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COMPETITIVE PROCESSES IN 1,4-DIRADICALS

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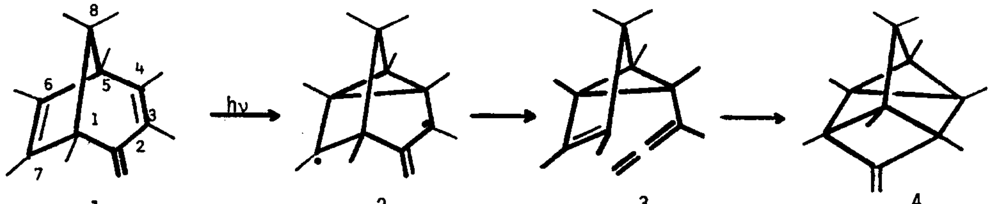
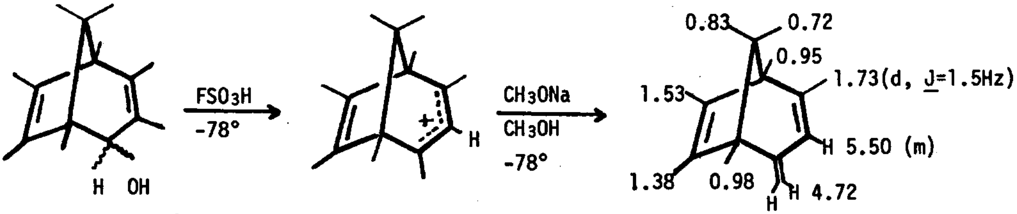
2-Methylenebicyclo[3.2.1]octa-3,6-dienes (eg. 1) photoisomerize to tetracyclic isomers (eg. 4).[1] Plausible (but presumed) intermediates in these isomerizations are the 1,4-diradicals 2 and the allenes 3. The photochemical part of the reaction proceeds *via* a triplet excited state.[1] Substitution of H for CH_3 at C4 or C5 in 1 is without effect on the reaction course; the yield of tetracyclic alkene in all three cases is essentially quantitative.[1,2] In contrast, substitution of H for CH_3 at C3 has a striking effect on the product composition. We describe here one such example found in the irradiation of 7 and discuss briefly the mechanistic significance of the results.



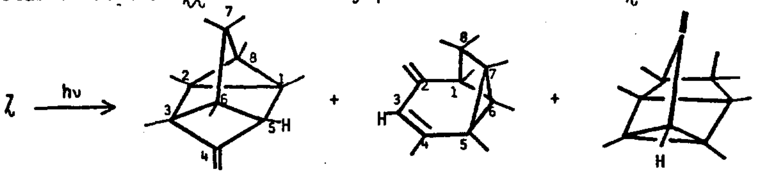
1 2 3 4

Dissolution of 5[1] in FSO_3H/SO_2ClF at -78° gave allylic ion 6[3] which was quenched (CH_3ONa/CH_3OH, -78°) to give a nearly quantitative yield of 7 (λ_{max}^{EtOH} 243 nm, ε13,000).[4] Irradiation of 7 (80 mg in 10 ml of ether, 450 W. Hanovia lamp)[5] gave three products assigned the



5 6 7

structures 8-10 shown. The reaction was faster with Vycor filtered light than with a Corex filter, and the product ratios depended on the filter used. Separate experiments showed that 8 was photostable but that 10 was formed by photoisomerization of 9.[6]

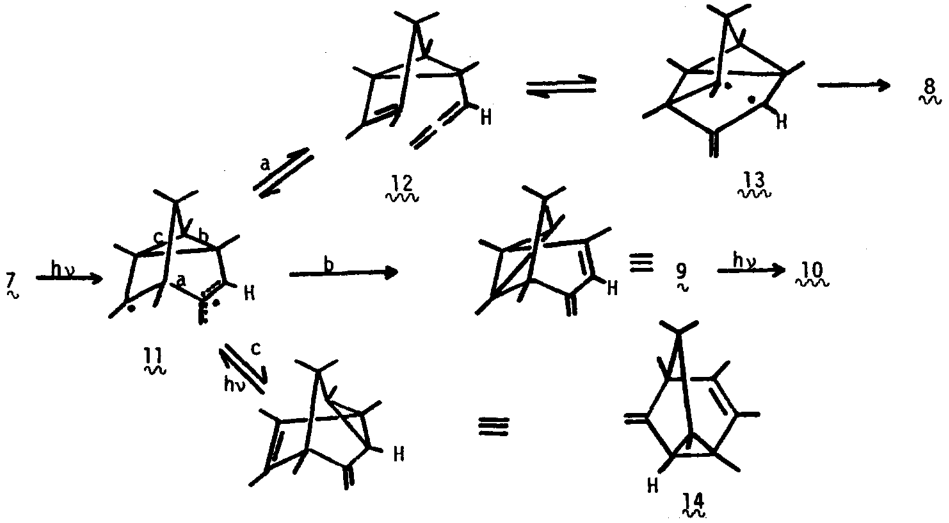


	8	9	10
Corex (12 hr)	45%	45%	10%
Vycor (6 hr)	45%	5%	50%

The structure of 8, the expected[1] photoproduct, is based on its spectral data [ir (CCl_4) 1678, 880 cm^{-1}; no λ_{max} >210 nm; nmr: no methyl signal below δ1.00; 7 sharp methyl singlets at δ0.62 and 0.67 (C7), 0.83 (C6), 0.88 (C3), 0.90 (C2), 0.93 (C1), 1.00 (C8); δ2.10 (1H, sl br, C5), δ4.23 and 4.32 (sl br, vinyls); irradiation at δ2.10 sharpened the signal at δ4.23].[7]

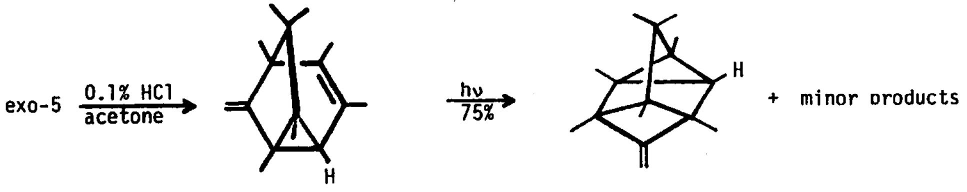
The structure of 9 follows from its spectral data, from mechanistic considerations, and from its photoconversion to 10 [ir (CCl_4) 1650, 885 cm^{-1}; λ_{max}^{EtOH} 244 nm (sh), ε2900; nmr: six sharp aliphatic methyl singlets at 0.57 and 0.67 (C8), 0.98, 1.02 and 1.07 (C5-7), 1.18 (C1); one allylic methyl at δ1.62 (d, *J*=2.0Hz, C4), three vinyl protons at δ4.48 and 4.58 (methylene) and δ5.35 (C3); irradiation of the peak at δ5.35 caused collapse of the peak at δ1.62, and sharpening of the δ4.48 signal].

Compounds 8 and 9 are formed competitively on irradiation of 7, possibly as a consequence of several reaction paths accessible to the initially formed 1,4-diradical intermediate 11.



Cleavage of bond a is the usual path, giving allene 12. If the allene adds to the cyclopentene moiety in a stepwise fashion, diradical 11 or 13 would be formed; ring closure of 13 to 8 is not reversed photochemically (λ_{max} <210 nm) or thermally at room temperature.

Two possible di-π-methane[8] paths may compete with allene formation. Cleavage of bond b leads to the observed product 9; this path is probably irreversible, since irradiation of 9 gives 10. Although on the basis of literature examples[8] one might have expected 14 to predominate over 9, the product from this alternate di-π-methane path (cleavage of c) was not observed. However separate irradiation of 15, a close analog of 14, under conditions similar to those used to photoisomerize 7, gave ca. 75% of 16[1] and some unidentified products. Consequently 14 may have gone undetected because if it were formed during the irradiation of 7, it probably would have been reconverted to 8 (and 9).



15 16

The question remains why the di-π-methane reaction (path b) competes with allene formation (path a) when the group at C3 in 7 is H, but not when it is CH_3 or ϕ. There are several possible explanations. The rate of formation of the monosubstituted allene 12 may be slower than that of a di-substituted allene (eq. 3), allowing the di-π-methane route to compete. Since allene formation is reversible, ring closure to 8 (if stepwise) may be slower than ring closure to 4 because the intermediate would have a secondary radical site (13). Or the di-π-methane path may be accelerated in rate because of the higher energy of the secondary radical 11 compared with the corresponding diradical when the substituent at C3 is CH_3 or ϕ. Any or all of these effects may contribute to the experimentally observed result.[9,10]

Acknowledgement. We are indebted to the National Science Foundation for support of this research.

REFERENCES

1. H. Hart and M. Kuzuya, Tetrahedron Lett., preceding paper.
2. Replacement of the methyl groups at C3 and C4, or C6 and C7 with phenyl groups also does not affect the reaction path.

3. The mechanism of this interesting rearrangement will be discussed in a separate paper; for analogous rearrangements see H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, **95**, 4096 (1973).
4. The pmr spectrum (δ units) was assigned by comparison with analogous compounds (ref 1); irradiation of the multiplet at δ5.50 caused collapse to a singlet of the doublet at δ1.73.
5. These conditions are entirely analogous to those used for the quantitative conversion of **1** to **4**.
6. Evidence for the structure of **10** and the mechanism of its formation from **9** will be discussed in another paper.
7. Compare the pmr spectrum with data for **8a**-**8e**, table in ref 1.
8. S. S. Hixson, P. S. Mariano and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
9. In the preceding paper (ref 1) we noted that substitution of H for CH_3 at C1 in **1** also diverts the photoisomerization away from the clean formation of allene. This observation is consistent with the proposed reaction scheme, since allene formation (cleavage of bond *a*) would be expected to be retarded by such a substitution, allowing other paths to compete. On the other hand, substitution of H for CH_3 at C4 or C5 would retard the di-π-methane path(s), but should be without a substantial rate effect on allene formation.
10. One can, of course, analyze all of the photochemical interconversions described here as concerted processes. The effect of substituent changes is more easily rationalized, however, in terms of diradical intermediates. Since the reactions proceed from triplet excited states, diradical mechanisms are probably preferred.