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The Mercury-Photosensitized Reaction of Cyclooctene Vapor

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In connection with the studies of the photoelimination of ethylene from cyclooctadienes,[1] we have examined the mercury-photosensitized reaction of cyclooctene and found a unique isomerization into bicyclic compounds, along with the elimination of ethylene. Cyclooctene vapor (99.5%, glc) was irradiated with a low-pressure mercury lamp in the presence of mercury vapor at room temperature. The photolysis products observed were hydrogen, ethylene, 1,5-hexadiene, 1,7-octadiene (I), bicyclo[4.2.0]octane (II), bicyclo[3.3.0]-octane (III), and cyclooctane. Of these products, I, II, and III were isolated by glc (PEG 6000, 80°C) and were identified by a comparison of the NMR, mass spectra, and glc with those of authentic samples which has been independently synthesized (II and III)[2,3] or obtained commercially I[(I)NMR(CCl_4 solution): τ 4.2 (2H, m), 5.0 (2H, m), 5.2 (2H, m), 8.0 (4H, m), and 8.6 (4H, m); mass spectrum; parent peak at *m/e* 110; (II) NMR: τ 7.7 (2H, m), *ca.* 8.2 (4H, m) and 8.5(8H, m), no peaks at τ less than 7.5; mass spectrum: important peaks at *m/e* 110, 82, 81, 67, 54, and 41; (III)NMR: τ 7.6 (2H, m) and *ca.* 8.5 (12H, m), and no peaks at τ less than 7.4; mass spectrum: important peaks at *m/e* 110, 82, 67, 54, and 41]. The product yields are shown in Table 1, together with the effects of added radical scavengers.

Because of the diversity of the photolysis products, several different mechanistic pathways should be considered. Scheme 1 for the formation of ethylene, 1,5-hexadiene, and I may be suggested from the observa-

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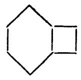
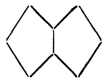
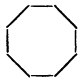
[1] S. Takamuku and H. Sakurai, *J. Phys. Chem.*, **73**, 1171 (1969); S. Takamuku, M. Utsunomiya, and H. Sakurai, *Chem. Commun.*, **1969**, 173; S. Takamuku and H. Sakurai, This Bulletin, **44**, 569 (1971).

[2] W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, **27**, 1910 (1962); R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962).

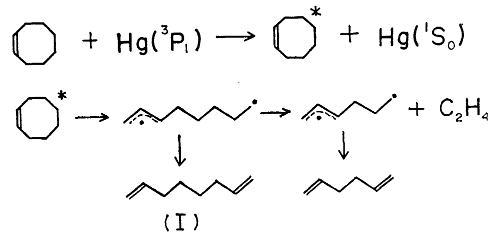
[3] P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, **30**, 3006 (1965).

Table 1. Mercury-photosensitized reaction of cyclooctene vapor (Cyclooctene 3.9 mmHg; Mercury *ca.* 0.5 g; 5 min; 100 m*l* quartz cell)

Product	None	NO[a]	O_2[b]	C_2H_4[b]
		μmol		
H_2	0.10	c)	c)	c)
C_2H_4	0.11	c)	c)	c)
	0.10	0.09	0.09	0.10
 (I)	0.97	0.89	0.69	1.13
 (II)	0.98	0.95	0.62	0.90
 (III)	0.17	0.18	0.10	0.12
	0.44	0.36	0.21	0.20

a) 5 mol% added,　b) 10 mol% added,　c) not determined

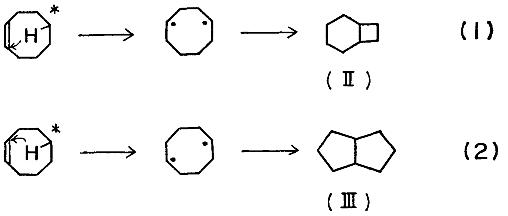
tions that (i) the products other than cyclooctane were not appreciably affected by the addition of several kinds of radical scavengers (though oxygen affects the formation of almost all products, this effect may be caused by the quenching of triplet cyclooctene), and (ii) the yields of ethylene and 1,5-hexadiene were equal within the limits of experimental error:



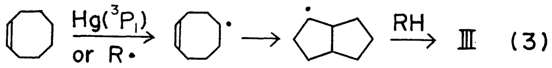
Scheme 1

In Scheme 1, a diradical intermediate, which is produced by the familiar allylic C–C bond cleavage, may undergo unimolecular isomerization to I or further C–C bond cleavage, yielding ethylene and a new diradical resulting in a similar isomerization to 1,5-hexadiene. Such an allylic diradical intermediate has been widely proposed in the mercury-photosensitized reaction of cyclopentene,[4] cyclohexene,[5] cycloheptene,[5] where the ring closure to the respective vinylcycloalkanes has been observed as one of the typical reactions of the intermediate. The yield of vinylcyclohexane expected from the intermediate was very low in the present photolysis of cyclooctene. Thus, the allylic diradical intermediate seems to show different reactivities depending on the vibrational excess energy or the molecular structure.

On the other hand, the most reasonable pathway for the formation of bicyclic compounds (II and III) is presumed to be the hydrogen transfer from an appropriate methylene group to the olefinic double bond with subsequent or simultaneous C–C bond formation. The transannular hydrogen abstraction from C-5 methylene *via* six- (1,5-shift) or five-center (1,4-shift) processes, leading to the formation of II or III through the respective diradical intermediates, is given below:



Though the mechanistic details, whether concerted or step-by-step, are not clear, the larger yield of II compared with that of III shows a preference for 1,5-hydrogen transfer *via* a six-center process over other hydrogen transfers.



An alternate diradical process (3), which is presumed by an analogy with a free radical transannular cycloaddition to 1,5-cyclooctadiene, thus forming bicyclo[3.3.0]octane derivatives,[6] may be ruled out on the basis of the experiments with radical scavengers.

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[4] W. A. Gibbons, W. F. Allen, and H. E. Gunning, *Can. J. Chem.*, **40**, 568 (1962).

[5] G. R. DeMare, O. P. Strausz, and H. E. Gunning, *ibid.*, **43**, 1329 (1965).

[6] R. Dowbenko, *Tetrahedron*, **20**, 1843 (1964).