Direct Photolysis of Cycloalkenes [1]

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The direct photolyses at 184.9 nm of cyclohexene (1a), cycloheptene (1b), and cyclo-octene (1c) were investigated in the vapour and liquid phases. The vapour-phase photolysis of these cyclo-alkenes gave the decomposition products (ethylene and butadiene from cyclohexene) or α,ω-dienes (2) and vinylcycloalkanes (3), the yields of which decrease with increasing pressure, along with minor amounts of the rearrangement products, methylenecycloalkanes (4) and bicyclo[*n*.1.0]alkanes (5; $n = 3$—5). Liquid-phase photolysis on the other hand afforded only the latter two rearrangement products and the *cis–trans*-isomer, when sterically allowed. On the basis of the pressure dependence of the product yields and other evidence, it is shown that the precursor of the decomposition products, α,ω-dienes, and vinylcycloalkanes is a vibrationally excited ground state of the cycloalkenes, which may be produced in a rapid internal conversion process from the excited singlet state generated initially. The rearrangement products were proved to be formed *via* a carbene intermediate (8) by the use of the deuteriated cycloheptane. Upon direct irradiation in the liquid phase, the *trans*-isomers of cyclohexene and cycloheptene were also generated, and trapped only in the presence of added acidic methanol to form the corresponding methoxycycloalkenes (6). The lifetime of *trans*-cycloheptene generated photochemically was determined to be 23 min at -10 ± 2 °C in a low-temperature experiment.

WHILE many studies have been made on the photochemistry of alkyl-substituted ethylenes, most of this published work has been concerned with triplet sensitization and therefore with the chemical reactivity of the alkene triplet thus generated. On the other hand, photochemical behaviour following direct excitation of these compounds is less understood partly because of the absence of effective absorption in the u.v. region above 230 nm. Limited studies on vapour-phase photolysis [2] have shown that, when directly irradiated, an alkene is promoted to an excited singlet state and then suffers fast

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[1] Preliminary report, Y. Inoue, S. Takamuku, and H. Sakurai, *J.C.S. Chem. Comm.*, 1975, 577.

[2] (*a*) P. Borrell and F. C. James, *Trans. Faraday Soc.*, 1966, **62**, 2452; P. Borrell and P. Cashmore, *ibid.*, 1969, **65**, 1595, 2412; P. Borrell, A. Cervenka, and J. W. Turner, *J. Chem. Soc.* (*B*), 1971, 2293; (*b*) J. P. Chesick, *J. Chem. Phys.*, 1966, **45**, 3934.

internal conversion to afford a vibrationally excited ground-state molecule; this species is known to undergo allylic C–C and/or C–H bond cleavage in addition to *cis–trans* isomerization by collisional deactivation. On liquid-phase direct photolysis, apart from *cis–trans* isomerization and allylic fission, stereospecific cyclodimerization of but-2-ene [3] and photorearrangement *via* carbene intermediates of tetrasubstituted alkenes [4] have recently been reported. However, few comparisons on vapour- and liquid-phase photolyses have been made, although such a study would make possible a comprehensive understanding of the fates of the excited states involved and their subsequent chemical reactions.

Further interest derives from the possible photochemical formation of highly strained *trans*-cyclohexene and *trans*-cycloheptene upon direct irradiation of their *cis*-isomers. In the field of cycloalkene chemistry, many efforts have been made to generate the strained *trans*-cycloalkenes.[5] These *trans*-cycloalkenes have been postulated in some cases as unstable intermediates which give rise to addition products with (acidic) methanol [6] or isobenzofuran derivatives.[5] However, it is uncertain whether free *trans*-cycloalkenes are formed under these conditions and, if they exist, what is their lifetime, since all the reactions employed were carried out in the presence of the trapping agents. In previous papers [7] we revealed that direct photolysis at 184.9 nm of *cis*-cyclo-octene in pentane gives the *trans*-isomer with the high photostationary *trans* : *cis* ratio of 0.96. Thus the *cis*-isomers of smaller-sized cycloalkenes are also expected to suffer *cis–trans* photoisomerization with higher efficiencies upon direct irradiation than the sensitized photoisomerization,[6] although the direct photolysis of cycloheptene in pentane solution has been reported to yield carbene-derived products.[1]

In the present paper, we report our studies on the direct photolysis at 184.9 nm of cycloalkenes (C_6–C_8) in the liquid phase together with the vapour-phase photolysis. We also present definitive evidence in support of the formation of highly strained *trans*-cyclohexene and *trans*-cycloheptene in their ground electronic states upon direct irradiation of pentane solution of the *cis*-isomers; the lifetime of *trans*-cycloheptene at a low temperature has been determined.

EXPERIMENTAL

Materials.—Commercially available cyclohexene (1a) cycloheptene (1b), and *cis*-cyclo-octene *cis*-(1c) were used after purification by fractional distillation through a spinning-band column and/or preparative g.l.c. to purities of >99.9, >99.9, and 99.5%, respectively. The sample of *cis*-cyclo-octene contained a small amount (0.46%) of cyclo-octane but was free from the *trans*-isomer.

trans-Cyclo-octene *trans*-(1c) was prepared by a three-step process starting from the *cis*-isomer, by the method described previously.[8] Fractional distillation under a reduced pressure of the product gave a sample of *trans*-(1c) which contained 0.38% of the *cis*-isomer as an impurity. A correction was made for this impurity in determination of product yields.

[1,2-$^2H_2$]Cycloheptene [$^2H_2$]-(1b) was prepared by a four-step synthesis. Cycloheptanone was converted to cycloheptane-1,2-dione by oxidation with selenium dioxide.[9] The deuteriated cycloheptene [$^2H_2$]-(1b) was synthesized by $LiAlD_4$ reduction of the cycloheptadione to [1,2-$^2H_2$]-cycloheptane-1,2-diol, followed by bromination of the diol with phosphorus pentabromide [10] to give [1,2-$^2H_2$]-1,2-dibromocycloheptane and subsequent debromination with zinc powder [11] to give the product (99.9% pure) in overall yield of 10%, the isotopic purity of which was confirmed as 99.0% by n.m.r. and mass spectrometry.

Solvent n-pentane was shaken with concentrated sulphuric acid, washed with water, dried over potassium carbonate, and fractionally distilled prior to use.

Analysis.—G.l.c. analyses of the reaction products from the direct photolyses of (1a—c) were carried out using a 9 m column of 20% β,β′-oxydipropiononitrile (ODPN) at 30 °C, a 6 m column of 15% polyethylene glycol 6 000 (PEG) at 70 °C, and a 6 m column of 20% ODPN at 70 °C, respectively. The analyses of the methoxycycloalkenes (6) were performed on a 3 m column of 15% PEG at 100—150 °C. All products, which can be separated from each other under these conditions, had retention times on g.l.c. and mass spectra identical with those of commercially obtained or independently synthesized authentic specimens. As internal standards, cycloheptane, cyclo-octane, and n-octane were employed for the liquid-phase photolyses of (1a, b, and c), respectively.

Vapour-phase Photolysis.—All experiments in the vapour-phase were carried out at room temperature and under static conditions. Cylindrical cells, 5 cm long and 5 cm in diameter, made of Suprasil and a mercury-free vacuum system were employed for vapour-phase photolysis. Irradiation at 184.9 nm was carried out using a spiral array of 30 W low-pressure mercury lamps with a Suprasil envelope, the light path being flushed with nitrogen gas during irradiation. The lamp was allowed to warm up for at least 30 min before each run in order to reach a stable operating condition. Control runs revealed that no detectable reaction occurred under irradiation through a Toshiba UV-25 filter which removes the 184.9 nm resonance line of mercury, suggesting the inability of the intense 253.7 nm resonance line to promote direct photolysis.

After each run, products were trapped in a capillary at −196 °C; small amounts of the non-condensable products

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[3] H. Yamazaki and R. J. Cvetanović, *J. Amer. Chem. Soc.*, 1969, **91**, 521; H. Yamazaki, R. J. Cvetanović, and R. S. Irwin, *ibid.*, 1976, **98**, 2198.

[4] P. J. Kropp, E. J. Reardon, jun., Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, *J. Amer. Chem. Soc.*, 1973, **95**, 7058; J. R. Fields and P. J. Kropp, *ibid.*, 1974, **96**, 7559; H. G. Fravel and P. J. Kropp, *J. Org. Chem.*, 1975, **40**, 2434.

[5] E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1965, **87**, 934.

[6] (*a*) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, 1967, **89**, 5199; P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, 1967, **32**, 3222; P. J. Kropp, *J. Amer. Chem. Soc.*, 1969, **91**, 5783; (*b*) R. Bonneau, J. Joussot-Dubien, L. Salem, and A. J. Yarwood, *ibid.*, 1976, **98**, 4329.

[7] Y. Inoue, S. Takamuku, and H. Sakurai, *J.C.S. Chem. Comm*, 1976, 423; *J. Phys. Chem.*, 1977, **81**, 7.

[8] Y. Inoue, K. Moritsugu, S. Takamuku, and H. Sakurai, *J.C.S. Perkin II*, 1976, 569.

[9] R. W. V. Harr, R. C. Voter, and C. V. Banks, *J. Org. Chem.*, 1949, **14**, 836.

[10] E. L. Eliel and R. G. Harber, *J. Org. Chem.*, 1959, **24**, 143.

[11] F. C. Whitmore and A. H. Homeyer, *J. Amer. Chem. Soc.*, 1933, **55**, 4556.

were discarded. The condensables were subjected to analysis on g.l.c.

Liquid-phase Photolysis.—A pentane solution containing 0.01M-cycloalkene (1) and a trace amount of the internal standard was irradiated at 184.9 nm by a 30 W U-shaped low-pressure mercury lamp fitted with an immersion reactor under nitrogen atmosphere. The product yields following direct irradiation was determined by g.l.c. analysis of portions removed from the irradiated solution. The liquid-phase photolyses of the deuterium labelled cycloheptene [$^2H_2$]-(1b) and non-deuteriated cycloheptene (1b) were run at a concentration of 0.066M in a Suprasil cell (1 × 1 × 5 cm) under external irradiation by the low-pressure mercury lamp.

Liquid-phase photolyses of 0.01M-cyclohexene and -cycloheptene in the presence of 0.50M-methanol and/or 0.03M-sulphuric acid were carried out in the immersion reactor under similar conditions. Control runs revealed that the substrate cycloalkenes (1a and b), and the products (4) and (5) as well, did not react with acidic methanol to give the methoxycycloalkanes (6) even after the acidic cycloalkene solution was left for one day without u.v. irradiation. However, strained *trans*-cyclo-octene *trans*-(1c) was found to react with acidic methanol in the absence of light to give methoxycyclo-octane in good yield after a few days at room temperature.

Photolysis at Lower Temperature.—Liquid-phase photolyses at -78 °C were carried out by an external irradiation method in the cylindrical Suprasil vessel used for vapour-phase experiments. A pentane solution (5 ml) containing 0.01M-cycloheptene was placed in the cylindrical cell, and then deaerated by five freeze–thaw cycles in a mercury-free vacuum system. The bottom half of the cell, where the solution lay, was cooled to -78 °C and the solution was irradiated externally through the top window of the cylinder by the spiral mercury lamp. After the irradiation, the irradiated solution was divided into the desired number of portions with continued cooling at -78 °C. In the determination of the lifetime of *trans*-cycloheptene, the divided portions were kept at -10 ± 2 °C for definite periods, and then chilled in turn to -78 °C. Subsequently, a large excess of pre-cooled methanol (at -78 °C) containing 5% concentrated sulphuric acid was added to the treated solution, and the mixture was gradually warmed to room temperature with vigorous shaking.

Independent Syntheses of Authentic Specimens.—All compounds synthesized were identified by means of n.m.r., i.r., and mass spectrometry. Hepta-1,6-diene (2b) was synthesized by pyrolysis of heptamethylene glycol diacetate at 500 °C according to the method of Marvel and Stille.[12] Octa-1,7-diene (2c) was obtained commercially. Vinylcyclopentane (3b) was synthesized by a Wittig reaction of cyclopentanecarbaldehyde.[13] Vinylcyclohexane (3c) was synthesized by pyrolysis of 2-cyclohexylethyl acetate, which was prepared by a Grignard reaction of ethylene oxide with cyclohexylmagnesium bromide[14] followed by esterification with acetyl chloride. Methylenecycloalkanes (4a—c) were prepared by a Wittig reaction of the corresponding cycloalkanone, *i.e.* cyclopentanone, cyclohexanone, and cycloheptanone.[15] Bicyclo[*n*.1.0]alkanes (5) (n = 3—5) were prepared by a Simmons–Smith reaction of the corresponding cycloalkene with di-iodomethane in the presence of zinc dust–copper(I) chloride mixture according to the method of Rawson and Harrison.[16] Methoxycycloalkanes (6) were prepared by the reaction of the corresponding cycloalkanol with sodium hydride and subsequent treatment with methyl iodide.

RESULTS

Vapour-phase Photolysis.—Direct photolysis at 184.9 nm of cyclohexene (1a) vapour gave ethylene and buta-1,3-diene as major decomposition products along with the rearrangement products, methylenecyclopentane (4a) and bicyclo[3.1.0]hexane (5a). The yield of butadiene was virtually equal to that of ethylene. The effect of the pressure of cyclohexene on product yields was examined up to 30 Torr in order to obtain information on the lifetime of the intermediate involved. The results are shown in Figure 1. The effect of the pressure on suppressing yields of ethylene and butadiene is evident from the data, while the yields of the rearrangement products (4a) and (5a) remained constant over the entire pressure range employed.

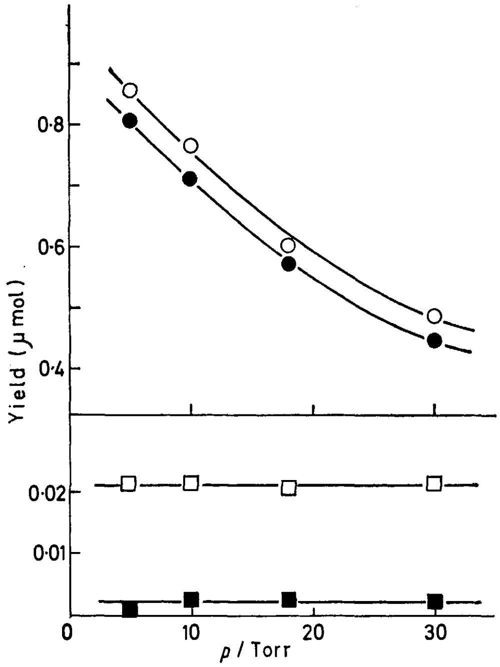

FIGURE 1 Product yield as a function of initial substrate pressure in vapour-phase photolysis of cyclohexene. Exposure time 3 min: ○, ethylene; ●, buta-1,3-diene; □, methylenecyclopentane (4a); ■, bicyclo[3.1.0]hexane (5a)

The products from the direct photolysis of cycloheptene (1b) vapour was hepta-1,6-diene (2b), vinylcyclopentane (3b), methylenecyclohexane (4b), and bicyclo[4.1.0]heptane (5b). The pressure dependence study was repeated. As shown in Table 1, the yields of heptadiene and vinylcyclopentane decrease with increasing cycloheptene pressure and the yields of methylenecyclohexane and bicycloheptane are practically pressure independent.

Direct photolyses of *cis*- and *trans*-cyclo-octene vapour

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[12] C. S. Marvel and J. K. Stille, *J. Amer. Chem. Soc.*, 1958, **80**, 1740.

[13] O. Grummitt, J. Liska, and G. Greull, *Org. Synth.*, 1964, **44**, 26.

[14] F. F. Blicke and F. B. Zienty, *J. Amer. Chem. Soc.*, 1939, **61**, 95.

[15] G. Wittig and U. Schoellkopf, *Org. Synth.*, 1960, **40**, 66.

[16] R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, 1970, **35**, 2057.

gave the *cis–trans*, isomer octa-1,7-diene (2c), vinylcyclohexane (3c), methylenecycloheptane (4c), and bicyclo[5.1.0]-octane (5c). On increasing the pressure by adding n-pentane as an inert gas, the yields of (2c) and (3c) were diminished, whilst an increase in the yield of the *cis–trans* isomer was observed; the yields of (4c) and (5c) were virtually invariant (see Table 2).

TABLE 1

Vapour-phase photolysis of cycloheptene (1b)

			[Product]/μmol			
p/Torr	*t*/min	Conversion (%)	(2b)	(3b)	(4b)	(5b)
3	3	1.6	0.105	0.181	0.038	*a*
9	3	0.43	0.062	0.120	0.033	0.008
15	3	0.22	0.049	0.097	0.034	0.008

[a] Yield not determined.

TABLE 2

Vapour-phase photolysis of *cis*- and *trans*-cyclo-octene (1c)

p/Torr					[Product]/μmol				
cis-(1c)	*trans*-(1c)	Pentane	*t*/min	Conversion (%)	(2c)	(3c)	(4c)	(5c)	*cis–trans* isomer
3	0	0	2	6.4	0.674	0.373	0.017	0.017	*a*
3	0	25	2	4.0	0.385	0.199	0.013	0.016	0.088
0	3	0	2	15.0	0.666	0.428	0.022	0.029	1.39
0	3	25	2	14.4	0.491	0.298	0.016	0.029	1.63

[a] Formation not detected.

TABLE 3

Liquid-phase photolysis of cycloalkenes (1a—c)

				Product (%) [a]		
Cycloalkene	Concentration/ M	*t*/min	Conversion (%)	(4)	(5)	*cis–trans* isomer
Cyclohexene (1a)	0.01	30	31	22	43	
Cycloheptene (1b)	0.01	30	30	34	27	
cis-Cyclo-octene *cis*-(1c) [b]	0.01	30	43	2.1	2.8	90
trans-Cyclo-octene *trans*-(1c) [b]	0.01	30	44	2.1	3.6	84

[a] Yield based on consumed cycloalkene. [b] Uncharacterized product (*ca.* 3%) was also observed.

TABLE 4

Liquid-phase photolysis of cycloheptene (1b) and its $[1,2\text{-}^2H_2]$ isomer

				Product (%) [a]		
Compound	Concentration/ M	*t*/h	Conversion (%)	(4b)	(5b)	Ratio (4b)/(5b)
(1b)	0.066	60	25	40	36	1.11
$[1,2\text{-}^2H_2]$-(1b)	0.066	60	38	38	38	1.0

[a] Yield based on consumed substrate.

Liquid-phase Photolysis.—The results of the direct photolysis at 184.9 nm of a pentane solution containing 0.01M-cycloalkene (1) are shown in Table 3. In sharp contrast to the vapour-phase photolyses of these compounds, formation of the decomposition products, α,ω-dienes (2) or vinylcycloalkanes (3) was not detected; the major photoproducts were the rearrangement products, *i.e.* methylenecycloalkanes (4) and bicyclo[*n*.1.0]alkanes (5; *n* = 3—5), and the *cis–trans* isomer of (1c).

In order to clarify the mechanism of formation of the rearrangement products, $[1,2\text{-}^2H_2]$cycloheptene $[^2H_2]$-(1b) was synthesized and subjected to direct photolysis. As shown in Table 4, the direct irradiation of pentane solution of $[^2H_2]$-(1b) gives a somewhat different product ratio from that obtained in the photolysis of non-deuteriated cycloheptene under similar conditions. A decrease in deuterium content was not observed for the products (4b) and (5b) on analysis by g.l.c.–mass spectrometry. The product $[^2H_2]$-methylenecyclohexane was separated by g.l.c. from the irradiated solution of $[^2H_2]$-(1b). The n.m.r. spectrum of the compound in CCl_4 shows only signals for four allylic protons at δ 2.05 (m) and six methylene protons at 1.45 (m), but lacks a signal for olefinic protons, indicating predominant deuteriation at the *exo*-methylene carbon of the methylenecyclohexane produced.

Direct Photolysis in the Presence of Acidic Methanol.—Since, as described above, the liquid-phase photolysis of *cis*-cyclo-octene gives the *trans*-isomer in good yield, it is to be expected that cyclohexene and/or cycloheptene also photoisomerize into the highly strained *trans*-isomers upon direct irradiation, although the main course of the photolyses of these cycloalkenes is the rearrangement to methylenecycloalkanes and bicycloalkanes. However, the spectroscopic detection of these simple *trans*-isomers is difficult because of the probable absence of efficient u.v. absorption above 230 nm and the relatively low yield of the products. It has been proposed in other systems that *trans*-cyclohexene and *trans*-cycloheptene, and their 1-phenyl derivatives, react rapidly with acidic methanol forming the corresponding methyl ethers as an addition product. Hence, the direct photolysis of cyclohexene and cycloheptene were performed in the presence of acidic methanol in search of their highly strained *trans*-isomers. Unfortunately, methanol has a weak absorption band in the vacuum u.v. region and therefore the secondary reactions induced by the decomposition of methanol following photoexcitation will be unavoidable; the extinction coefficient at 185 nm of methanol is 140 l mol^{-1} cm^{-1},[17] while those of the cycloalkenes are in the range of 5 500—10 000 l mol^{-1} cm^{-1}.[18]

The results of the direct photolyses of cyclohexene and cycloheptene in the presence of neutral methanol and of acidic methanol are shown in Tables 5 and 6. The corresponding methyl ethers, *i.e.* methoxycyclohexane (6a) and methoxycycloheptane (6b), were obtained in significant yields only on photolysis with acidic methanol. Since the direct irradiation of methanol is known to produce some radicals,[19] the increase of the conversion rate and the decrease in the yields of the rearrangement products (4) and (5) may be attributed to the subsequent radical-induced reactions which consume the substrate alkenes. Of course, these cycloalkenes (1a and b) and the rearrangement products did not react with acidic methanol after standing for at least one day under similar conditions without u.v. irradiation.

TABLE 5

Liquid-phase photolysis of cyclohexene (1a) in the presence of acidic methanol

Concentration/M				Conversion	Product (%)[a]		
(1a)	MeOH	H_2SO_4	t/min	(%)	(4a)	(5a)	(6a)
0.01	0	0	30	31	22	43	*b*
0.01	0.50	0	30	49	9.0	20	0.7
0.01	0.50	0.03	30	46	9.6	22	4.4

[a] Yield based on consumed cyclohexene. [b] Formation not detected.

TABLE 6

Liquid-phase photolysis of cycloheptene (1b) in the presence of acidic methanol

Concentration/M				Conversion	Product (%)[a]		
(1b)	MeOH	H_2SO_4	t/min	(%)	(4b)	(5b)	(6b)
0.01	0	0	30	30	34	27	*b*
0.01	0.50	0	30	54	9.1	12	0.6
0.01	0.50	0.03	30	53	9.4	11	5.0

[a] Yield based on consumed cycloheptene. [b] Formation not detected.

Direct Photolysis of Cycloheptene at Lower Temperature.—The direct irradiation of pentane solution containing 0.01M-cycloheptene was carried out for 3 h in a dry ice–acetone bath. Treatment after irradiation and the results are shown in Table 7. It was revealed that the precursor of methoxycycloheptane (6b) has a long enough lifetime at −78 °C to react with added acidic methanol after the end of irradiation. Even when acidic methanol was added after the above irradiated solution of cycloheptene had been allowed to stand for 20 h at −78 °C, the decrease in the yield of methoxycycloheptane was <20%.

TABLE 7

Liquid-phase photolysis of cycloheptene at −78 °C

Treatment following the photolysis at −78 °C	Conversion (%)	Product (%)[a]		
		(4b)	(5b)	(6b)
Warm (to room temperature)	9	23	24	*b*
Warm ⟶ add acidic methanol	9	23	23	0.5
Add acidic methanol ⟶ warm	9	25	24	4.7

[a] Yield based on consumed cycloheptene. [b] Formation not detected.

The low-temperature experiment was repeated in order to determine the lifetime of *trans*-cycloheptene at low temperatures. The determination of the lifetime at −10 °C of *trans*-cycloheptene was done by adding acidic methanol to the portion removed from the irradiated solution which was kept at −10 °C after the irradiation at −78 °C. The logarithm of relative yields of methoxycycloheptane produced is plotted as a function of the time at −10 °C in Figure 2; a good linear relation was obtained, indicating unimolecular decay of *trans*-cycloheptene. The lifetime of *trans*-cycloheptene can be calculated from the data to be 23 min at −10 °C.

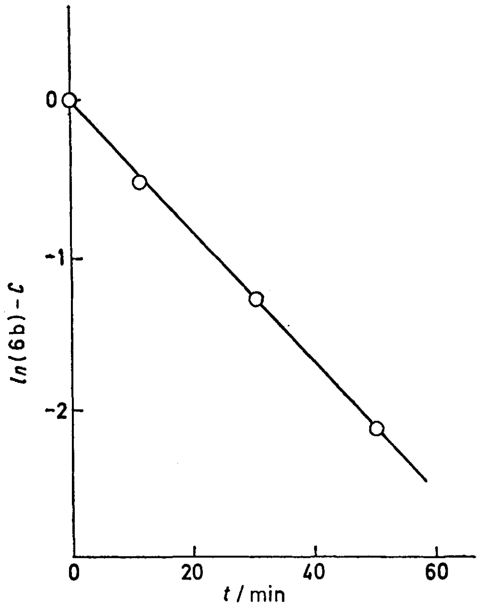

FIGURE 2 Logarithm of relative yield of methoxycycloheptane (6b) *versus* the time of standing at −10 °C

For similar attempts with cyclohexene methoxycyclohexane was not detected by g.l.c. suggesting the lower stability of *trans*-cyclohexene.

DISCUSSION

Vapour-phase Photolysis.—Two distinct mechanisms should be operative for the direct photolysis of cycloalkenes in the vapour phase, since apparent differences in the effects of pressure on the product yields are seen from the data shown in Figure 1 and Tables 1 and 2. The products resulting from the vapour-phase photolysis of the cycloalkenes (1) may be classified according to the pressure dependence of their yields; the decomposition products, α,ω-dienes (2), and vinylcycloalkanes (3) are produced only on vapour-phase photolysis and their yields decrease with increasing pressure, while the yields of the rearrangement products (4) and (5) are practically pressure independent and these become the major photoproducts in liquid-phase photolysis. The pressure effects observed depend upon whether or not the precursor involved has a lifetime long

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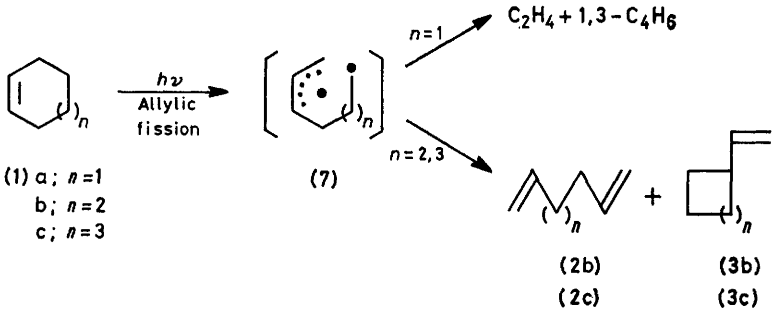
[17] A. J. Harrison, B. J. Cederholm, and M. A. Terwilliger, *J. Chem. Phys.*, 1959, **30**, 355.

[18] L. C. Jones, jun., and L. W. Taylor, *Analyt. Chem.*, 1955, **27**, 228.

[19] R. P. Porter and W. A. Noyes, jun., *J. Amer. Chem. Soc.*, 1959, **81**, 2307.

enough to suffer deactivating collision. Hence, the decomposition products, α,ω-dienes, and vinylcycloalkanes are inferred to be formed *via* an intermediate having a relatively long lifetime. In other systems,[2] it is known that with simple alkenes an electronically excited singlet alkene undergoes rapid internal conversion into a vibrationally activated ground state, and with molecules of this size the lifetime should be long enough to permit collisional deactivation of any energetic ground-state species which may be formed in an internal conversion process. Crandall and Watkins[20] reported that the vapour-phase pyrolyses of the cycloalkenes (1b and c) gave the corresponding α,ω-dienes (2) and vinylcycloalkanes (3) as the major products. It is therefore concluded that the precursor of these pressure-dependent products is a vibrationally excited ground-state cycloalkene, which is produced *via* the internal conversion of the electronically excited state generated initially by direct irradiation. This conclusion is also supported by the observation that only the rearrangement products (4) and (5) are formed on liquid-phase photolysis, in which the excess of vibrational energy is quickly removed by collision with solvent molecules.



Scheme 1

In our previous study[21] on the direct photolysis of *cis-* and *trans*-4,5-dimethylcyclohexene vapour, we showed that the decomposition of the cyclohexenes into *cis-* or *trans*-but-2-ene and buta-1,3-diene undergoes *via* a short-lived allylic biradical on the basis of the non-stereospecific formation of but-2-ene. It was also deduced that the intermediate of the decomposition products in the present photolysis of cyclohexene itself is a short-lived allylic biradical (7a) produced by an allylic C–C bond cleavage of the vibrationally-activated cyclohexene. Similarly, the formation of the α,ω-dienes (2) and the vinylcycloalkanes (3) may be accounted for in terms of the competitive intramolecular disproportionation and recombination reaction of the analogous allylic biradicals (7b and c) as shown in Scheme 1.

A quantitative treatment of the pressure dependence study on the photolysis of cyclohexene vapour gives additional information on the lifetime of the vibrationally activated cyclohexene in its ground electronic state. The sequence (i)—(v) is proposed for the formation of ethylene and buta-1,3-diene, the small amounts of the rearrangement products being neglected, where the superscripts S_1 and $S_0{}^*$ represent the electronically excited singlet and the vibrationally activated ground states, respectively.

$$(1a) \xrightarrow[184.9\ \text{nm}]{h\nu} (1a)^{S} \qquad \text{(i)}$$

$$(1a)^{S_1} \xrightarrow[\text{conversion}]{\text{Internal}} (1a)^{S_0*} \qquad \text{(ii)}$$

$$(1a)^{S_0*} \longrightarrow C_2H_4 + 1{,}3\text{-}C_4H_6 \qquad \text{(iii)}$$

$$\longrightarrow (1a) \qquad \text{(iv)}$$

$$\xrightarrow{(1a)} (1a) \qquad \text{(v)}$$

A steady-state treatment of the sequence (i)—(v) leads to equation (vi) for the reciprocal of the yields of the products ethylene and butadiene.

In Figure 3, the reciprocals of the product yields are plotted against the cyclohexene pressure and a good

$$1/\phi = \frac{k_{iii} + k_{iv}}{k_{iii}} + \frac{k_v}{k_{iii}}[(1a)] \qquad \text{(vi)}$$

linear relation is obtained. From the slope and intercept, we obtain the value, $(k_{iii} + k_{iv})/k_v = 26.3$ Torr, for the vapour-phase photolysis of cyclohexene. Assuming that the deactivation of the vibrationally excited cyclohexene occurs at each collision, *i.e.* $k_v = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, the value $k_{iii} + k_{iv}$ is calculated to be 0.83×10^{-8} s^{-1}. Thus the vibrationally excited ground state of cyclohexene has a lifetime of 1.2×10^{-8} s.

The same treatment can be applied for the vapour-phase photolysis of cycloheptene, although only limited data are available for the pressure dependence of the product yields. The lifetime of the vibrationally excited cycloheptene (1b) ^{S_0*} can be estimated to be 3.3×10^{-8} s by a similar calculation from the combined yield of hepta-1,6-diene (2b) and vinylcyclopentane (3b).

On the other hand, the rearrangement products (4) and (5) are formed in a pressure independent process, probably from an electronically excited state which has a short lifetime compared with the effective time between deactivating collisions even at higher pressures; the lifetime of the electronically excited state involved

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[20] J. K. Crandall and R. J. Watkins, *J. Org. Chem.*, 1971, **36**, 913.

[21] Y. Inoue, S. Takamuku, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1975, **48**, 3101.

may be around 10^{-10} s. However, the superposition near 185 nm of the R $\leftarrow$ N band over the continuum of the V $\leftarrow$ N band in the absorption spectra of the cycloalkenes complicates the situation. We cannot conclude from the available data whether the electronically excited state involved in the present photorearrangement is the excited singlet state or the $\pi,R(3s)$ Rydberg (R) excited state of the cycloalkenes.* The detailed mechanism of this rearrangement reaction will be discussed below.

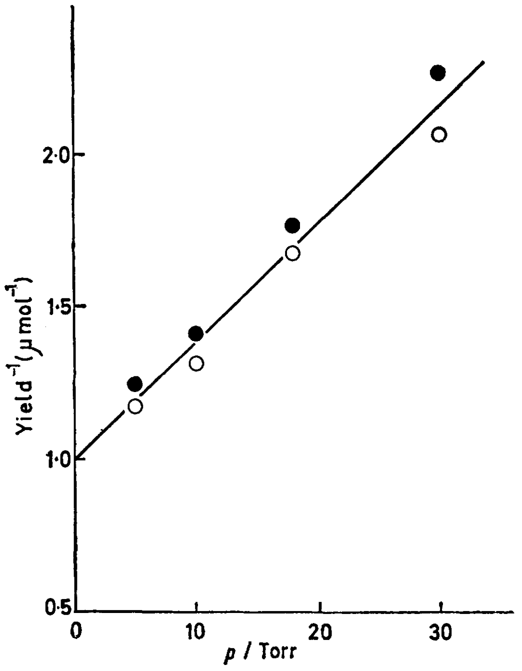
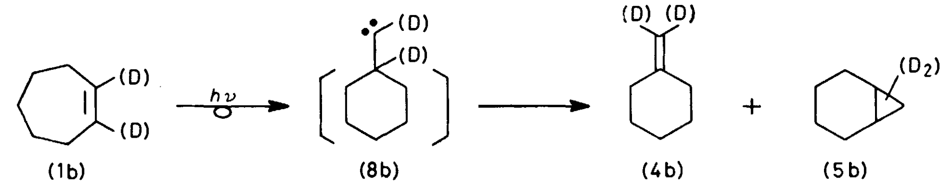


FIGURE 3 Reciprocal of yield of ethylene (○) and buta-1,3-diene (●) as a function of pressure in vapour-phase photolysis of cyclohexene

Liquid-phase Photolysis.—The direct photolyses of the cycloalkenes in the liquid phase give the rearrangement products and, when the *trans*-form is stable at room temperature, the predominant formation of the *cis–trans* isomer of (1c) is observed (Table 3). The formation of the stereoisomers of (1c) is interpreted in terms of the photoisomerization *via* the excited singlet state, as demonstrated previously.[7] The mechanism of formation of these rearrangement products is of interest. The mechanism is inferred to involve competing rearrangements to (4) and (5) *via* the carbene intermediate which is produced by the [1,2] shift of an allylic C–C bond of the excited cycloalkene (see Scheme 2).



SCHEME 2

Direct photolysis of the deuteriated cycloheptene $[^2H_2]$-(1b) provides definitive evidence in support of the generation of the carbene (8b). $[^2H_2]$Methylenecyclohexane produced in the photolysis of $[^2H_2]$-(1b) carries the deuterium atoms only on the *exo*-methylene carbon, supporting the mechanism involving hydrogen (deuterium) transfer to the carbene centre in the intermediate (8b). Furthermore, the photolysis of $[^2H_2]$-(1b) gives a somewhat different product distribution from that obtained in the photolysis of non-deuteriated cycloheptene as shown in Table 4. The decrease in yield of (4b) and the increase in yield of (5b) can be explained in terms of competing hydrogen transfer and insertion to C–H bond of the carbene (8b), since deuteriation at the 1- and 2-positions of (1b) caused the rate of the hydrogen transfer in the carbene to be slow, leading to a decrease in the yield of $[^2H_2]$-(4b). Assuming that the rate of the intramolecular insertion of the carbene (8b) to the C–H bond is not affected by deuteriation, the isotope effect on the hydrogen transfer process in the carbene, denoted by k_H/k_D, is calculated to be 1.11; the value should be compared with the isotope effect, $k_H/k_D = 1.12$, observed for the transfer of a tertiary hydrogen atom in isopropylcarbene which is generated by the photolysis of the corresponding diazoalkane.[22] Likewise, analogous carbenes (8a) and (8c) are also postulated in the photolysis of the other cycloalkenes (1a) and (1c) as the precursor of the rearrangement products (4) and (5).

Highly Strained trans-*Cycloalkenes.*—The efficient photochemical conversion of *cis*-cyclo-octene to its *trans*-isomer prompted us to search for highly strained *trans*-isomers of the smaller cycloalkenes (1a and b) in liquid-phase photolysis. Since spectroscopic detection of these

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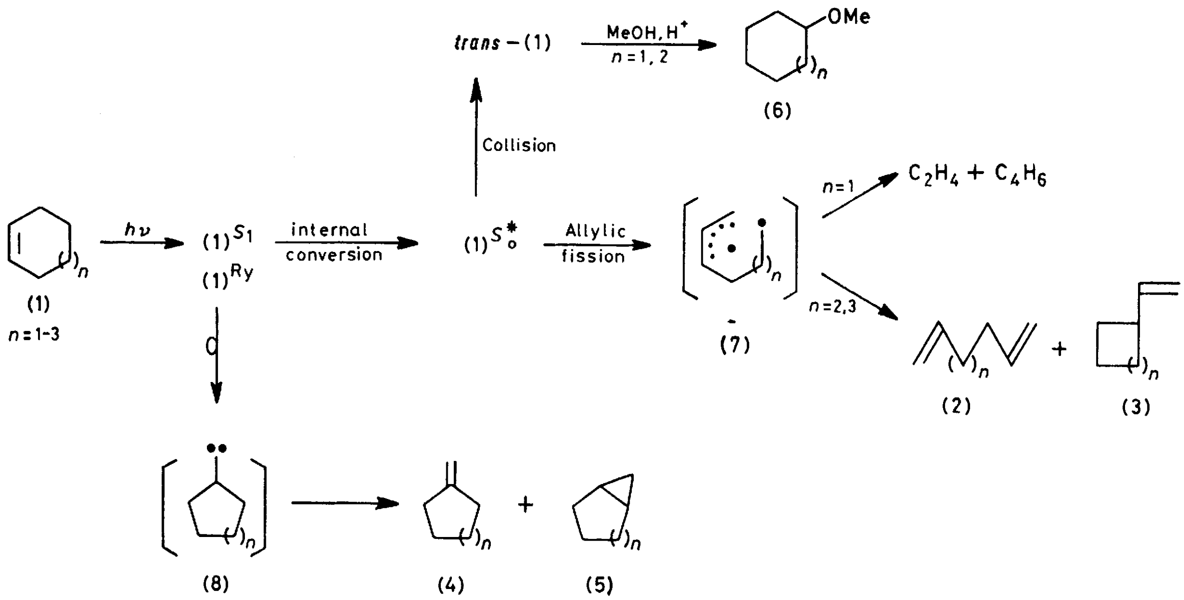
* Recently, Kropp *et al.*[4] have reported that tetrasubstituted alkenes, *e.g.* 2,3-dimethylbut-2-ene, undergo a similar photorearrangement involving a carbene intermediate, probably *via* a Rydberg state, on direct irradiation at >220 nm. Although they observed the photorearrangement of several tetrasubstituted alkenes to carbene-derived products, similar behaviour of di- or tri-substituted alkenes is not known. In our preliminary experiments on the benzoate photosensitization of simple alkenes, it is shown that methyl benzoate acts as a singlet sensitizer to generate an excited singlet state of alkene, probably *via* a singlet exciplex. On the basis of the fact that, in the benzoate sensitization of cyclo-octene (1c), only the *cis–trans* isomerization occurs without the photorearrangement to the carbene-derived products (4c) and (5c), the excited state involved in the present photorearrangement may be inferred to be the Rydberg excited state of the cycloalkenes (1).

[22] W. Kirmse, H. D. Von Scholz, and H. Arnold, *Annalen*, 1968, **711**, 22.

trans-isomers is difficult because of the lack of effective absorption in an accessible u.v. region, chemical trapping of *trans*-cyclohexene and *trans*-cycloheptene by acidic methanol was applied to the liquid-phase photolysis of their *cis*-isomer. As shown in Tables 5 and 6, methoxycycloalkanes (6a and b) are obtained in significant yields only on photolysis in the presence of acidic methanol, although the introduction of methanol to the reaction system reduces the yields of the rearrangement products (4) and (5).

While the addition products with methanol are obtained on direct photolysis of the cycloalkenes (1a and b) in the presence of the trapping agent, it remains uncertain whether the precursor of these adducts is really the ground state *trans*-isomer or, a minor possibility, the electronically excited state of the alkene itself. Further support for the formation of *trans*-cycloheptene in its ground state comes from the direct photolysis of *cis*-cycloheptene at low temperatures and the subsequent addition to the irradiated solution of acidic methanol after irradiation (see Table 7). Considerable amounts of methoxycycloheptane (6b) are obtained even when acidic methanol is added after leaving the irradiated solution for 20 h at —78 °C. It is obvious that the precursor of methoxycycloheptane is the highly strained *trans*-cycloheptene and has a long enough lifetime at —78 °C to react with added acidic methanol after irradiation. The lifetime of *trans*-cycloheptene is calculated to be 23 min at —10 °C. This is the first evidence which suggests the formation and the trapping of *trans*-cycloheptene in the ground state.



SCHEME 3

The reactions of cycloalkenes following direct excitation at 184.9 nm are summarized in Scheme 3.

[6/1816 *Received, 27th September,* 1976]