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STRUCTURES OF PHOTOLYSIS PRODUCTS OF CAMPHOR (1)

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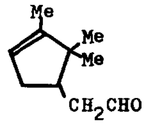
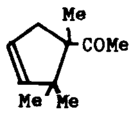
Ciamician and Silber's classical paper (2) on the photolysis of camphor (I) described the formation of several products, two of which were shown to have structures II and III on the basis of degradative experiments. Recently, Srinivasan (3) carried out a mechanistic study on this photolysis reaction, and found a solvent dependency of a ratio of quantum yield of II and III. Consequently, the formation of both was generally accepted in literatures (4). Because we required III for a synthetic purpose, we repeated the irradiation experiment in hydrocarbon solvent, which is said to be suitable for the formation of III (3) and found that the reaction was rather complex, and showed some interesting features. The results are briefly reported herein.

Irradiation of I in 5% in cyclohexane with a 450 watt high pressure mercury lamp fitted with a pyrex filter, produced predominantly II (maximum content reached to 30% after 6-10 hours) in the early stages. The gradual decay of II resulted in the formation of more than ten products. Of these photoproducts eight were isolated by gas chromatography and characterized as the following:



(II)



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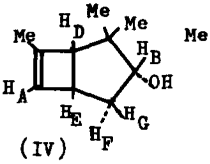
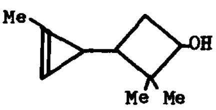
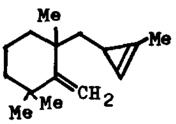


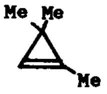
(IV)



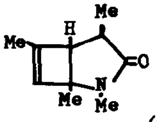
(IVa)



(V)



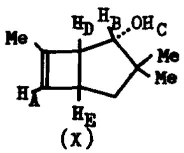
(VI)



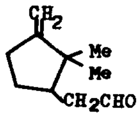
(VII)

(VIII) X:Cl

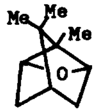
(IX) X:D



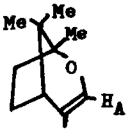
(X)



(XI)



(XII)



(XIII) H_B

Photoproduct A (IV) [r.r.t. (retention time relative to camphor at 170° on 20% PEG 4000 on fire brick 5m X 2.8mm) 2.21] (yield; 6.6%) has a geminal dimethyl group [ν 1380, 1360 cm^{-1}, δ Me_{I}=0.89, δ Me_{II}=0.94 ppm (5)], an ethylenic linkage (ν 1650 cm^{-1}, δ Me_{III}= 1.58, H_A=5.20 ppm) and a hydroxyl group (ν 3400 cm^{-1}, δ H_B=3.80 ppm) but no carbonyl function, indicating that the molecular framework is bicarbocyclic. The following signals, other than described above, were observed in its NMR spectrum. H_C=3.93 (O<u>H</u>, removed by D_2O treatment), H_D=2.89, H_E=2.71, H_F=2.18 and H_G=1.77 ppm. Extensive application of spin-spin decoupling experiments (6), together with the fact that H_D has only one vicinal coupling, revealed the following coupling constants. $J_{AMe_{III}}$=1.4, $J_{DMe_{III}}$=1.3, J_{AD}=2.1, J_{DE}=6.7, J_{EF}=6.7, J_{EG}=9.3, J_{FG}=13.0, J_{FB}=6.4 and J_{BG}=2.5 Hz, and the structure IV could be deduced (7). In IV, J_{AD} is assigned to an allylic coupling and not a vicinal coupling. This assignment is not in accord with the result of a recent revision on the assignment of the proton signals of cyclobutene (11). However, the result obtained from monocyclic system may not be applicable to such a strained bicyclic derivative like IV. Actually, in the NMR spectra of VII (12), VIII and IX (13), vinylic proton at 6.10, 5.98 and 6.12 ppm, respectively, revealed allylic couplings and the methyl group of VII appeared as virtually a triplet (J=1.5 Hz). All of these observations support the illustrated arrangement in IV. A clear display of M-type long range coupling between H_B and H_D (J=1.2 Hz) permits the deduction of the stereochemical structure shown.

Photoproduct B (X) (r.r.t. 1.58) (yield; 11.5%), also showed a geminal dimethyl group (ν 1385, 1375 cm^{-1}, δ Me_{I}=0.89, Me_{II}=0.93 ppm), an ethylenic linkage (ν 1643 cm^{-1}, δ Me_{III}=1.63, H_A=5.24 ppm) and hydroxyl group [ν 3500 cm^{-1}, δ H_C=3.61 (OH), H_B=4.03 ppm] suggesting a skeleton similar to that in IV. H_D was coupled with Me_{III}, H_A, H_B and H_E at 2.30 ppm (multiplet) (J=1.5, 1.5, 6.0 and 4.5 Hz) and H_B has no other vicinal coupling. These observations lead to the structure X. Photoproducts C (XI) (r.r.t. 0.89) (yield; 12.6%) and D (II) (r.r.t. 0.83) were identified as β- and α-campholenal by direct comparison with authentic samples (2,14).

Photoproduct E (XII) (r.r.t. 0.62) (yield; 5.6%) showed no absorption due to carbonyl, hydroxyl or ethylenic linkage in the UV and IR spectra. But characteristic absorption due to the oxetane structure was observed at 951 cm^{-1} (15) and furthermore, NMR spectrum of XII was quite evident to suggest a symmetric structure, <u>i.e.</u> δ 0.79 ppm integrated for

6H is very sharp singlet, third methyl is at 1.36 ppm suffering a strong shielding effect by lone pair electrons of ethereal oxygen, and 2H at 4.12 ppm (multiplet) was ascribed for protons at ethereal carbon. Remaining protons (5H) were at around 1.83 ppm (multiplets). Therefore, its structure was deduced as XII.

Photoproduct F (XIII) (r.r.t. 0.35) (yield; 20.3%) was an enol ether derivative, showing strong $\nu_{C=C}$ at 1640 cm^{-1} in IR spectrum. In NMR spectrum, there are three singlet methyls at 0.96, 1.03 and 1.12 ppm, and two vinylic protons, H_A at 5.87 ppm and H_B at 4.74 ppm were coupled in each other (J=6.0 Hz), of which only H_B has further splitting with the adjacent methine (J=6.0 Hz). Observed magnitude of vicinal coupling falls in the category of dihydropirane (16,17), therefore, smaller ring sharing the oxygen is six-membered. The above evidence suggests the structure for XIII.

Photoproduct G (XIV) (r.r.t. 0.28) (yield; 6.1%) is evidently the decarbonylation product already reported by Srinivasan (3), the NMR spectrum of XIV revealed methyl groups at 0.81, 0.86 and 0.97 ppm. Further irradiation of II, resulted in the production of XI, XII and XIII, but not of IV suggesting that the last compound is derived from a different path way, although the immediate precursors of IV and XI were probably cyclohepadiene derivatives (18), relatively complex steps would be involved, in the formation of IV and XI, including a rearrangement previously recognized during the photoisomerization of eucarvone (19). The photochemical formation of XI from II would be of particular interest, since such a photoisomerization has been believed to occur through an intermediate having a strained trans-double bond (20). This is the first example encountered in a cyclopentene derivative. Precursor of XIII is considered to be a carbene which is analogous to one already observed in photolysis of cyclocamphor (21).

Contrasting with previous reports, III was not detected in our experiment although, we detected a ketonic product at r.r.t. 2.68 [δ 2.11 ppm (3H singlet)], but this was not III. The structure of this compound will be the subject of a separate paper in the near future.

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References

1) This paper was read at 20th Annual Meetings of Chemical Society of Japan, Apr. 1, 1967, Tokyo. See Abstract of Papers Vol. III, p. 196 (1967).

2) G. Ciamician and P. Silber, *Ber.*, **43**, 1310 (1910).

3) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 1546 (1959). *Idem.*, *ibid.*, **83**, 2604 (1961).

4) W. A. Noyes, G. S. Hammond, J. N. Pitts edited, *Advances in Photochemistry*, Vol. I, p. 369. Interscience Publishers, New York (1963), also cf. J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, **87**, 5218 (1965).

5) Chemical shifts (δ) were expressed from the tetramethylsilane as internal standard.

6) This was performed by Dr. M. C. Woods, Varian Associates.

7) Although it might appear less probable from the mode of genesis the structure IVa for this compound was eliminated on the following. a) It has been pointed out that $\nu_{C=C}$ of cyclopropenone exists at 1775-80 cm^{-1} (8) but IV has none in that region, b) in both compounds V (9) and VI (10), vinylic methyls of cyclopropene system appeared at 2.1 and 2.0 ppm while that of IV appeared at much higher field and c) further discrepancy of chemical shifts of methine proton of IV and V (H_D: 2.89 and 0.9 ppm) against the IVa.

8) G. L. Closs, L. E. Closs and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

9) G. Büchi and J. D. White, *ibid.*, **86**, 2884 (1964).

10) K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

11) J. D. Roberts and E. A. Hall, *ibid.*, **89**, 1056 (1967).

12) L. A. Paquette, *ibid.*, **86**, 500 (1964).

13) L. A. Paquette, J. H. Barrett, R. P. Spitz and R. Pitcher, *ibid.*, **87**, 3417 (1965).

14) M. Nakazaki and K. Naemura, *Bull. Chem. Soc. Japan*, **37**, 532 (1964).

15) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, p. 118. J. Wileys & Sons, New York (1958).

16) NMR Catalog No. 111, edited by Varian Associates.

17) For ring-size effect of J-cis in cycloalkenes, see a) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963), b) G. V. Smith and H. Krilloff, *ibid.*, **85**, 2016 (1963), c) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

18) W. G. Dauben, *J. Am. Chem. Soc.*, **82**, 4333 (1960).

19) D. I. Schuster, M. J. Nash and M. L. Kantor, *Tetrahedron Letters*, 1375 (1964).

20) R. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

21) P. Yates and L. Kilmurry, *Tetrahedron Letters*, 1739 (1964).