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PHOTOCHEMISTRY OF δ,γ-UNSATURATED KETONES IN SOLUTION[1,2]

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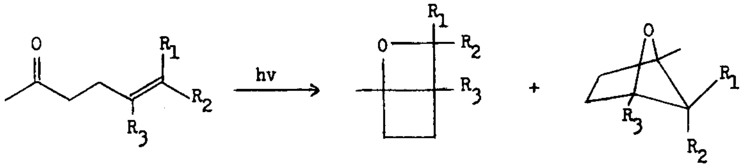
Photochemical addition of carbonyl compounds to unsymmetrical olefins yields a mixture of isomeric oxetanes. The major isomer is the one with the oxygen linked to the lesser substituted end of the olefinic bond.[4] Previous investigations on intramolecular oxetane formation from the photolysis of δ,γ-unsaturated ketones showed that 2-oxabicyclo[2,2,0]hexanes (II) were the major or the only non-ketonic products.[5,6] We wish to report that both oxabicyclo[2,2,0]hexanesand oxabicyclo[2,1,1]hexanes(III) are formed in the photolysis of δ,γ-unsaturated ketones.[7]



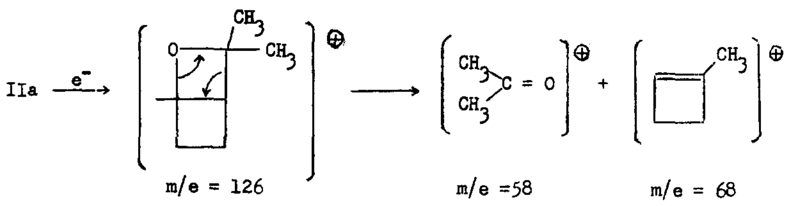
Ia (R_1=R_2=CH_3, R_3=H)
Ib (R_1=R_2=R_3=H)
Ic (R_3=CH_3, R_1=R_2=H)
Id (R_2=CH_3, R_1=R_3=H)

IIa(R_1=R_2=CH_3, R_3=H)
IIb(R_1=R_2=R_3=H)
IIc(R_3=CH_3, R_1=R_2=H)
IId(R_2=CH_3, R_1=R_3=H)

IIIa(R_1=R_2=CH_3, R_3=H)
IIIb(R_1=R_2=R_3=H)
IIIc(R_3=CH_3, R_1=R_2=H)
IIId(R_2=CH_3, R_1=R_3=H)

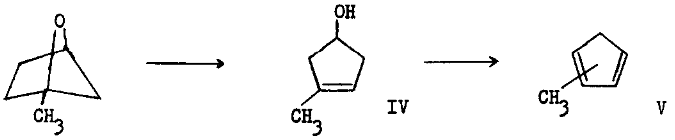
Irradiation of 6-methyl-5-hepten-2-one (Ia) in pentane (15g. in 115ml.) with a 450 w. Hanovia mercury lamp for 137 hours yielded an oxetane fraction (56%) and a non-volatile fraction (24%) together with some unreacted ketone (7%).[8] The oxetane fraction was resolved by preparative v.p.c. into two components, IIa and IIIa in a ratio of 2:5 respectively. Both compounds gave satisfactory elemental analyses and were characterized by physical methods. Compound IIa, 1,3,3-trimethyl-2-oxabicyclo[2,2,0]hexane, exhibits n.m.r. bands at 8.67τ(singlet), 8.65τ(singlet) and 7.3-8.0τ(multiplet) with a relative ratio of 3:6:5 respectively. Compound IIIa, 1,6,6-trimethyl-5-oxabicyclo[2,1,1]hexane, exhibits n.m.r. bands at 9.31τ(singlet), 8.85τ (singlet), 7.95-8.60τ(multiplet) and 6.08τ(doublet, J = 1.5 c.p.s.) with a relative ratio of 3:3:3:4:1 which may be assigned to the endo-6-CH_3, exo-6-CH_3, 1-CH_3, 2- and 3-methylenes and 4-H respectively. Both compounds exhibit infrared absorption in the 950 cm^{-1} region assignable to the oxetane.

Further characterization of IIa and IIIa was provided by mass spectrometry.[9] The two compounds exhibit overall similar mass spectra except that IIa exhibits intense peaks at m/e = 58 (4.45% of Σ_{14}) and m/e = 68 (3.25% of Σ_{14}) which are much weaker for IIIa [m/e = 58 (0.14% of Σ_{14}) and m/e = 68 (0.44% of Σ_{14})]. The difference may be attributed to the following fragmentation reactions of the IIa molecule ion which is not possible for the IIIa molecule ion.



The formation of IIIa as the major photoproduct from Ia may be visualized as analogus to the Paterno-Büchi Reaction in which the reactive intermediate is the $\underline{n} \rightarrow \pi^*$ excited ketone. The relatively more electron deficient oxygen adds to the lesser substituted end of the olefinic bond with the concerted formation of the second bond.

Irradiation of 5-hexen-2-one (Ib) under similar conditions led to the formation of an oxetane fraction (44%). The n.m.r. of this fraction exhibits two sharp methyl bands at 8.72τ and 8.83τ and a multiplet in the 5-6τ region assignable to the α-protons of ethers with a relative ratio of methyl protons to α-protons of ethers of 6:3.2 respectively. Since pure IIb exhibits a sharp methyl band at 8.72τ and a typical ABX pattern in the 5-6τ region for the C_3-methylenes with a relative ratio of 3:2,[5] the n.m.r. data are indicative of the formation of both IIb and IIIb. The mixture is unstable toward v.p.c. and fractional distillation even under very mild conditions. Compound IIb may be isolated in pure form by v.p.c. together with IV and V but we have not been able to isolate IIIb. The structure of IV was established by physical data, elemental analysis and comparison with an authentic sample.[10] Fraction V was shown to be a mixture of methylcyclopentadienes. The formation of IV and V may be easily rationalized from the decomposition of IIIb. On the basis of the n.m.r. spectrum of the initial mixture, the relative proportions of IIb to IIIb was estimated to be 6:4.



Irradiation of 5-methyl-5-hexen-2-one (Ic) and trans-hepten-2-one (Id) followed by v.p.c. analyses led to the isolation of IIc and IId[6] and products similar to IV indicating that IIIc and IIId may also be formed in the original irradiation mixture.

REFERENCES

(1) A preliminary report of this work was presented at the "Symposium on Organic Photochemistry" in Strasbourg, France, July, 1964.

(2) The work was supported by a grant from the National Science Foundation. The MS-9 high resolution mass spectrometer used in this work was purchased on the grants from the National Science Foundation and from the Louis Block Fund of the University of Chicago. The authors wish to acknowledge their support to make this work possible.

(3) National Science Foundation Postdoctoral Fellow, 1964-1965.

(4) For a review on the photochemical addition of carbonyl compounds to olefins, see N. C. Yang, M. Nussim, M. J. Jorgenson and S. Murov, Tetrahedron Letters, 3657 (1964).

(5) R. Srinivasan, J. Am. Chem. Soc., 82, 775 (1959).

(6) H. Morrison, J. Am. Chem. Soc., 87, 932 (1965).

(7) A related reaction has been reported recently which involves the formation of 1,6,6-trimethylbicyclo[2,1,1]hexan-5-al from citral, P. Cookson, J. Hudec, S. A. Knight and B. R. D. Whitear, Tetrahedron, 19, 1995 (1964).

(8) The quantum yield of decomposition of Ia was estimated to be of the order of 0.003 by the use of 2-hexanone as the secondary standard.

(9) The mass spectral measurements were kindly performed by Professor P. E. Eaton on an MS-9 high resolution mass spectrometer. The spectra were obtained at an ionizing potential of 70 ev. The symbol Σ_{14} represents the total ionic intensity of the spectrum scanned from m/e=14.

(10) The α-naphthylurethane of IV was kindly supplied by Mr. Michael Marx of the Department of Chemistry, Columbia University.