External *vs.* Internal Cyclopropyl Bond Cleavage in the Photosensitized Epimerization of Bicyclo[3,1,0]hex-2-enes

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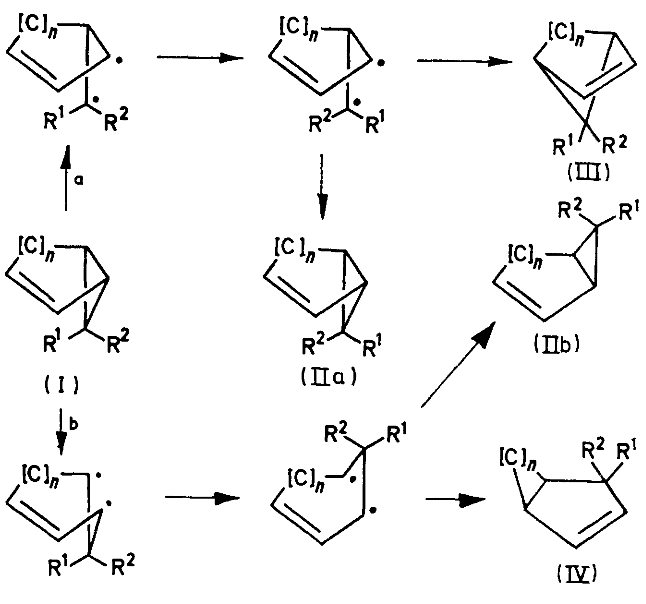
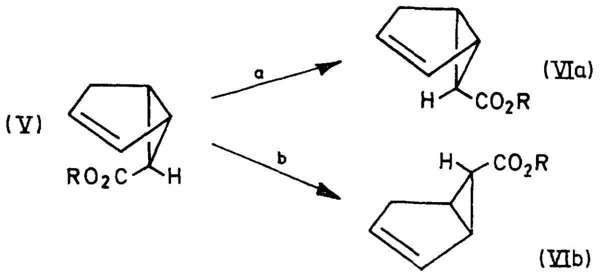
Summary The photosensitized epimerizations of bicyclo-[3,1,0]hex-2-ene-6-*endo*-carboxylic acid and its methyl ester occur exclusively by cleavage of the external cyclopropyl bond.



We recently reported our results on the photosensitized epimerization of several bridge-substituted bicyclo[*n*,1,0]-alk-2-enes (I) which can occur *via* the cleavage of the external or internal bond of the cyclopropane ring (paths a and b, respectively).[1] Internal cyclopropyl bond cleavage can result in the formation of bicyclo[*n*,1,0]alkenes(IV).[3,2] External cyclopropyl bond cleavage could be expected to result in the formation of bicyclo[*n*,2,1]alkenes (III). Frustated by our inability to obtain (III), we decided to determine the path of the epimerization reaction. If the epimerization was proceeding *via* cleavage of the external cyclopropyl bond, added functionality or substitution on (I) might promote rearrangement to (III). Predictions of the preferred mode of cleavage on the basis of orbital overlap in the ground state or degree of substitution has been discussed in detail elsewhere and can be erroneous in these systems.[2,3] The epimerization paths can be distinguished by the irradiation of optically active (I) since the products of path a and path b [(IIa) and (IIb) respectively] are enantiomeric.



Optically active bicyclo[3,1,0]hex-2-ene-6-*endo*-carboxylic acid (V; R = H) was obtained by partial resolution with (−)-ephedrine in chloroform–ether.[4] Treatment with ethereal diazomethane produces the corresponding optically active methyl ester (V; R = Me). Both the acid and the ester were subjected to photosensitized irradiation.[1] The methyl ester product mixture was separated; samples were collected *via* preparative g.l.c., and rotations were measured. Acid product mixtures were first treated with diazomethane to convert them into the corresponding methyl esters and then separated in the same fashion, and rotations were measured. These data are summarized in the Table. In order to determine the relative amounts of (VIa) and (VIb) formed in the photochemical reactions of (V), it was necessary to determine the rotation of pure (VIa) corresponding to (V). A sample of the optically active methyl ester (V; R = Me) was subjected to base-catalysed epimerization (LiOBu^t–Me_2SO) to produce (VIa; R = Me). The results are also shown in the Table. In summary, the products of the photochemical epimerizations (VI; R = Me) have the same optical rotation as that of the base-catalysed epimer-

Table

Reaction	Sample	Starting material	$[\alpha]^{25}_{D}$	Product	$[\alpha]^{25}_{D}$	Recovered starting material	$[\alpha]^{25}_{D}$
Irradiation of (V; R = Me) ..	1	(V; R = Me)	+191°	(VI; R = Me)	+137°	(V; R = Me)	+190°
	2	(V; R = Me)	+191	(VI; R = Me)	+136	(V; R = Me)	+192
Irradiation of (V; R = H) ..	1	(V; R = H)	+217*	(VI; R = Me)	+137	(V; R = Me)	+191
	2	(V; R = H)	+217	(VI; R = Me)	+137	(V; R = Me)	+192
	3	(V; R = H)	+217	(VI; R = Me)	+138	(V; R = Me)	+191
Base catalysed	1	(V; R = Me)	+191	(VIa; R = Me)	+137	(V; R = Me)	+192
Epimerization of (V; R = Me)	2	(V; R = Me)	+191	(VIa; R = Me)	+138	(V; R = Me)	+192

All rotations were taken on an O. C. Rudolph Model 80 Polarimeter using concentrations from 0·43 to 1·68% in 95% EtOH.

* Optical activity = 51% based on a determination of the activity of the pure enantiomorph (+425); the corresponding methyl ester (prior to reaction) had $[\alpha]^{25}_{D} = +191$.

ization. Further, recovered starting materials (isolated as the methyl esters) showed no change in optical activity. Thus, the photochemical epimerization of bicyclo[3,1,0]hex-2-ene-6-*endo*-carboxylic acid and its methyl ester occur by cleavage of the external cyclopropane bond exclusively (path a).

Several examples of photosensitized epimerizations in systems similar to (I) have recently been reported.[5-7] These examples may not be analogous to those we have reported owing to the specific nature of their functionality; however, the transformations leading to epimerization of the bridge substituents can be formally depicted as proceeding *via* cleavage of the external cyclopropane bond. Nonetheless, products analogous to (III) have not been obtained.

The diradical intermediate proposed in path a appears to prefer to bond 1,3 [giving (IIa)] rather than 1,5 [giving (III)]. This same preference is observed in the triplet carbene addition to conjugated olefins which gives similar diradical intermediates and leads to the predominant formation of cyclopropanes [*e.g.* (IIa)]; there are only two documented cases of 1,4 carbene addition to give (III), both involving extensively conjugated systems and highly stabilized diradical intermediates.[8]

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