

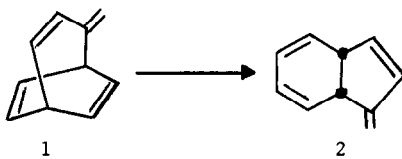
MECHANISTIC STUDY OF THE SINGLET EXCITED STATE PHOTOREARRANGEMENT OF  
2-METHYLENE-BICYCLO[3.2.2]NONA-3,6,8-TRIENE. AN UNUSUAL [1,3] VINYL SHIFT.

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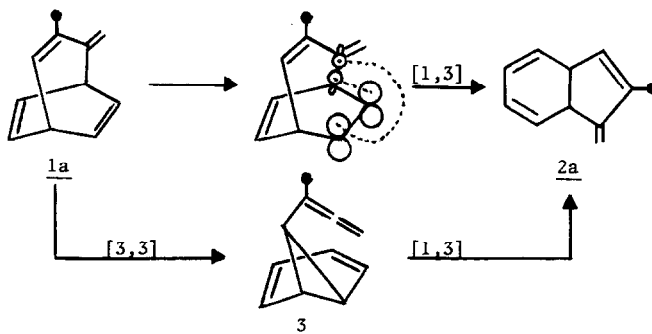
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In the preceding communication, we reported an interesting singlet state photochemical interconversion of methylenomobarrelene 1 and dihydroindene 2.<sup>1</sup>

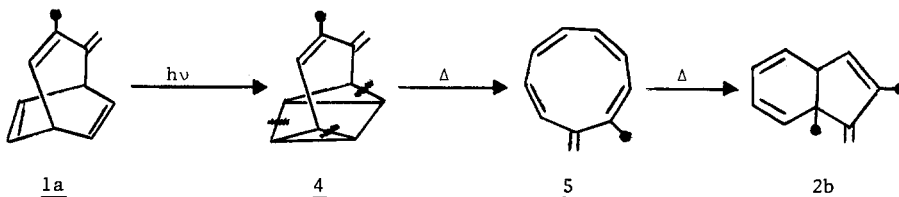


Two fundamentally different mechanisms for this interconversion seem to be possible *a priori*: Mechanism A whereby a vinyl shift takes place either directly as a photochemically allowed suprafacial [1,3] sigmatropic shift, or consecutively by a [3,3] sigmatropic shift to norcaradienyl allene 3 followed by a [1,3] shift to give 2a (Scheme I), and Mechanism B where photochemical  $\pi_2^s + \pi_2^s$  cycloaddition to form 4 is followed by thermal  $\sigma_2^s + \sigma_2^s + \sigma_2^s$  opening to nonafulvene (5), which recloses by a thermal disrotatory reaction to 2.<sup>2</sup> (Scheme II).

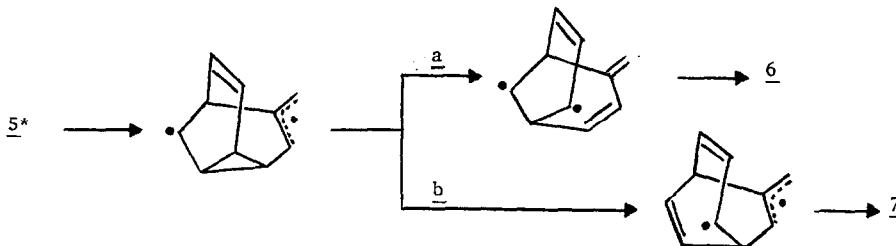
Scheme I. Mechanism A.



Scheme II. Mechanism B.



Formation of 6 and 7 by a sensitized irradiation of 5 represents another example of an unambiguous triplet excited state di- $\pi$ -methane rearrangement of a "free rotor" bridged cycloheptadiene system.<sup>12,13</sup> Furthermore, we note here an exceptional case of a non-regiospecific di- $\pi$ -methane rearrangement. Apparently, the two alternative pathways a and b (represented by Zimmerman qualitative valence bond mechanism), have similar excited state potential energy surfaces.<sup>14</sup>



Mechanistic aspects of the singlet rearrangement 5 $\rightarrow$ 9 are discussed in detail in the following communication.

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#### REFERENCES

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- 2) P. Ahlberg et al., *ibid.*, 94, 7063 (1972).
- 3) J.C. Barborak, J. Daub, D.M. Follweiler and P.v.R. Schleyer, *ibid.*, 91, 7760 (1969).
- 4) Rayonet RPR-100 reactor, "3000Å" lamps, pyrex filter.
- 5) Olefin 5: m/e 130;  $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$  233 nm ( $\epsilon$  8500), 260 sh (5670); nmr ( $\text{CDCl}_3$ )  $\delta$  3.38 (1H,q), 3.67 (1H,t), 4.34 (1H,s), 5.01 (1H,d), 6.02 (1H,q), 6.20 (2H,t), 6.50 (2H,t). Cf. Ref.12. Satisfactory elemental analysis.
- 6) J. Grutzner and S. Winstein, *ibid.*, 94, 2200 (1972). M.J. Goldstein and B.G. Odell, *ibid.*, 89, 6356 (1967).
- 7) Gpc analyses and separations were conducted using a 5% Carbowax 20M columns, at 90°.
- 8) Olefin 6: m/e 130; nmr ( $\text{CDCl}_3$ )  $\delta$  1.68 (1H,m), 2.12 (1H,q), 2.34 (1H,d,q), 3.70 (1H,d,d), 4.82 (1H,s), 4.94 (1H,s), 5.40 (1H,d,d), 5.74 (2H,m), 6.34 (1H,d). Cf. Ref. 12.
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- 10) L.G. Greifenstein, J.B. Lambert, M.J. Broadhurst and L.A. Paquette, *J. Org. Chem.*, 38, 1210 (1973).
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- 13) For a recent discussion of the "free rotor" effect see H.E. Zimmerman and G.A. Epling, *J. Amer. Chem. Soc.*, 94, 8749 (1972), and references cited therein.
- 14) H.E. Zimmerman and A.A. Baum, *ibid.*, 93, 3646 (1971)