

PHOTOISOMERIZATION OF BIS(PERFLUOROMETHYL)BICYCLO[2.2.2]OCTA-
2,5-DIENES TO TETRACYCLO[4.2.0.0^{2,8}.0^{5,7}]OCTANES

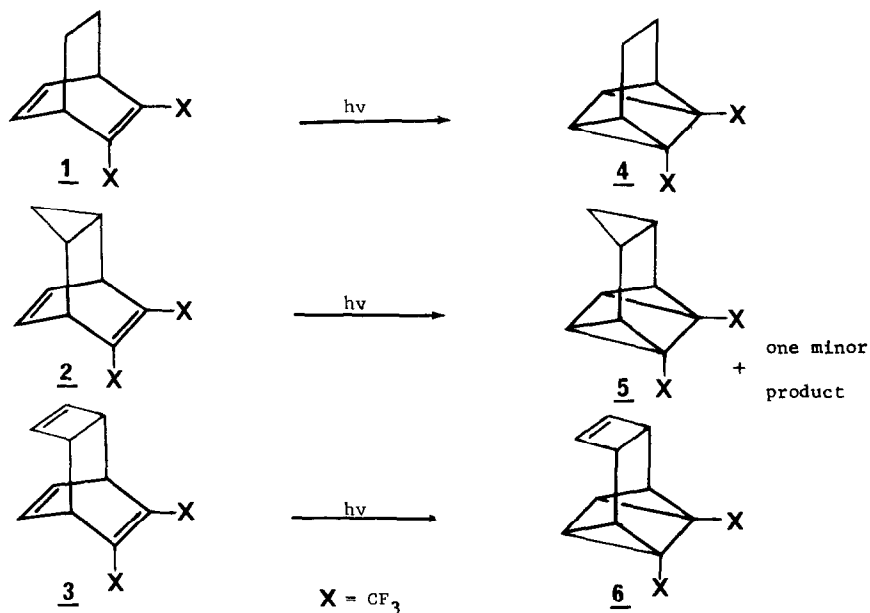
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The reaction of photoisomerization of norbornadiene and its derivatives to the corresponding quadricyclanes, brought about either by direct irradiation or triplet sensitization is well known (1). However, similar isomerizations involving the related bicyclo[2.2.2]octa-2,5-diene system are not known. Studies in this area have apparently led to complete failure of reaction or only to side products (2). Recently, in the study of Diels-Alder reactions with perfluoro-2-butyne as dienophile, several bis(perfluoromethyl)bicyclo[2.2.2]-octadienes, 1-3, become available to us (3). We have now found that these compounds upon direct irradiation indeed undergo internal cycloaddition in a manner analogous to that of norbornadiene. These photochemical reactions can be represented by the following equations:



The uv spectrum (in acetonitrile) of compound 1 only shows a shoulder (234 m μ , ϵ = 950) on a strong end absorption, e.g. at 200 m μ , ϵ = 5,900. Irradiation of a 25% solution of 1 in an inert solvent such as dioxane, THF, acetonitrile or pentane in a quartz tube with a low pressure Hg lamp led to efficient formation of one product. The reaction can be conveniently followed by nmr (when irradiated in a deuterated solvent) (4) or by glc (5 ft. 3% SE-30 column, 50°). It reaches a maximum 85% conversion after 20 hrs of irradiation (5). Based on the H¹ nmr spectrum and its thermal behavior, structure 4 has been assigned to the photoproduct. Compound 4 was isolated by preparative glc. Its 60 Mc nmr spectrum (in CCl₄) shows no low field signals for vinyl or doubly allylic protons. It shows two groups of signals at 2.03 (an unresolved multiplet) and 1.31 ppm (a broad doublet) of relative intensities 3:1, indicating two of the four cyclopropyl protons with chemical shift close to those of the ethano bridge protons. Compound 4 is thermally labile. At 80.5°, it reverts to 1 with a rate constant of $2.1 \times 10^{-3} \text{ sec}^{-1}$.

Similar to 1, the uv spectrum of 2 shows only end absorption: 200 m μ (ϵ = 1,710); 220 (670); 250 (180). Irradiation of 2 by the same procedure as described for 1 produces a mixture of two products in an approximate ratio of 1.5 to 10 (by glc, the same silicone column). The major product, a low melting white solid when pure, reverts to 2 at slightly elevated temperatures ($k = 3.3 \times 10^{-4} \text{ sec}^{-1}$ at 80.5°); therefore its isolation is possible only by preparative glc using column temperatures below 60°. Its nmr spectrum (in CCl₄; 60 Mc) is most indicative of the structure, consisting of a broad doublet at 1.84 ppm (4H), a broad band between 1.1-1.4 (2H), a multiplet between 0.6-0.9 (1H) and a quartet, due to two overlapping triplets ($J = 4.0, 4.0 \text{ Hz}$), at 0.13 (1H). They are consistent with the structure 5 with the high field signals accounted by the two methylene cyclopropyl protons. Figure I shows the 100 Mc spectrum of 5 and the results of partial decoupling experiments (6). Although the close chemical shifts of the three higher field groups of signals makes complete decoupling impossible, the results clearly show that the signals at 1.1-1.4 ppm are coupled to the two methylene cyclopropane protons; therefore, they must be due to the two adjacent tertiary cyclopropane protons. The minor product has not been isolated in sufficient quantities for structural assignment (7).

Irradiation of 3 in a similar manner yielded one photoproduct. A maximum of approximately 80% conversion was achieved after two days of irradiation (5). The nmr spectrum of the product (in THF-d₈) (4) shows a singlet at 6.61 ppm (2 cyclobutenyl vinyl protons), a multiplet at 3.17

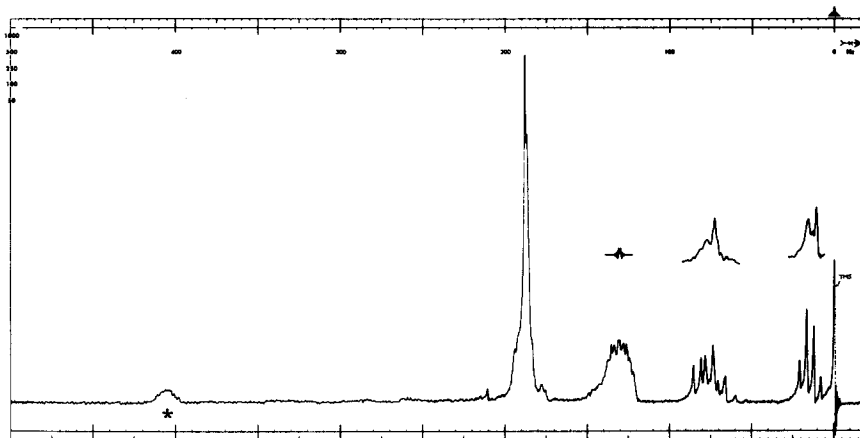


Figure I. 100 Mc nmr spectrum of 5 (CCl_4 , TMS internally); upper, decoupled spectrum. *, signals due to small amount of 2.

(2H) and two coupled groups of signals centered at 2.17 and 1.76 (2H each). It is consistent with the structure 6. Upon heating at 80.5° , 6 reverts to 3 with a rate constant of $4 \times 10^{-3} \text{ sec}^{-1}$. In view of the facile photosensitized ring closure of the cyclooctatetraene-maleic anhydride adduct (8), the selective direction of ring closure in compound 3 is somewhat unexpected.

Quite in contrast with norbornadiene, we have found that the observed isomerizations of compounds 1-3 cannot be sensitized, e.g. not even by acetone, a high triplet energy sensitizer. This, coupled with the thermal instability of the photoproducts, could explain some of the difficulties experienced by previous workers with the bicyclo[2.2.2]octadiene system.

The chemical properties of the new tetracyclic ring system are presently under investigation.

REFERENCES

1. See e.g. J. R. Edman, *J. Org. Chem.*, 32, 2920 (1967) and literatures cited therein.
2. H. Prinzbach, *Pure & App. Chem.*, 16, 17 (1968).
3. R. S. H. Liu, *J. Am. Chem. Soc.*, 90, 215 (1968); R. S. H. Liu and C. G. Krespan, *J. Org. Chem.*, accepted for publication.
4. We are grateful for a generous sample of THF-d₈ given by Professor Scheuer.
5. Failure to reach 100% conversion could be due to possible formation of minute amounts of benznoid compounds, which may either act as an internal filter or singlet sensitizers for the reverse reaction. The conversion of quadricyclane to norbornadiene can be sensitized efficiently by singlet donors: See S. Murov and G. S. Hammond, *J. Phys. Chem.*, 72, 3797 (1968).
6. We wish to acknowledge Mr. K. N. Somasekharan's assistance in obtaining the decoupled spectrum. The HA-100 spectrophotometer was obtained under Grant GM 14533-01 supported by the National Institute of Health.
7. That the nmr spectrum of a sample of the minor product contaminated with 2 failed to show additional new high field signals suggests that the original cyclopropyl group has participated in the reaction to form the minor product.
8. S. Masamune, H. Cuts and M. G. Hogben, *Tet. Letters*, 1017 (1966).