison of retention times and infrared spectra with those of known samples of 1,3-cyclohexadiene and 1,3,5-hexatriene[15] established the identity of the products.

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[12] (a) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). (b) It is possible that some oxetane and/or dimer was formed in this reaction, but these would not have been detected by our method of analysis: D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); D. R. Arnold, R. L. Hinman, and A. H. Glick, *ibid.*, 1425 (1964).

[13] R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2806 (1961); **82**, 5063 (1960).

[14] G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

[15] G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **70**, 3394 (1948); J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *ibid.*, **82**, 2537 (1960).

Photolysis of 1,3-Cyclohexadiene.—A commercial sample of diene was redistilled before use (b.p. 80°) and this material was homogenous by g.l.c. Photolyses of diene were carried out as described above. With a Pyrex filter, the ratio of diene to 1,3,5-hexatriene after 10 hr. was 270:8.5. This ratio is similar to that observed in irradiation of III under the same conditions. This mixture was photolyzed further after removal of the filter. After an additional 5 hr., the ratio of diene to triene was 25:162; after 6 hr. 40 min., the ratio was 1.0:8.25. The final photomixture was concentrated under reduced pressure, and the residue was separated by g.l.c. on a Dow 710 column at 69°. The materials of retention times 4.5 and 5.9 min. were collected in a liquid nitrogen trap connected to the gas outlet. The colorless liquids had infrared and ultraviolet spectra in excellent agreement with those reported for *cis*- and *trans*-1,3,5-hextriene.[15]

In runs where diene and triene were removed by distillation, substantial amounts of high-boiling material remained. While we have no evidence that this material results from photolysis and not from "dark" reactions of cyclohexadiene and triene, the presence of this material is consistent with reports of the photochemical formation of dimers and other high-boiling compounds.[16,17]

Analysis for Benzene in the Photomixtures.—Benzene is not cleanly separated from 1,3-cyclohexadiene and 1,3,5-hexatriene by g.l.c. on the columns mentioned above, but is separated on a PDEAS column (phenyldiethanolamine succinate). A 2% solution of benzene in ether was prepared to compare with the photolysis mixture. The latter, alone, gave a single peak at 2.84 min. (mixture of diene and triene), while a mixture of equal amounts of the dilute benzene solution and the concentrated photomixture gave two distinct peaks at 4.5 (benzene) and 2.84 min. Thus, to the limit of the validity of this analysis, benzene is not present in the photomixture from photolysis of ketone III. A similar experiment eliminates benzene from the photomixture formed on photolysis of cyclohexadiene.

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(16) G. O. Schenck, S.-P. Mannsfield, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.*, **19b**, 19 (1964).

(17) R. J. De Kock, N. G. Minnaard, and E. Havinga, *Rec. Trav. Chim.*, **79**, 922 (1960).

The Cyclization of Epoxy Olefins. II. The Attempted Formation of a Bornenol System[1]

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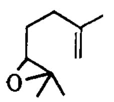
Treatment of 2,3,3-trimethyl-4-vinylcyclopentene, prepared unambiguously from α-campholenaldehyde, with perphthalic acid yields an inseparable mixture of stereoisomeric monoepoxides. Acid-catalyzed rearrangement of the oxide mixture yields only 2,3,3-trimethyl-4-vinylcyclopentanone and 2,2,3-trimethyl-4-vinylcyclopent-3-enol. No bicyclic cyclization product is found. From the relative proportions of the *cis* and *trans* isomers of the cyclopentanone, however, a minimum value for the isomer composition of the starting epoxide may be obtained.

The acid-catalyzed cyclization of epoxy olefin systems as a model for terpenoid biogenesis has been accomplished in a number of cases. Boron fluoride treatment of geraniolene monoepoxide (**1**) resulted in the partial formation of cyclic products,[3] and the use of another Lewis acid, stannic chloride, caused the formation of only the cyclic compounds **2** and **3**.[4] Subsequently, van Tamelen was able to isolate bicyclic products from the reaction of epoxyfarnesyl acetate with boron fluoride and other acid catalysts.[5]



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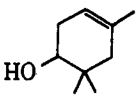

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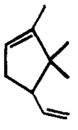
Although the familiar bridged bicyclic system of camphor and related terpenes is probably not derived naturally by an *oxidative* cyclization, it was of interest to explore the possibility of forming this structure from an epoxy olefin. To this end we chose for a starting material the monocyclic diene **4**. This compound has been previously reported[6] as a product from the Hofmann elimination of N,N-dimethyl-α-camphylamine. The yield of **4** was so low, however, that the compound was characterized by a boiling point only. It was necessary, therefore, to prepare the diene unambiguously and in preparative yield. Pyrolysis of the acetate **5** afforded a material of the expected elemental composition in 85% yield which differed in boiling point from the substance previously reported to be **4**. Spectral measurements, however, showed that the expected diene was indeed the product of pyrolysis. In the infrared, bands at 918 and 1005 cm.$^{-1}$ demonstrated the presence of the vinyl grouping, and four vinyl hydrogens in the appropriate pattern were displayed in the n.m.r. spectrum between 4.9 and 5.98 p.p.m. Conversion of the diene to the epoxy olefins **6a** and **b** was effected with monoperphthalic acid. The usual difference in reactivity of mono- and polysubstituted double bonds predicts the formation of principally this epoxidation product.[7] Confirmation was again afforded by spectral evidence.



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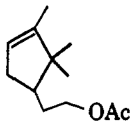

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6a

6b

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(2) Taken in part from the Ph.D. Thesis of C. J. C., Wayne State University, Detroit 2, Mich.

(3) D. J. Goldsmith, *J. Am. Chem. Soc.*, **84**, 3913 (1962).

(4) D. J. Goldsmith and T. J. Lajiness, unpublished observation.

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