Photochemical Rearrangement of Cycloheptene

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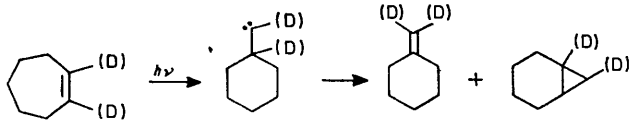
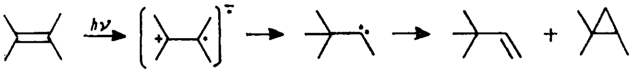
Summary Direct photolysis of cycloheptene gives methylenecyclohexane and bicyclo[4.1.0]heptane by a novel photorearrangement *via* a carbene intermediate, and hepta-1,6-diene and vinylcyclopentane *via* a vibrationally excited ground state.

Work on the sensitised photolysis of cycloalkenes in the vapour phase has been reported previously,[1,2] but little is known of the direct photolysis. We now report the photochemical rearrangement of cycloheptene (**1**) by direct irradiation in the vapour and liquid phases.



(1) (6) (4) (5)

The products and yields from the direct photolysis of (**1**) are shown in Table 1 and 2. Hepta-1,6-diene (**2**) and vinylcyclopentane (**3**) were obtained only from the vapour-phase irradiation and their yields decreased with increasing pressure of the substrate. Methylenecyclohexane (**4**) and bicyclo[4.1.0]heptane (**5**) were obtained in both vapour and liquid-phase photolysis and their yields were independent of the pressure in the vapour-phase irradiation. Based on these results and the observation of Crandall and Watkins[3] that pyrolysis of (**1**) affords (**2**) and (**3**) as the main products, the formation of (**2**) and (**3**) in the vapour-phase photolysis is concluded to be the result of the thermal cracking of vibrationally excited ground-state cycloheptene, which is generated by a rapid internal conversion from the electronically excited state initially formed.



Scheme

Although the electronically excited state involved is not certain because of the superposition near 1849 Å of the R ← N band over the continuum of the V ← N band in the absorption spectrum of cycloalkenes,[4] the formation of (**4**) and (**5**) can be interpreted in terms of competing rearrange-

Table 1

Vapour-phase photolysis of (**1**)[a]

Compound	Pressure /torr	Exposure time/min[b]	Conversion /%	Product/µmol (2)	(3)	(4)	(5)
(1)	3	3	1·6	0·105	0·181	0·038	c
(1)	9	3	0·43	0·062	0·120	0·033	0·008
(1)	15	3	0·22	0·049	0·097	0·034	0·008

[a] A cylindrical Suprasil cell, 5 cm long and 5 cm in diameter, and a mercury-free vacuum system were used. [b] Direct irradiation at 1849 Å was performed using a spiral array of 30 W low-pressure mercury lamps, the light path being flushed with nitrogen gas. [c] Not determined.

TABLE 2

Liquid-phase photolysis of (**1**) and [$^2H_2$]-(**1**)[a]

Compound	Solvent	Exposure time/h	Conversion /%	Product/%[b] (**2**)	(**3**)	(**4**)	(**5**)	Dimers[c]
(**1**)	none[e]	215	6	d	d	33	31	22
(**1**)	n-pentane[f]	60	25	d	d	40	36	10
[$^2H_2$]-(**1**)	n-pentane[f]	60	38	d	d	38	38	10

[a] Light source is a U-shaped 30 W low-pressure mercury lamp. [b] Based on the conversion. [c] Composed of bicycloheptyl, cycloheptylcycloheptene, and bicycloheptenyl. [d] Not detected. [e] Suprasil tube, 2 mm in diameter, used. [f] Suprasil vessel, 1 cm × 1 cm × 5 cm, containing 33 mg of (**1**) or [$^2H_2$]-(**1**) in 5 ml pentane used.

ments of the excited state *via* a carbene intermediate (**6**).† Direct photolysis of [1,2-$^2H_2$]cycloheptene {[$^2H_2$]-(**1**), isotopic purity of 99·0%} provided additional evidence to support the generation of the carbene (**6**). Liquid-phase photolysis of [$^2H_2$]-(**1**) gave a different product distribution from that obtained in the photolysis of (**1**) under similar conditions (Table 2). The decrease in yield of (**4**) and the increase in yield of (**5**) can be explained in terms of the competing rearrangements *via* the carbene intermediate (**6**), since deuteriation at the 1- and 2-position of (**1**) causes the rate of the hydrogen (deuterium) transfer from (**6**) to be slow, leading to the decrease in the yield of [$^2H_2$]-(**4**).

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† Recently, Kropp *et al.* have reported that tetrasubstituted alkenes, *e.g.* 2,3-dimethyl-but-2-ene, undergo a similar photorearrangement involving a carbene intermediate, probably *via* a π,R(3*s*) Rydberg excited state, on direct irradiation in pentane solution (Scheme); P. J. Kropp, E. J. Reardon, Jr., Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, Jr., *J. Amer. Chem. Soc.*, 1973, **95**, 7058; T. R. Fields and P. J. Kropp, *ibid.*, 1974, **96**, 7759 (Scheme). Although they observed the photorearrangement of several tetrasubstituted alkenes to carbene-derived products, similar behaviour of di- or trisubstituted alkenes is not known.

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[2] S. Takamuku, K. Moritsugu, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1971, **44**, 2562; Y. Inoue, M. Kadohira, S. Takamuku, and H. Sakurai, *Tetrahedron Letters*, 1974, 459; Y. Inoue, S. Takamuku, and H. Sakurai, *Bull. Chem. Soc. Japan*, submitted for publication.
[3] J. K. Crandall and R. J. Watkins, *J. Org. Chem.*, 1971, **36**, 913.
[4] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, 1969, **69**, 639.