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BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 1147—1148 (1976)

Vapor-Phase Photolysis of *cis*-Cyclononene

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(Received September 12, 1975)

Synopsis. Direct and sensitized photolyses of *cis*-cyclononene (**1c**) vapor were investigated. The direct irradiation of **1c** gave 1,8-nonadiene(**2**) and vinylcycloheptane *via* the thermally-activated ground state produced by rapid internal conversion from the excited singlet state initially generated. On the other hand, the sensitized photolysis of **1c** gave **2** and five bicyclononanes, which are interpreted in terms of intramolecular hydrogen transfer reactions.

We have investigated the direct and sensitized photolyses of alkenes.[1] On direct irradiation in the vapor phase, the excited singlet alkene generated was reported to suffer rapid internal conversion to thermally-activated ground state molecule.[1e,2] On the other hand, the vibrationally-excited triplet alkene produced in vapor-phase photosensitization has been demonstrated to undergo intramolecular hydrogen transfer reactions[1a,d,f] along with the well-known *cis-trans* isomerization and allylic bond cleavage.[3] As for the photochemistry of cycloalkenes, little is known of the photochemical behavior of medium-ring alkenes, although considerable study has been made of the sensitized photolysis of common-ring alkenes.[4] We wish now to report the results of the direct and sensitized photolyses of cyclononene vapor.

Experimental

All the experiments were carried out at room temperature and under static conditions. The apparatus and basic procedures employed were the same as described previously.[1d,e] The light source of the direct photolysis at 1849 Å was a 30 W low-pressure mercury lamp fitted with a Suprasil envelope. In the sensitized photolyses, radiation from the lamp was filtered by a Toshiba UV-25 filter. The products were analyzed by GLC on a 6 m column of 15% polyethylene glycol-6000 and a 3 m column of 15% tritolyl phosphate. All the products had retention times on GLC identical to those of the authentic specimens or, in the case of *cis*- and *trans*-bicyclo[5.2.0]nonanes, to those reported in the literature.[5] Attempts for the separation on GLC of *trans*-cyclononene from the *cis*-form were unsuccessful.

Preparation of cis-*Cyclononene (1c).* Cyclononanone, prepared from dimethyl azerate according to procedures similar to those described in "Organic Syntheses,"[6,7] was reduced with $LiAlH_4$ to cyclononanol. The alcohol was heated with phosphoric acid to yield *cis*-cyclononene(**1c**), which was purified to 99.5% by preparative GLC.

Preparative Photolysis. The mercury photosensitization of *cis*-cyclononene(**1c**) with 10% nitric oxide was carried out at the pressure of 1.5 Torr for 12 h using the 30 W mercury lamp and a preparative irradiation apparatus which was made up of a 5 l Pyrex vessel, two quartz cells for irradiation, and a thermosiphone for circulation of the gas. Isolation of the products, **2**, **5c** and **6c**, was performed by preparative GLC. The NMR and mass spectra of the products separated above made the identification certain.

Independent Syntheses of the Authentic Specimens. *1,8-Nonadiene(2)* was synthesized by pyrolysis of nonamethylene glycol diacetate at 500 °C according to the method of Marvel and Stile.[8]

Vinylcycloheptane(3) was synthesized by pyrolysis of **1c** at 800 °C.[9]

cis-*Bicyclo[4.3.0]nonane(4c)* was prepared by hydrogenation of indene on Raney nickel W-2 at 180°C for 3 h at the hydrogen pressure of 200 atm in an autoclave.

trans-*Bicyclo[4.3.0]nonane(4t)* was prepared by acetone-sensitized photoepimerization of **4c**.[10]

cis-*Bicyclo[6.1.0]nonane(6c)* was synthesized by a Simmons-Smith reaction of cyclooctene with diiodomethane in the presence of zinc-copper(II) chloride mixture, according to the procedure described by Rawson and Harrison.[11]

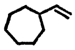
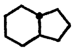
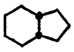
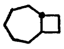
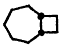
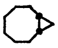
Results and Discussion

The products resulting from the direct and sensitized photolyses of *cis*-cyclononene(**1c**) vapor are shown in Table 1.

On direct photolysis of **1c** at 1849 Å, 1,8-nonadiene (**2**) and vinylcycloheptane(**3**) were obtained as the major products. The formation of **2** and **3** was also observed in the pyrolysis of **1c** at 520—720 °C.[9] The electronically-excited singlet state of simple alkenes has been shown in other systems to undergo rapid internal conversion.[1e,2] Thus, it may be inferred that the electronically-excited singlet of **1c** generated by the direct irradiation suffers rapid internal conversion to a thermally-activated ground state, which gives the products similar to those from the pyrolysis of **1c**. The absence of the bicyclic products, **4**, **5**, and **6**, indicates the low efficiency of the S→T intersystem crossing process, since the photoisomerization to the bicyclic products is characteristic of the triplet species, as shown below in the photosensitization of **1c**.

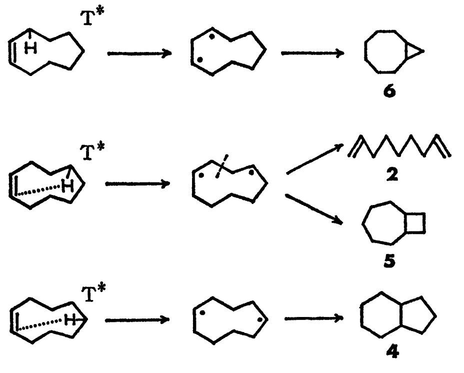
In sensitized photolysis, mercury and benzene vapor were used as the sensitizers. The products of the photosensitization of **1c** were 1,8-nonadiene(**2**), *cis*- and *trans*-bicyclo[4.3.0]nonanes (**4c** and **4t**), *cis*- and *trans*-bicyclo[5.2.0]nonanes(**5c** and **5t**), and *cis*-bicyclo[6.1.0]nonane(**6c**), as shown in Table 1. The marked difference in the product distribution between the mercury and benzene sensitizations is attributable to the different triplet energies of the sensitizers; the triplet energies of mercury and benzene are 113 and 84 kcal/mol, respectively. Since the benzene sensitization of **1c** in the liquid phase did not afford any of these products, it is considered that the intermediate

Table 1. Photolyses of *cis*-cyclononene(**1c**)

Photolysis mode	Pressure, Torr	Exposure time, min	Product, μmol						
						 			H_2
			2	**3**	**4t**	**4c**+**5t**	**5c**	**6c**	
Direct[a]	1.0	3.0	0.29	0.13	c)	c)	c)	c)	d)
Mercury-sensitization	1.0	2.0	0.07	c)	0.11	0.12	0.54	1.18	0.04
Benzene-sensitization[b]	1.0	30	0.05	c)	0.23	0.08	0.02	0.02	c)

a) A small amount (0.04μmol) of unidentified C_9H_{16} product was also obtained. b) One Torr of benzene vapor was added as the sensitizer. c) Not detected (<0.01μmol). d) Not determined.

involved in the vapor-phase photosensitization is a vibrationally-excited triplet of **1c** and that the vibrational activation in the triplet state enhances the photorearrangement. Similarly to the mechanism shown in the norcarane formation in the mercury photosensitization of cycloheptene,[1b)] the formation of **6c** is interpreted in terms of a 1,2-shift of allylic hydrogen followed by ring closure of the resulting 1,3-biradical (Scheme). The intramolecular hydrogen abstractions by the excited C=C double bond *via* two possible six-membered transition states give cyclic 1,4- and 1,6-biradicals, and the subsequent β-cleavage or recombination of the resulting biradicals leads to the products **2**, **5**, and **4**.



Scheme.

It is thus confirmed in this system that the 1,2-shift of allylic hydrogen and the intramolecular hydrogen abstractions *via* six-membered transition states are the main course of the photo-sensitization of simple alkenes in the vapor phase.

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