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THE PHOTOCHEMISTRY OF HOMOCONJUGATED CYCLIC DIENES. I.
THE PHOTOISOMERIZATION OF 1,4-CYCLOOCTADIENE.

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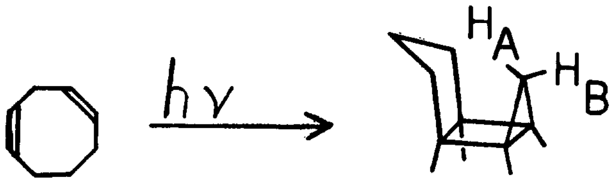
Internal photocycloadditions in non-conjugated dienes are well-known (1). Only recently, however, have the products of the mercury ($^3P_1$) sensitized photolysis of open chain 1,4 dienes been shown to include compounds with the highly strained bicyclo[2.1.0] skeleton (2,3). In view of these studies we would like to report the formation of a highly strained analogue of the bicyclo[2.1.0] system from the unsensitized solution photolysis of 1,4-cyclooctadiene (I). The latter was prepared by a simplified method developed in our laboratories (4).

Eight hour irradiation of a 0.045 M ether solution of I, in a quartz immersion apparatus fitted with a Vycor filter and a medium pressure mercury arc lamp, quantitatively converted the starting diene to a single product. The photoproduct, isolated by preparative gas chromatography, showed infrared bands at 3020 and 3045 cm^{-1}, indicative of a fused cyclopropane ring (5). The nmr spectrum showed absorptions centered at τ 7.32 (2H, multiplet), 8.6 (8H, multiplet), 9.12 (1H, doublet) and 9.80 (1H, quartet). The spectral data is compatible with the structure, cis,syn,cis-tricyclo[3.3.0.$0^{2,4}$]octane (II) for the photoproduct. The basis for this assignment will be discussed below.

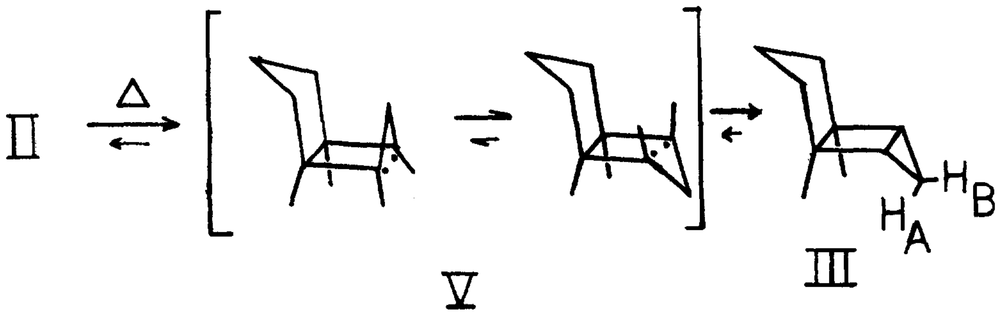


I II

The appearance of a second major peak of varying intensity, upon vpc analysis of the photolysis mixture, suggested that the initially-formed photoproduct was undergoing partial thermal rearrangement to a product other than the starting material. This was confirmed by the fact that the nmr spectrum of the crude photolysis product, prior to injection on vpc, showed absorptions due, essentially, only to II. The thermolysis was studied by heating a carbon tetrachloride solution of pure II in a sealed nmr tube at 100°. Periodic recordings of the nmr spectrum of the solution clearly showed that the suspected rearrangement was taking place. The half-life was estimated to be approximately 20 hr.

The thermolysis product was isolated by preparative gas chromatography and its nmr and ir spectra recorded. The latter showed two bands at 3035 and 3005 cm^{-1}, again indicative of a fused cyclopropane ring (5). The nmr spectrum showed absorptions centered at τ 7.9 (2H, multiplet), 8.5 (6H, multiplet), 9.0 (2H, doublet) and 9.45 (2H, multiplet). This nmr spectrum is in complete agreement with that reported by both Winstein (6) and Meinwald (7) for a compound which was assigned the structure *cis*,*anti*,*cis*-tricyclo[3.3.0.$0^{2,4}$]octane (III).

The stereochemical assignments of II and III rest, in part, on Traynham and co-workers' recent nmr study (8) of the chemical shifts of secondary cyclopropyl protons in *cis*-bicyclo[n.1.0]alkanes (analogous to H_A and H_B in II and III). These workers found that the presence of a cis ring, large enough to interact with H_A, shifts that absorption to higher field relative to H_B. Therefore, II would be expected to show cyclopropane bands much more highly separated than those in III. A comparison of the nmr absorptions assignable to H_A and H_B in II, i.e. τ 9.80 and τ 9.12, respectively, with those of III, consisting of two overlapping bands extending from τ 9.23 to τ 9.67, are in good agreement with expectations. Traynham's work also included a study of the nmr spectrum of bicyclo[2.1.0]pentane (IV), a compound expected to show H_A and H_B band positions similar to those in III. The nmr absorptions at τ 9.6 (H_A) and 9.3 (H_B) in IV further substantiate the assignment of the *anti* configuration to III leaving the *syn* configuration for II.



Previous work (9,10) indicates that the thermal rearrangement of II to III involves an intermediate which may be represented by the equilibrating diradical, V. Regeneration of the tricyclic system from V, under thermal conditions, should lead to the thermodynamically more stable product. From steric considerations, it appears that the *anti* isomer should be more stable than the corresponding *syn* analogue. The assignment of the *anti* configuration to the thermolysis product, purely on thermodynamic grounds, is therefore in complete agreement with that concluded from spectral data.

The evidence amassed thus far points to a concerted mechanism analogous to the photochemically allowed (11) cycloaddition of two ethylene molecules. Inspection of models suggests that, in a concerted photoreaction of this type, the ground state geometry of I would favor formation of the observed *syn* photoproduct.

Studies now in progress will attempt to shed further light on the generality as well as the detailed mechanism of this photoreaction. A full account of these investigations will be forthcoming in a future publication.

REFERENCES

1. For excellent reviews on this subject see: (a) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966): (b) H. Prinzbach, *Pure Appl. Chem.*, **16**, 17 (1968).
2. J. Meinwald and G. W. Smith, *J. Am. Chem. Soc.*, **89**, 4923 (1967).
3. R. Srinivasan and K. H. Carlough, *ibid.*, **89**, 4932 (1967).
4. S. Moon and C. Ganz, *J. Org. Chem.*, in press.
5. S. A. Liebman and B. J. Gudzinowicz, *Anal. Chem.*, **33**, 931 (1961).
6. J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).
7. J. Meinwald and B. E. Kaplan, *J. Am. Chem. Soc.*, **89**, 2611 (1967).
8. J. G. Traynham, J. S. Dehn and E. E. Green, *J. Org. Chem.*, **33**, 2587 (1968).
9. J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962).
10. C. Steel, R. Zand, P. Hurwitz and S. G. Cohen, *ibid.*, **86**, 697 (1964).
11. R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).