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MERCURY SENSITIZED PHOTOREARRANGEMENT OF
3,3,6,6-TETRAMETHYL-1,4-CYCLOHEXADIENE

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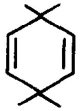
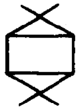
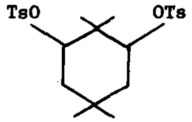
Although the photochemistry of nonconjugated dienes has received limited attention compared with the conjugated analogs[1,2], several interesting transannular cyclcoaddition reactions have been recorded. The isomerism of norbornadiene[3] and 1,5-cyclooctadiene[4] are particularly noteworthy in this regard. Since norbornadiene has a rigid folded structure, it is not representative of simple cyclic dienes and we therefore chose to study the photochemical tranformations of 3,3,6,6-tetramethyl-1,4-cyclohexadiene (I)[5]; in this case reactions analogous to those cited above would lead to the tricyclohexane isomers II and/or III. This communication outlines our initial findings in this investigations.


I


II

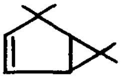

III



IV

Diene I was not prepared by the acetate pyrolysis procedure originally described for its synthesis[6,7], due to the concurrent thermal decomposition of I to para xylene[8]. Instead, we have found that treatment of the corresponding ditosylate (IV) with potassium tert.-butoxide in anhydrous DMSO[9] gave I in good yield.

The photolysis of I was effected in the vapor phase with mercury sensitization, using 2537 Å resonance lamps in a Srinivasan-Griffin reactor. After 12-20 hr exposure in either vycor or quartz reaction vessels, I was partially but cleanly converted to an isomeric hydrocarbon. A minor photoproduct was also obtained, but not in sufficient quantity to permit identification. Purification of the major photoisomer was accomplished by glpc at 120° on a 6 ft column packed with 20% Apiezon L on Chromosorb W. No reaction was observed by irradiation of the liquid phase or a benzene solution of I.



V

VI

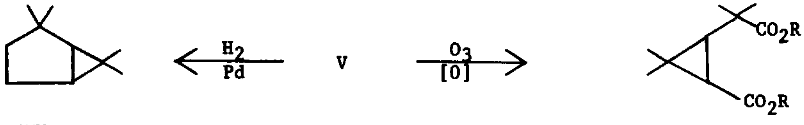
Assignment of structure V to the major photoisomer rested on infrared absorption at 3048, 1590, 1365 (doublet) and 755 cm^{-1}; ultraviolet absorption at 308 mμ (ε 5,400); nmr signals at τ 4.45 (multiplet) and ca. 8.9 (sharp asymmetric multiplet superimposed on a small AB quartet) with an area ratio of 1:7 respectively; and a mass spectrum having a molecular ion at m/e 136 (the main peaks in this spectrum are listed in Table I and are consistent with structure V). The ultraviolet absorption spectrum of V is characteristic of vinyl cyclopropane systems[10], and the infrared spectrum indicates a cis-disubstituted olefin. The nmr spectrum is also consistent with V, but does not permit a clear decision between this structure and the isomeric bicyclo[2.1.1]hexene VI. Since VI has C_{2v} symmetry while V is asymmetric, the former structure could be ruled out if the presence of four structurally non-equivalent methyl groups could be demonstrated. The nmr spectrum of the photoproduct was not significantly affected by a change in solvent from carbon tetrachloride to benzene, and it was therefore necessary to chemically modify the compound in order to achieve a distinction.

Table I

The Mass Spectrum of V

m/e	Relative Abundance	m/e	Relative Abundance
136 (M^+)	42.4	79	44.9
121	100.0	78	11.0
106	13.6	77	37.6
105	41.2	65	12.4
93	52.3	55	13.0
91	39.0	53	21.4
80	10.7	51	18.5

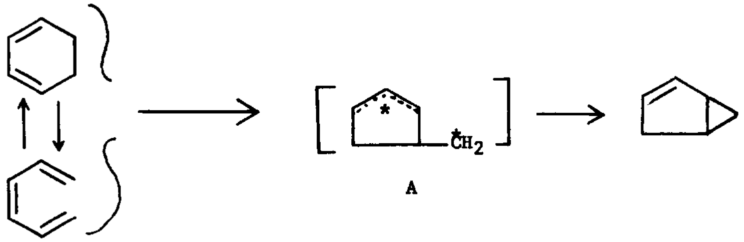
In the presence of a palladium catalyst one equivalent of hydrogen was rapidly taken up by V, and the purified dihydro derivative (VII) was identified by its mass spectrum (parent ion at m/e 138, most abundant ion at m/e 123) and nmr spectrum. The latter displayed a complex multiplet at τ 8.1-8.8, four sharp singlets of equal amplitude at τ 8.85, 8.93, 8.98 and 9.08 and two smaller peaks at τ 9.25 and 9.37. The relative area ratios of these resonance signals were 3.5:12.5:2; apparently part of the methylene multiplet lies under the methyl singlets. These findings remove any ambiguity concerning the assignment of structure V to the photoproduct. Before the hydrogenation study had been completed, additional evidence supporting V was obtained by oxidation of the photoproduct to the diacid VIII (R=H). The methyl ester (R=CH_3) was purified by glpc and exhibited infrared, nmr and mass spectra in accord with the assigned structure.



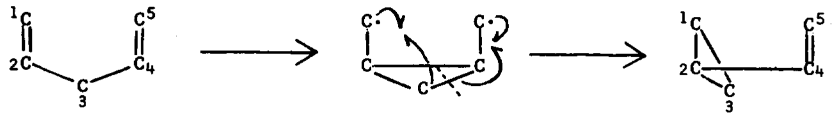
VII VIII

Discussion. Bicyclo[3.1.0]hexene photoproducts have been reported from a variety of conjugated trienes and 1,3-cyclohexadienes[1,10c,11], and recent studies suggest that independent routes to the rearranged product are possible from each substrate class (equation 1). A symmetrical intermediate was, however, ruled out[12]. If a stepwise mechanism for these rearrangements is accepted then an intermediate of type A must be involved. However, the formation of an intermediate of this kind from I is difficult to rationalize. We prefer to view the rearrangement of I as an example of the general reaction type outlined in equation 2. Other noteworthy examples are found in the photorearrangement of barrelene and bicyclo[4.2.2]-deca-2,4,7,9-tetraene to semibullvalene[13] and bullvalene[14] respectively.

(1)



(2)



Since the 4,5- double bond is unchanged in the rearrangement product, this feature of the substrate may be part of an aromatic ring, as demonstrated by the rearrangement of benzonorbornadienes[15] and dibenzobicyclo[2.2.2]-octatrienes[16].

REFERENCES

1. W. G. Dauben, Nineteenth Organic Chemistry Symposium, Tempe, Arizona (1965).
2. R. Srinivasan, *Advances in Photochemistry*, **Vol. 4**, 113, Interscience, New York (1966).
3. [a]W. G. Dauben and R. Cargill, *Tetrahedron*, **15**, 197 (1961); [b]G. Hammond, P. Wyatt, C. DeBoer and N. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).
4. R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964).
5. The tetramethyl derivative avoids the problem of double bond isomerization which complicates teh parent diene.
6. W. Reusch, M. Russell and C. Czurella, *J. Org. Chem.*, **29**, 2446 (1964).
7. F. Grant, R. Gleason and C. Bushweller, *J. Org. Chem.*, **30**, 290 (1965).
8. Grant, et.al.[7] report less decomposition even at higher temperatures, perhaps due to a shorter contact time.
9. C. Snyder and R. Cargill, *Tetrahedron*, **15**, 197 (1961).
10. [a]P. K. Freeman, M. Grostic and F. Raymond, *J. Org. Chem.*, **30**, 771 (1965); [b]K. Crowley, *Tetrahedron Letters*, 2863 (1965); [c]J. Meinwald, A. Eckell and K. Erickson, *J. Am. Chem. Soc.*, **87**, 3532 (1965).
11. E. F. Ullman, W. Henderson, Jr., and K. Huffman, *Tetrahedron Letters*, 935 (1967).
12. J. Meinwald and P. Mazzocchi, *J. Am. Chem. Soc.*, **89**, 1755 (1967).
13. H. E. Zimmerman, R. Binkley, R. Givens and M. Sherivin, *J. Am. Chem. Soc.*, **89**, 3932 (1967).
14. M. Jones and L. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967).
15. J. R. Edman, *J. Am. Chem. Soc.*, **88**, 3454 (1966).
16. E. Ciganek, *J. Am. Chem. Soc.*, **88**, 2882 (1966).