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THE PHOTOSENSITIZED ISOMERIZATION OF BRIDGE SUBSTITUTED BICYCLO[n.1.0]ALK-2-ENES[1]

David L. Garin and K. O. Henderson[2]
Department of Chemistry, University of Missouri-St. Louis, St. Louis, Missouri, U.S.A.

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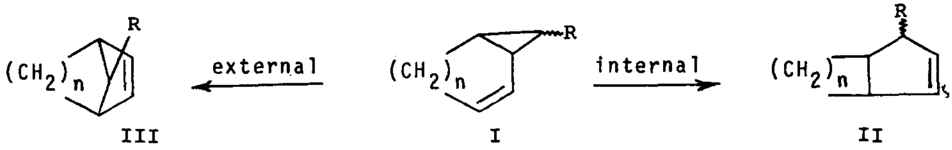
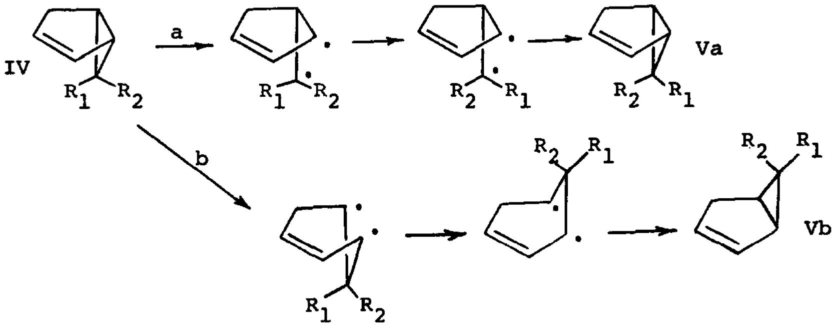
Photochemically excited cyclic vinylcyclopropanes (I, bicyclo[n.1.0]alk-2-enes) can be expected to undergo rearrangements leading to products resulting from involvement of the internal and/or external bond of the cyclopropane ring, II and/or III, respectively (3,4).

It is obvious that external cyclopropane bond cleavage can lead to epimerization of the bridge carbon atom (path a) and internal rearrangement to the "epimerization" of the cyclopropane ring (path b). We have observed that the photosensitized irradiation of bridge substituted cyclic vinylcyclopropanes does lead to epimeric products. The reaction appears to be general and will have to be considered a competitive reaction for photochemically induced rearrangements of I.





The photosensitized irradiation of the endo isomers of I (n=1, R=CO_2Me, CO_2H, CH_2OH and n=2, R=CO_2Et) produce the corresponding exo isomers as the major products in yields of 29-76%. The exo isomers rearrange to the endo isomers to a much lesser extent where R=CH_2OH and not at all when R is an ester function.

Irradiations of ca. 0.50% solutions (20 ml of hexane-benzene, 4:1) at ambient temperature were conducted in a Rayonet reactor using 2537Å light. All irradiations were continued until at least 50% of the starting material (endo isomers) had been consumed as determined by integration of vapor phase chromatograms. Prolonged irradiation leads to a decrease in volatile products. Typical results are described in Table 1.

Table 1.

Irradiation of I(5).

n	R	Product distribution after 2.5 hr % epimerized product	% starting material
1	endo-CO_2H(VI)	29	33
1	endo-CO_2Me(VII)	61	13
1	exo-CO_2Me(VIII)	0	75
1	endo-CH_2OH(IX)	46	30
1	exo-CH_2OH(X)	10	59
2	endo-CO_2Et(XI)	76	20
2	exo-CO_2Et(XII)	0	92

Solutions of higher concentration (ca. 1%) were used for preparative runs necessitating longer periods of irradiation. Samples of products were separated and collected by preparative vpc on a Wilkens A-700 (autoprep) instrument utilizing silicone gum rubber (SE-30) and fluoro-silicone (QF-1) as stationary-phase materials. Preparative size product mixtures of the carboxylic acids (I, n=1, R=CO_2H) were treated with ethereal diazomethane and analyzed as the corresponding methyl esters.

Compounds VI, IX, XI, and XII were prepared by reported procedures (6,7,8). The endo methyl ester VII, prepared from the corresponding acid by treatment with diazomethane, had b.p. 56-58°/2.0 mm, nmr ($CDCl_3$):δ5.6 (s, 2H), 3.55 (s,3H), and no absorptions above 1.5 ppm, consistent with that reported for the ethyl ester (9). The ester can be hydrolyzed back to the acid (VI) in aqueous sodium hydroxide without epimerization as reported (9). The exo methyl ester VIII had an nmr ($CDCl_3$) spectrum consistent with that reported for the ethyl ester (9): δ5.6 (m, 1H), 6.0 (m, 1H), 3.55 (s, 3H), and 1.0 ppm (t, J=3 Hz, 1H). Hydrolysis of VIII with aqueous sodium hydroxide followed by acidification with 5N HCl gave bicyclo(3.1.0)hex-2-ene-6-exo-carboxylic acid m.p. 78-79° (hexane), lit. m.p. 79-79.5° (9). The exo hydroxymethyl compound X, identical to the alcohol obtained by the lithium aluminum hydride reduction of VIII, had nmr ($CDCl_3$): δ6.1 (m, 1H), 5.5 (m, 1H), 3.5 (d, J=7 Hz, 2H), and 0.55 ppm (m, 1H).

The lack of previous reports in the literature on the photochemical isomerization of cyclic vinylcyclopropanes to produce epimeric compounds (e.g.,IV → V) is undoubtedly due to the fact that many of the compounds investigated by other workers do not contain different substituents at the bridge position or some resolvable tag in the molecule. Thus, "epimerization" would lead to a product identical to starting material, a no-reaction reaction (e.g., IV → V where $R_1=R_2$).

The pathway(s) of the epimerization of I may be resolved by irradiation of optically active IV since the products of path a and path b (Va and Vb, respectively) are then not identical but enantiomeric. We are continuing our investigations in this area.

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