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A NOVEL INTRAMOLECULAR ADDITION OF PHOTOCHEMICALLY OR THERMALLY GENERATED KETENE TO A [4π + 2σ] ELECTRONIC SYSTEM

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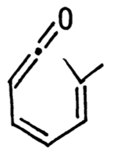
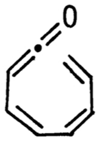
The photochemical or thermal reaction of exo-6-methoxy-1,5,6-trimethyl- or exo-6-methoxy-1,3,5,6-tetramethyltricyclo[3.2.1.0^{2,7}]-oct-3-en-8-one resulted in the novel formation of rapidly equilibrating valence isomers of norcaradiene-cycloheptatriene derivative via a ketene intermediate.

It is well established that several 2,4-cyclohexadienones photoisomerize to the ketenes of general structure A, which undergo intramolecular cycloaddition to afford the starting dienones or bicyclo[3.1.0]hex-2-en-4-ones.1) The photochemistry of 2,4,6-cyclooctatrienone also involves a ring opening to the ketene B which has been directly observed by low-temperature infrared spectroscopy and recyclized to the starting trienone upon warming.2) All of these ketenes involve π-bonds to intervene in the electrocyclization, whereas little notice has been focused on the reactions of ketene with electronic systems which involves both π-bonds and constrained or polar σ-bond except cyclopropane ring.3) Previously we have investigated the photoreaction of 1,5-dimethyl-6-oxacyclopropylidenetricyclo[3.2.1.0^{2,7}]-oct-3-en-8-one (1). The compound 1 photoisomerized to the ketene 2 which was detected by low-temperature infrared spectroscopy. The ketene 2 collapsed to the lactone 3 by an intramolecular ene-type reaction involving the epoxide ring.4)

Further interest in the chemical behaviors of ketenes to the intramolecular electronic system containing both π-bonds and constrained or polar σ-bond prompted us to investigate the photochemical or thermal reaction of exo-6-methoxy-1,5,6-trimethyl- and exo-6-methoxy-1,3,5,6-tetramethyltricyclo[3.2.1.0^{2,7}]oct-3-en-8-ones (4a and 4b).5) We would like to present here an example of the ketene which undergoes a facile intramolecular addition to a [4π + 2σ] electronic system to result in the formation of rapidly equilibrating valence isomers of norcaradiene-cycloheptatriene derivative.


A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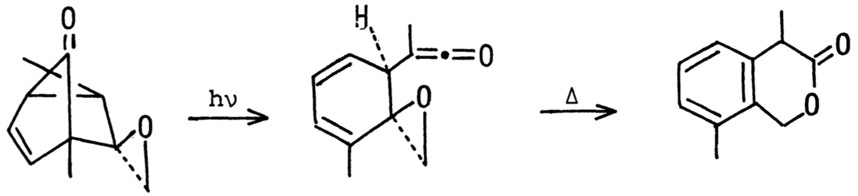
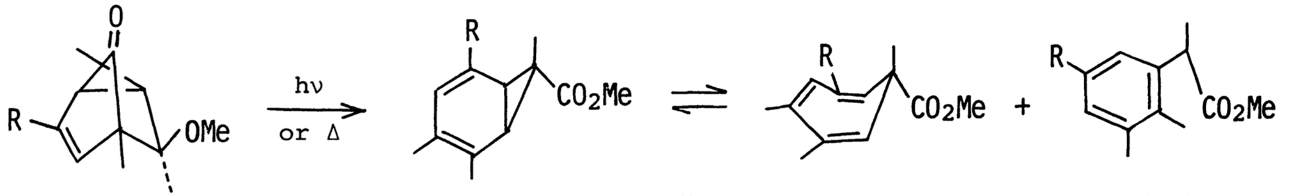


1 2 3

Irradiation of 4a in anhydrous acetonitrile (0.5 mol dm^{-3}) using 300 nm lamps[6) for 10 h and the following preparative TLC afforded 5a and 6a in 31 and 8% yields,[7) respectively, with the recovery of 4a in a 38% yield. Similarly 4b gave 5b and 6b in 36 and 6% yields, respectively, along with 17% of the starting ketone 4b. The structures of the photoproducts 5a and 5b were confirmed as equilibrating valence isomers of norcaradiene-cycloheptatriene derivative on the basis of the spectral data which have been reported by Schmid and his coworkers.8) The prolonged irradiation



4a,b a: R=H b: R=Me 5a,b 6a,b

of 4a and 4b in acetonitrile for 50 h resulted in the formation of 6a or 6b in 40% or 55% yield along with unidentified material. This result seems to suggest that 5a,b are the primary photoproducts and 6a,b might be the secondary products originated from 5a,b.

To confirm this point, the photoreaction of 4a,b was carried out in CD_3OD and monitored by NMR spectroscopy. As shown in Fig. 1, the initial decrease of 4a accompanied the increase of 5a. Upon prolonged irradiation, 6a increased gradually, and 5a decreased gradually. Much the same was observed in the case of the photoreaction of 4b. Therefore it is suggested that 6a,b should be the secondary products originated from 5a,b. This type of reaction has been reported in the phtochemistry of norcaradiene derivatives.9) Furthermore CD_3O group was not incorporated instead of CH_3O group of 5a,b or 6a,b.

The compounds 4a,b have a skeleton of 1 or photolabile 3-methylcar-4-en-2-one which has been shown to photoisomerize to a ketene derivative.10) Therefore a ketene should be the reasonable intermediate. Support for the intermediacy of the ketene 7 was obtained by conducting the irradiation of the film of 4a at 77 K. After irradiation of 4a for 20 min with a high pressure mercury lamp through CaF_2 cell window for infrared spectroscopy, the infrared spectrum was recorded to exhibit a ketene band at 2105 cm^{-1}. On warming to room temperature, the 2105 cm^{-1} band disappeared completely to show a new band at 1718 cm^{-1} corresponding to 5a. The carbonyl absorption corresponding to 6a was not observed. These facts clearly indicate that the ketene 7 was formed by photochemical process, which then thermally rearranged to 5a. Exactly the same discussion would be possible for the

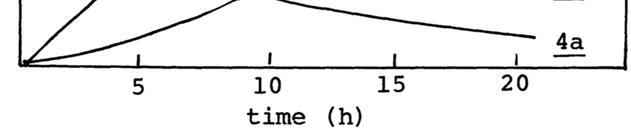
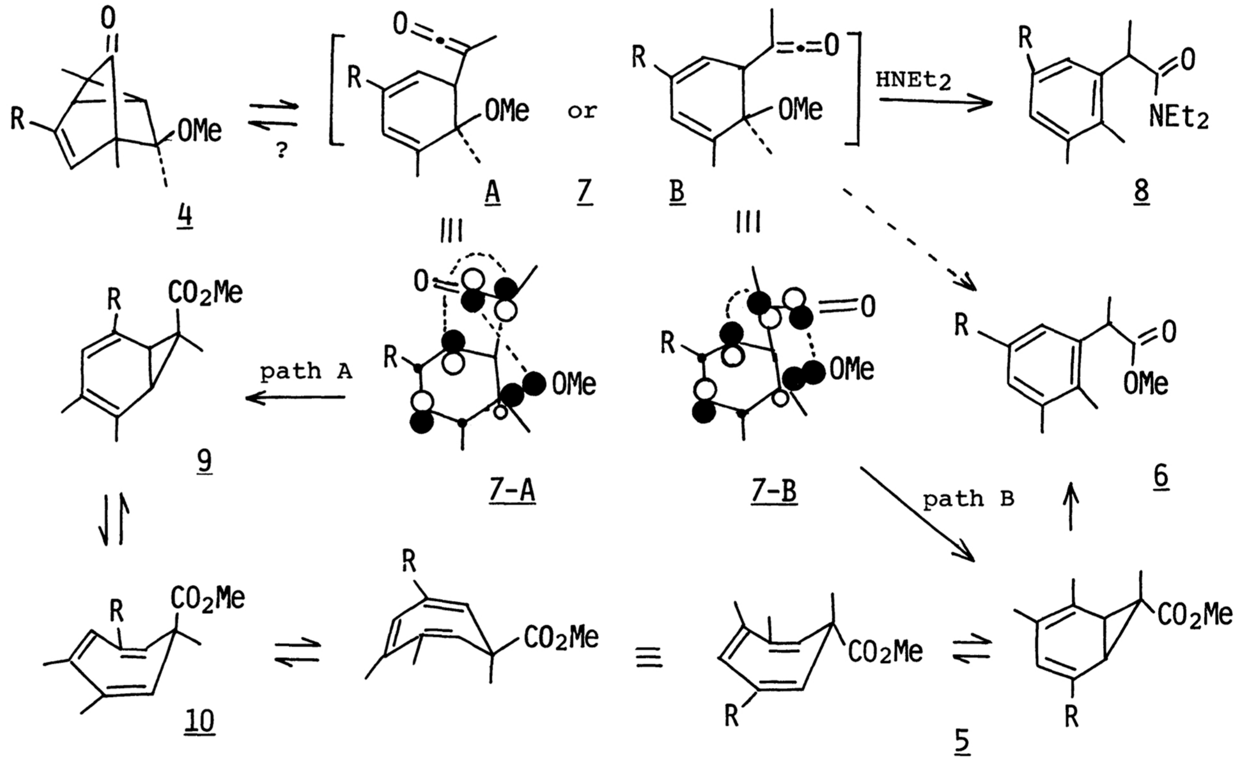


Fig. 1. The composition of 4a, 5a and 6a on the photoirradiation of 4a in CD_3OD at various times.

Scheme 1



photoreaction of 4b.

Furthermore, in photoirradiation of 4a in acetonitrile-diethylamine (9/1), the ketene 7 was trapped to afford an amide 8, of which structure was identical with the authentic sample.[12] The compound 8 should be derived from the nucleophilic addition of diethylamine to 7 and the subsequent base ($HNEt_2$) induced elimination of methanol.

Similar to the photochemical reactions of 4a,b, the heating of 4a in refluxing 1,2-dichlorobenzene for 20 h afforded 5a and 6a in 48 and 9% yields, respectively. Prolonged heating (50 h) of 4a under similar conditions resulted in the disappearance of 4a or 5a, and in formation of 6a[11] in 47% yield along with unidentified material after purification by TLC. The thermal reaction of 4b also afforded the similar results to those of 4a. These thermal reaction should also involve the initial Cope rearrangement of 4a,b to the ketene 7.

The mechanism of the photochemically or thermally generated ketene 7 to afford 5 is of considerable interest. Few examples are known for the reaction of ketene with C-OR bond. Triethyl orthoformate is known to react with a ketene to give the adduct.[13] In the present photolysis of 4a,b in CD_3OD, no solvent addition product to the ketene and no incorporation of CD_3O group instead of CH_3O group of 5a,b or 6a,b were observed. Therefore the conversion of 7 to 5 seems to be an intramolecular process. An attractive reorganization pathway should be path A or path B via the conformer 7-A or 7-B, respectively, as depicted in Scheme 1. The formulae 7-A and 7-B represent an interaction of the LUMO of a ketene moiety and the HOMO of a hexadienyl system involving [4π + 2σ] electrons. The conformation of 7-A seems to be favorable for a Diels-Alder reaction to recyclize to the starting ketone 4. No evidence for this process is obtained at the present stage. The path A can afford 9 in which CO$_2$Me group is located in the endo position. A facile ring opening of 9 to cycloheptatriene 10, and the subsequent ring inversion[14] of 10 to the more stable form can give equilibrating valence isomers 5. The path B can afford 5 directly. It is not determined here whether path A or path B is operative in the conversion of 7 to 5. The formation of 6 is explained by thermal[11] and photochemical[9] cleavage of cyclopropane ring of the norcaradiene form in 5. The detail concerning selective cleavage of the 6-7 bond as compared to the 1-7 bond is obscure. Another possible pathway affording 6 is an ene-type reaction as in the case of ketene 2. However this pathway seems to be less favorable based on the low-temperature photolysis or the experimental result presented in Fig. 1.

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