

THE PHOTOCHEMICAL ISOMERIZATION AND FRAGMENTATION
OF DEHYDRONORCAMPHOR

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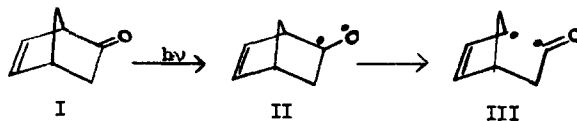
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In connection with studies of the mechanisms of a number of photochemical reactions, particularly of structurally interesting unsaturated ketones, we have studied the photolysis of dehydronorcamphor, bicyclo[2.2.1]hept-5-en-2-one (I). We were led to study this particular compound in order to determine what role the highly strained bicyclo[2.2.1]heptyl skeleton would play in influencing the course of reaction following excitation, in comparison with the course of photochemical reactions of relatively unstrained cyclic and open-chain ketones. In addition, studies of the optical properties of dehydronorcamphor show that it is a prime example of a compound containing an inherently dissymmetric chromophore as a structural unit, in which there is considerable interaction between the pi-systems of the β,γ -double bond and the carbonyl group (1,2). This interaction, which is indicated by physical data such as the ultraviolet spectrum and optical rotatory dispersion and circular dichroism curves of a number of β,γ -unsaturated ketones, has been rationalized from a molecular orbital viewpoint (2). We were interested in the chemical consequences of this electronic interaction as demonstrable through photochemical reactions of this class of compounds.

Since the time this study was undertaken, a report has appeared (3) describing a study of the photolysis of dehydronorcamphor (I) in several solvents: cyclohexane, methylcyclohexane, methanol, ethanol and isopropyl alcohol. Since our findings differ significantly from those of Schenck and Steinmetz (3) we wish to report our salient results at this time.

The only reaction observed by Schenck and Steinmetz (3) was the formation, quantitatively and stoichiometrically, of cyclopentadiene and ketene (isolated respectively as the maleic anhydride adduct and as acetanilide after reaction with aniline). These products were suggested (3) to be derived from direct decomposition of the mesomeric biradical III which is produced by the expected fragmentation toward the bridgehead of the excited state which was pictured as II (3). No other products or intermediates were reported to be present in "nachweisbaren Mengen" (3).



We initially studied the photolysis of I in ether and followed the reaction by withdrawing small samples at frequent intervals without interrupting the photolysis and injecting these samples before and after removal of most of the solvent into an F and M Gas Chromatograph using a Silicon Gum Rubber column. The irradiation was carried out in an immersion apparatus utilizing a Hanovia 450-watt high-pressure quartz mercury-vapor lamp with a pyrex filter. The stirred ether solution was purged with oxygen-free

nitrogen for an hour prior to irradiation and a slow rate of passage of nitrogen through the solution was maintained during the photolysis. In each run we used solutions of approximately 4 g. of I in 250 ml. of solvent. Our samples of I were completely homogeneous by gas chromatography, and physical and spectral properties agreed in all details with those reported by several groups of workers (1,2).

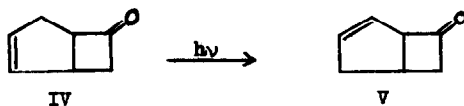
We observed that the gas chromatography peak due to I began to decrease in size immediately on irradiation and a shoulder appeared with a slightly higher retention time. This shoulder increased in size as the peak due to I decreased until, after about 90 minutes, the peak due to I was only a shoulder on the peak due to the new component. Further photolysis led to the reduction in the amounts of both I and the new component until, after about 3 hours, only traces of the two components remained. During this entire time, several peaks with very short retention times appeared and continuously increased in size during the photolysis. These are due, in part, to cyclopentadiene and ketene, identified respectively as in the work of Schenck and Steinmetz (3) via the maleic anhydride adduct and acetanilide, and both identical in physical properties with authentic materials.

When the runs were stopped after 60 or 90 minutes and the ether removed carefully by distillation, the residue accounted for the bulk of I used initially, indicating little formation of more volatile materials at this time. Distillation of this material through a spinning-band column afforded fractions which gave two clearly distinct peaks on gas chromatography, corresponding in retention times to I and the new compound (photo-ketone, see below) observed above. We thus obtained samples which consisted

of well over 90% photoketone and less than 10% I. The infrared spectrum of the photoketone shows a strong carbonyl band at 1780 cm^{-1} , characteristic of cyclobutanones and 7-ketobicyclo[2.2.1]heptanes (4). The elemental analysis of photoketone purified by preparative gas chromatography (Found: C, 77.66; H, 7.47. Calcd. for C_7H_8O : C, 77.75; H, 7.46) indicates that the photoketone is indeed an isomer of I. Further support for this assignment is given by the mass spectrum of our purest sample of photoketone. This shows a parent peak at m/e 108 and the strongest peak in the spectrum at m/e 66, corresponding to the loss of ketene. Complete analysis of this fragmentation pattern and those of I and related compounds will be reserved for a future communication, but it will suffice here to point out that it is in complete accord with the structure of the photoketone (V) given below. The n.m.r. spectrum, while also consistent with our proposed structure, was quite complex and not of great help to us in assigning structure. The ultraviolet spectrum in isooctane has a shoulder at $284\text{ m}\mu$ (ϵ 73) and maxima at 297 (ϵ 142), 306 (ϵ 160) and $317\text{ m}\mu$ (ϵ 112),*similar to but definitely different from the spectrum of I. This intense quartet has been recognized to be characteristic of the enhanced $n \rightarrow \pi^*$ transition of a number of β,γ -unsaturated ketones (2). Finally, a 2, 4-dinitrophenylhydrazone was prepared, m.p. $149-151^\circ$ (Found: C, 54.38; H, 4.10; N, 19.27. Calcd. for $C_{13}H_{12}N_4O_4$: C, 54.16; H, 4.20; N, 19.43). This material was shown by depression of the mixture melting point and by thin layer chromatography to be different from I-DNPH, m.p. $171-173$ (5) and is different from that reported for the isomeric IV-DNPH, m.p. $114-115$ (6) (IV is the product of cycloaddition of ketene to cyclopentadiene). These data taken

* These intensities are clearly minimum values as the samples of photoketone used were about 90-95% pure.

together lead us to propose that the structure of the photoketone is bicyclo[3.2.0]hept-2-ene-7-one (V, below).



The photoketone V is an intermediate not only in photolyses in ether solution, but we have shown it to be formed in dioxane and cyclohexane, and, by implication, in most if not all of the solvents studied by Schenck and Steimetz (3). Since V is produced rapidly at first and then subsequently reacts further, analyses for V and its isolation must be carried out in the early stages of the reaction (less than three hours photolysis under our conditions) when its concentration is at a maximum.

If, as a working hypothesis, we assume that the biradical III, or some similar intermediate, is produced on photolysis of I, structure V is then seen as derived by recombination of the radical fragments at the other end of the allylic system of III. This type of photochemical isomerization has ample precedent in the transformation of VI to VII reported by Büchi and Burgess(7). The subsequent photochemical decomposition of ketone V into ketene and cyclopentadiene (which is also seen as the main mode of decomposition



of V mass spectrometrically) is easily visualized as a reverse cycloaddition. It is interesting to speculate that the reason for the formation of IV and not V in the thermal addition of ketene to cyclopentadiene (6) may be that V, which decomposes readily under our conditions, may be unstable under the conditions of the thermal reaction and may revert back

to starting materials, funnelling all of the thermal reaction into the more stable product IV. We doubt if IV plays any important role in the photochemical reaction, although we cannot rule it out at this time.

We have not yet shown conclusively that all of the ketene and cyclopentadiene in the photochemical reaction is derived from V and none from I directly by cleavage, but this is suggested by the low initial yields of ketene while the concentration of V was building up. We also do not mean to imply any mechanism at this time for any of the transformations involved or a structure for the excited state, but we hope to do so eventually after completing a number of experiments now in progress on this and related systems.

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