



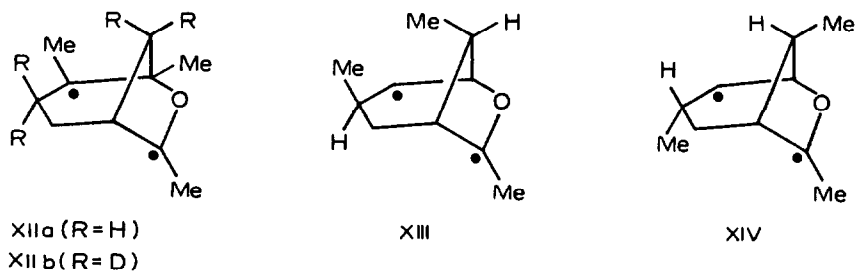
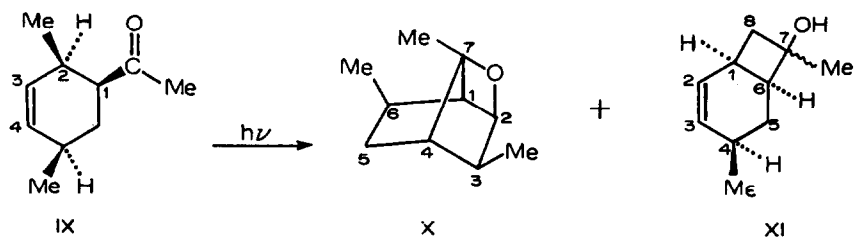
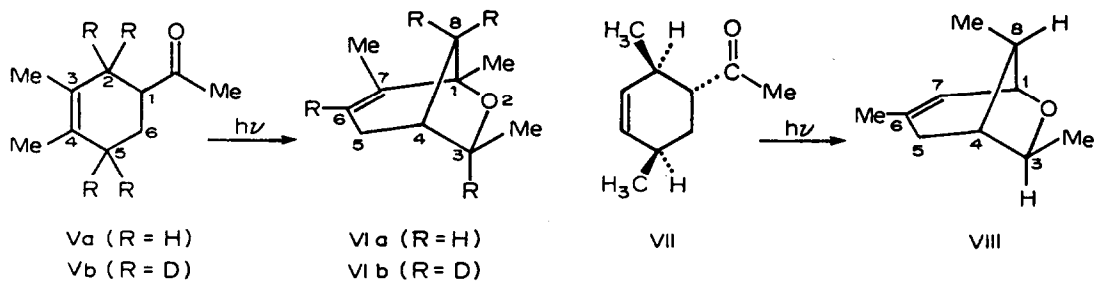
6.1 (quartet, 1,  $J = 6$  Hz,  $C_3$  methine), 7.9 (m, 3,  $C_5$  methylene and  $C_4$  methine), 8.3 (m, 5, vinyl methyl and  $C_8$  methylene), 8.6 (s, 3,  $C_1$  methyl), and 8.9 (doublet, 3,  $J = 6$  Hz,  $C_3$  methyl)(7).

The structure of VI as well as the mechanism of its formation was further indicated by the photolysis of the tetra-deutero analogue Vb (8) which gave VIb with no loss in overall deuterium content (mass spectrum). The nmr spectrum of VIb showed no vinyl hydrogen signal, no quartet due to the  $C_3$  methine, and a triplet ( $J = 1$  Hz) due to the  $C_3$  methyl, all of which are consistent with the proposed structure.

Photolysis of Diels-Alder adduct VII (4) as above led to the formation of two volatile products which could be separated and isolated in low yield by preparative glpc. The major product was deduced to have the structure VIII (6) in analogy to VI and on the basis of the following nmr spectrum ( $CCl_4$ ):  $\tau$  4.4 (m, 1, vinyl), 6.0 (m, 2,  $C_1$  and  $C_3$  methines), 7.7-8.3 (m, 4,  $C_5$  methylene and  $C_4$  and  $C_8$  methines), 8.3 (s, 3, vinyl methyl), 8.8 (d, 3,  $J = 6$  Hz,  $C_3$  or  $C_8$  methyl), and 9.0 (d, 3,  $J = 6$  Hz,  $C_3$  or  $C_8$  methyl). The minor photoproduct, very likely a double bond isomer of VII, has not yet been fully characterized.

Finally, photolysis of the all cis Diels-Alder adduct IX (4) led to two major volatile photoproducts, X and XI, neither of which possess the 2-oxabicyclo[3.2.1]oct-6-ene ring system previously observed. The structures of X and XI were assigned on the basis of their spectra (6,9) and represent the more familiar photochemical processes of cyclobutanol and intramolecular oxetane formation.

The formation of photoproducts VI and VIII from V and VII, the deuterium labeling results, and the different course of reaction in the case of IX can be well accommodated by the following mechanistic interpretation: Photolysis of V and VII leads to biradical intermediates XII and XIII respectively (10) which possess the requisite stereochemistry to undergo the intramolecular hydrogen atom transfer leading to VI and VIII (11). Biradical XIV however, formed from IX, is stereochemically incapable of this process and as a result bonding occurs between the radical centers giving oxetane X. That  $\gamma$ -hydrogen abstraction leading to cyclobutanol XI is competitive in the case of IX is not unexpected.



#### ACKNOWLEDGEMENT

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## REFERENCES

1. For part X see J.R. Scheffer and R.A. Wostradowski, *J. Org. Chem.*, **37**, 4317 (1972).
2. J.R. Scheffer, J. Trotter, R.A. Wostradowski, C.S. Gibbons, and K.S. Bhandari, *J. Amer. Chem. Soc.*, **93**, 3813 (1971).
3. J.R. Scheffer, K.S. Bhandari, R.E. Gayler, and R.H. Wiekenkamp, *ibid.*, **94**, 285 (1972).
4. A.A. Pettov and N.P. Sopov, *J. Gen. Chem. Russia*, **22**, 653 (1952). The relative stereochemistries of VII and IX were assigned on the basis of epimerization studies assuming the all *cis* isomer IX to be the less stable. Thus thermolysis (180° for 21 hrs) or base treatment of either VII or IX gave an equilibrium mixture of VII:IX = 2:1.
5. Photolyses (450 W Hanovia lamp fitted with a Corex filter sleeve) were carried out in pentane or hexane solution at a concentration of 1-2 mg/ml. All samples were thoroughly degassed prior to photolysis.
6. All compounds described gave satisfactory analyses and mass spectral parent ion peaks.
7. The stereochemistry at C<sub>3</sub> (*exo*-methyl) follows from the lack of coupling between the C<sub>3</sub> and C<sub>4</sub> methines. For a discussion of this point in a system very similar to VI see W.C. Agosta and A.B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).
8. This material was prepared using 2,3-dimethylbutadiene-1,1,4,4-d<sub>4</sub> which was in turn prepared by the general procedure of A.C. Cope, G.A. Berchtold, and D.L. Ross, *J. Amer. Chem. Soc.*, **83**, 3859 (1961).
9. Photoproduct X showed the following: ir (film) no OH or C=O absorption; nmr (CDCl<sub>3</sub>) τ 5.8 (d, 1, J = 4 Hz, C<sub>2</sub> methine), 7.5-8.4 (m, 6, methines at C<sub>1</sub>, C<sub>3</sub>, C<sub>4</sub> and C<sub>6</sub> plus methylene at C<sub>5</sub>), 8.5 (s, 3, C<sub>7</sub> methyl), 9.0 (d, 3, J = 11 Hz, C<sub>3</sub> or C<sub>6</sub> methyl), and 9.1 (d, 3, J = 10 Hz, C<sub>3</sub> or C<sub>6</sub> methyl). This data does not unequivocally rule out the less likely oxetane structure resulting from oxygen addition to C<sub>4</sub>. Photoisomer XI exhibited the following: ir (film) 3375 cm<sup>-1</sup> (OH), no C=O; nmr (CDCl<sub>3</sub>) τ 4.4 (m, 2, vinyls), 6.8-8.4 (m, 7), 8.8 (s, 3, C<sub>7</sub> methyl), and 9.0 (d, 3, J = 7 Hz, C<sub>4</sub> methyl).
10. The intermediacy of 1,4-biradical species in oxetane formation between alkyl ketones and electron rich olefins seems well accepted. See for example N.J. Turro and P.A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).
11. Intramolecular hydrogen atom transfers in acyclic oxatetramethylene and thiatetramethylene diradical intermediates have been observed. H.-S. Ryang, K. Shima, and H. Sakurai, *Tetrahedron Lett.*, 1091 (1970), and C.C. Liao and P. De Mayo, *Chem. Commun.*, 1525 (1971). To the best of our knowledge our work represents the first example of such a process in a cyclic oxatetramethylene diradical intermediate.