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ON THE PHOTOISOMERIZATION OF BICYCLO[3.2.1]OCTADIENONES

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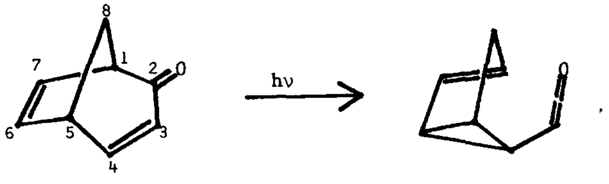
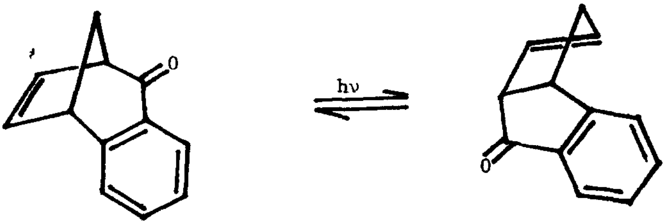
Bicyclo[3.2.1]octadienones with the general structure 1 photoisomerize to ketenes 2 and give products derived therefrom.[1-3] The corresponding 3,4-benzoöctadienones 3 undergo reversible



1 2

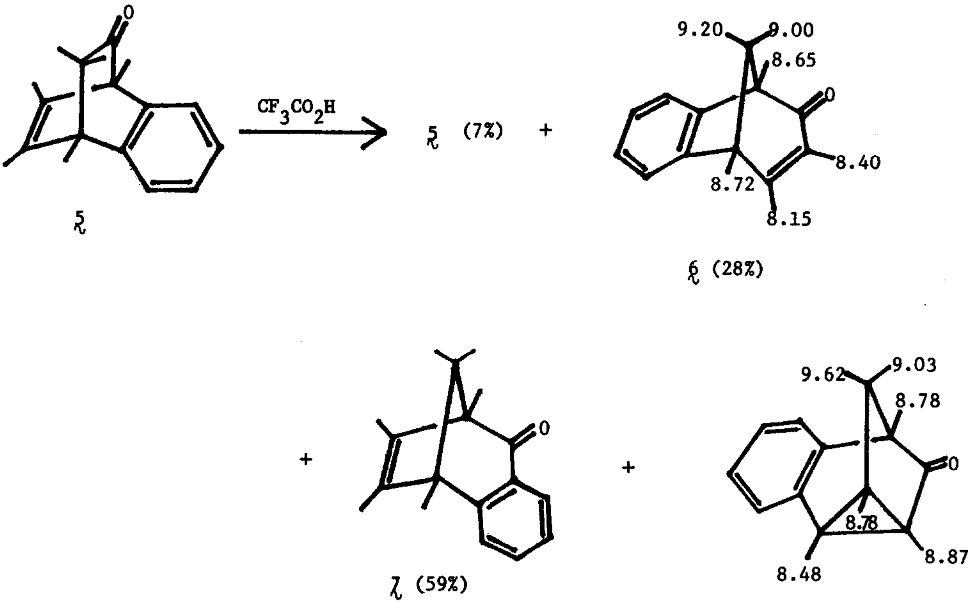
1,3-acyl shifts ($3 \rightleftharpoons 4$).[4] We now wish to report that the other possible (i.e., 6,7-) benzo



3 4

derivatives of 1 undergo a facile photoisomerization which is both synthetically useful and mechanistically interesting.

Acid-catalyzed rearrangement of the hexamethyl[2.2.2]dienone 5[5] gives a mixture of ketones 5 - 8.[4,6] A degassed solution of 6 (200 mg) in 5 ml of spectroscopic grade acetone, when irradiated (Pyrex, 450 watt Hanovia lamp, 50 min) gave a 100% yield of 8.[7] Similar



5

5 (7%) +

6 (28%)

+

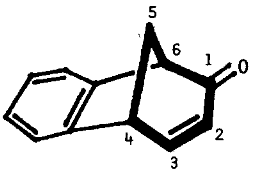
7 (59%)

+

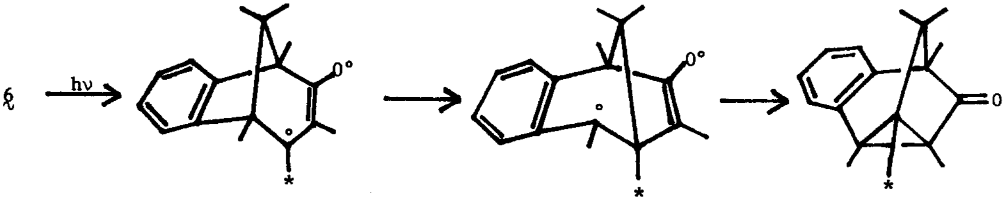
8 (6%)

results were obtained in ether, hexane, or carbon tetrachloride.

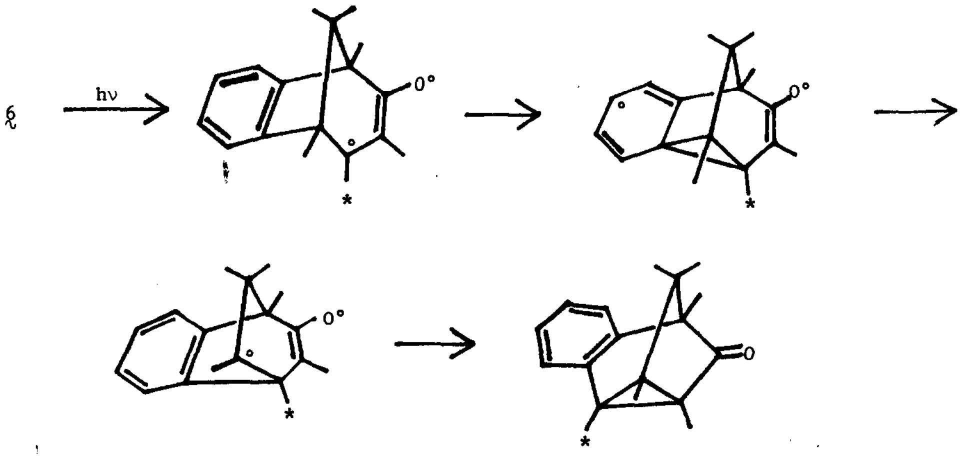
Ketones of the type 6 can be regarded as 4-arylcyclohexenones, compounds whose photochemistry has been extensively studied.[8,9] Rearrangement of 6 to 8 may occur by either a Type A or an Aryl Migration mechanism;[9] in this unusual example, the product would be structurally identical by either path:



Type A Mechanism[10]



Aryl Migration Mechanism



To decide between these alternatives, ketone 6 was treated (overnight reflux) with 3M NaOCH$_3$ in CH$_3$OD to convert the allylic methyl group responsible for the nmr peak at τ 8.15 to a CD$_3$ group. Irradiation of labeled 6 (the label is designated by an asterisk in the mechanistic schemes) gave 8 whose nmr spectrum lacked only the singlet at τ 8.48. Accordingly, the photo-isomerization must occur exclusively by the aryl migration mechanism. It seems quite possible that, because of the rigid geometry of the system, excitation may involve the aryl as well as the enone system. It is also perhaps noteworthy that the geometry of the system constrains the migrating aryl group to an endo relationship with the cyclopentanone ring in the product. In cases where both geometries are possible, the endo product is strongly favored.[9]

The reaction appears to be exceptionally efficient. For synthetic purposes, one can irradiate the mixture of 5-8 obtained from the acid-catalyzed isomerization of 5. Although ketones 5 and 7 can both photoisomerize,[4,11] they are essentially unaffected in the short time necessary to convert all the 6 to 8 (making 8 available from 5 in about 35% yield).

We plan to undertake a quantitative study of the reaction, and to study some chemistry of the interesting tricyclic ring system which it generates.

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4. H. Hart and G. M. Love, *Tetrahedron Lett.*, 2267 (1971).
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6. The numbers in formulas **6** and **8** refer to the chemical shifts of the methyl singlets, in τ units (CCl_4 solution). Europium shift reagents were used to assist in the assignments.
7. Identity with the product from the acid-catalyzed rearrangement of **5** was established by comparison of vpc retention times, ir and nmr.
8. For a review of earlier work, see P. J. Kropp, *Organic Photochemistry* (Ed. by O. Chapman), **1**, 1 (1967), especially pp. 72-74.
9. H. E. Zimmerman and W. R. Elser, *J. Amer. Chem. Soc.*, **91**, 887 (1969); H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969); H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968); H. E. Zimmerman, R. D. Rieke and J. R. Scheffer, *ibid.*, **89**, 2033 (1967).
10. We use open dots in both these mechanisms for convenience only and without any attached mechanistic significance; a more precise definition of the nature of the reactive intermediates must await the conclusion of a quantitative study of the reaction.
11. R. K. Murray, Jr. and H. Hart, *Tetrahedron Lett.*, 4995 (1968); H. Hart and R. K. Murray, Jr., *ibid.*, 379 (1969).