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PHOTOISOMERIZATION OF DICHLOROCARBENE ADDUCTS OF 2,4-CYCLOHEXADIENONES

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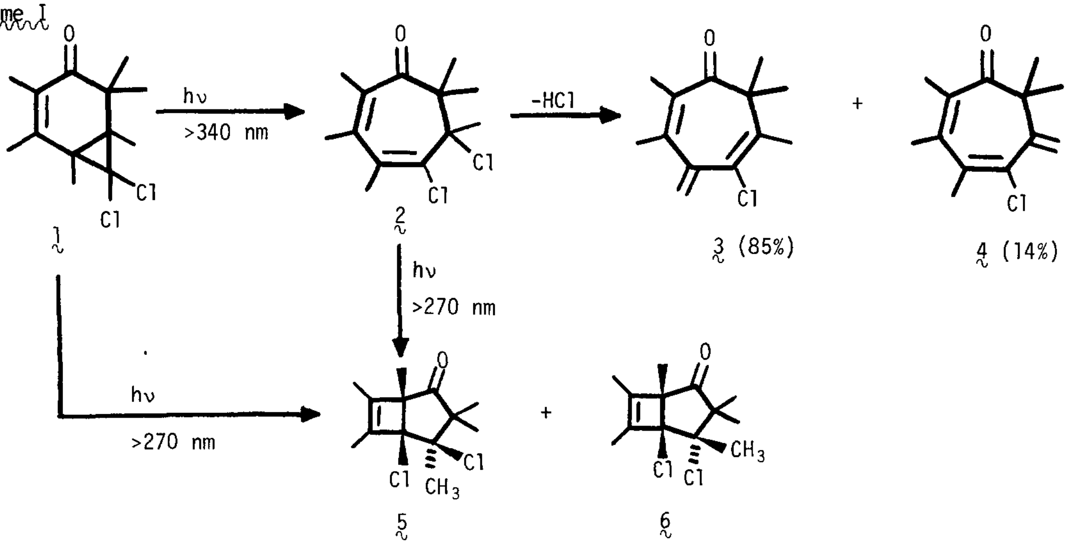
Summary: Irradiation of the nπ* band of the dichlorocyclopropyl enones 1 and 7 resulted in ring expansion and 1,2-chlorine migration to give 2 and 8 respectively, whereas the dihydrogen analog 11 gave the vinylcyclopropane-cyclopentene rearrangement product 12.

The photoisomerization of allyl halides to cyclopropyl halides has attracted attention because of the mechanistic questions it raises, particularly with regard to radical vis-à-vis ionic pathways.[1-3] We wish to describe here examples of the reverse process, photoisomerization of a cyclopropyl chloride to an allyl chloride. We compare our results with those reported earlier for a related cyclopropyl system lacking the halogen substituents.[4]

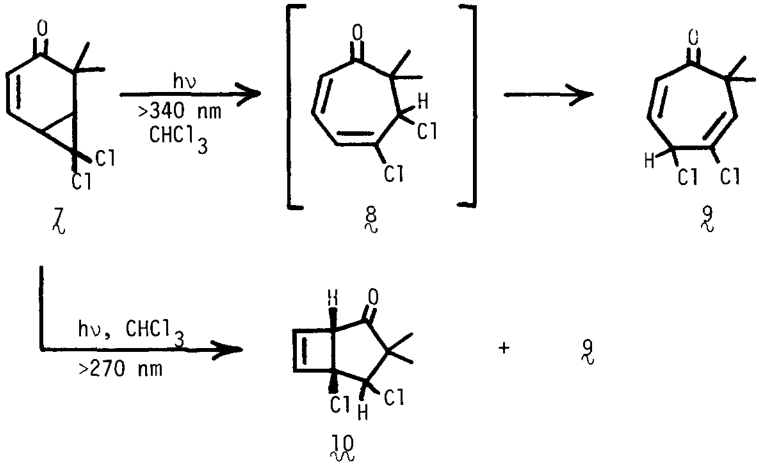
Addition of dichlorocarbene to hexamethyl-2,4-cyclohexadienone[5] under Makosza conditions[6] gave adduct 1 in good yield.[7,8] Adduct 1 was irradiated in chloroform through a uranium glass filter (λ>340 nm) to give, after vpc collection of the product, 85% of 3[8] and 14% of 4[9] (Scheme I). NMR examination of the crude photolysate showed no 3 or 4 (no vinyl protons), but

Scheme I



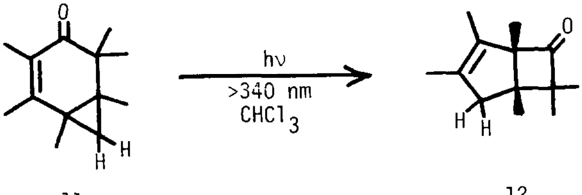
was consistent with structure **2**.[10] When the irradiation was carried out in hexane and followed by UV, the disappearance of the maximum at 255 nm due to **1** was accompanied by the formation of new maxima at 230 and 290 nm due to **2** (isosbestic points at 242 and 273 nm). Irradiation of **2** or **1** in hexane through Corex (λ>270 nm) gave nearly equal amounts of two new products, **5**[8] and **6**[8] each of which contained both chlorines.[11]

In a similar manner, irradiation of **7**,[8,12] at >340 nm gave a single product, the isomer **9**.[8] By carrying out the irradiation in hexane it was clear (by UV) that the actual photoproduct was **8**, and that **9** arose by allylic rearrangement during work-up. Irradiation of **7** through Corex gave, in addition to **9** (39%), the bicyclic ketone **10**[8] (only one isomer was isolated, 25%). Consequently the observed photoisomerization is general and does not require methyl substituents.



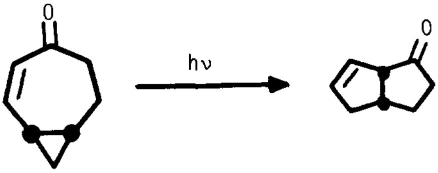
7 **8** **9** **10** **9**

In contrast, irradiation of **11**[8,13] gave mainly **12**,[8] as might have been expected by analogy



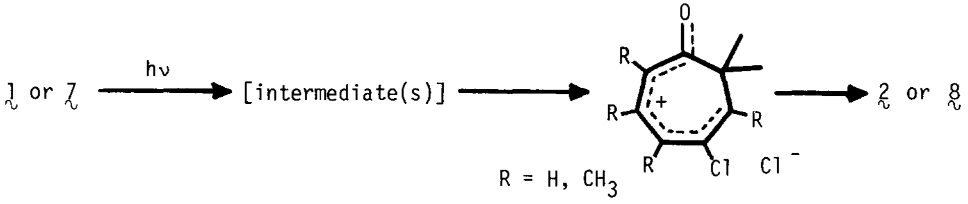
11 **12**

with Paquette's previous result for **13**.[4,14]



13 **14**

As to the mechanism for the photoisomerization of **1** and **7**, it seems that irradiation of the enone nπ* chromophore results in cleavage of the cyclopropane bond common to both rings. Halogen migration occurs specifically to the 'remote' carbon of the homodienone chromophore. The difference between **1** and **7** compared with **11** (and **13**) is a consequence of the presence of a leaving or migrating group on the cyclopropane ring. It is possible that ion-pairs are intermediates in this process.[15] The interesting question[1d] of possible stereospecificity of the halogen migration is under study.

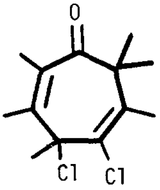


Acknowledgement. We are indebted to the National Institutes of Health, grant GM15997, for support of this research. We thank Mr. Edwin S. Perry for first preparing compound **1**.

References and Notes

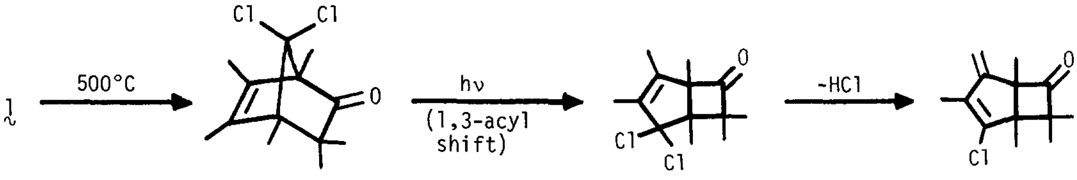
1. (a) S. J. Cristol and G. A. Lee, J. Am. Chem. Soc., **91**, 7554 (1969); (b) S. J. Cristol, G. A. Lee and A. L. Noreen, ibid., **95**, 7067 (1973); (c) S. J. Cristol and C. S. Ilenda, Tetrahedron Lett., 3681 (1976); (d) S. J. Cristol, L. Tenud and R. J. Daughenbaugh, ibid., 1099 (1977); (e) S. J. Cristol, R. J. Daughenbaugh and R. J. Opitz, J. Am. Chem. Soc., **99**, 6347 (1977); (f) S. J. Cristol and R. P. Micheli, ibid., **100**, 850 (1978).
2. Similar questions arise in many other photosolvolyses; for recent examples and leads to considerable earlier literature, see S. J. Cristol and R. M. Strom, J. Am. Chem. Soc., **102**, 5577 (1980) and D. C. Appleton, B. Brocklehurst, J. McKenna, J. M. McKenna, M. J. Smith, P. S. Taylor, S. Thackeray and A. R. Walley, Chem. Commun., 108 (1977).
3. Some allyl chlorides are reported not to photoisomerize to cyclopropyl derivatives; see S. J. Cristol and R. P. Micheli, J. Org. Chem., **40**, 667 (1975).
4. L. A. Paquette, G. V. Meehan, R. P. Henzel and R. F. Eizember, J. Org. Chem., **38**, 3250 (1973).
5. H. Hart, R. M. Lange and P. M. Collins, Org. Syn. Coll. Vol. 5, 598 (1973).
6. M. Makosza and M. Wawrzyniewicz, Tetrahedron Lett., 4659 (1969).
7. That the carbene had added to the C4-C5 double bond of the dienone was clear from the spectra of **1**; $\nu_{C=O}$ 1660 cm^{-1}, λ_{max} (hexane) 255 nm.
8. The compound had a satisfactory elemental analysis and/or high resolution mass spectrum and other spectral properties.

9. The product had satisfactory spectral properties.
10. Gem dimethyl at δ 1.26 and 1.27, homoallylically coupled quartets at δ 1.84 and 1.90, and methyl singlets at δ 1.88 and 1.95.
11. This result and the UV spectrum eliminates i as a possible structure for the first photoproduct.



i

12. Prepared[6] in 38% yield from 6,6-dimethyl-2,4-cyclohexadienone.
13. Prepared by reduction of the corresponding dibromocarbene adduct with tri-n-butyltin hydride.
14. The analogous product iii was not formed on irradiation of **1** although it could easily have been detected, since it was synthesized independently. Pyrolysis of **1** (500°C, 0.06 Torr) gave ii, which, on irradiation through Corex gave iii, isolated (vpc) as its dehydrohalogenation product iv.



ii iii iv

Comparison of these pyrolysis results with those observed for **1** [L. A. Paquette, R. P. Henzel and R. F. Eizember, J. Org. Chem., **38**, 3257 (1973)] is deferred to a full paper.

15. Similar allylic cations conjugated with a carbonyl group appear to be preferred intermediates in the acid catalyzed rearrangements of epoxyenones; for examples, see H. Hart, I. Huang and P. Lavrik, J. Org. Chem., **39**, 999 (1974); H. Hart and E. M. Shih, ibid., **40**, 1128 (1975); H. Hart, S.-M. Chen and S. Lee, ibid., **45**, 2906 (1980).

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