Photochemistry of Cyclohepta-1,3-diene and Cyclohepta-1,3,5-triene. Photochemical Formation and Chemical Reactivity of the Strained *trans*-Isomer[1]

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The direct and sensitized photolyses of *cis,cis*-cyclohepta-1,3-diene and *cis,cis,cis*-cyclohepta-1,3,5-triene have been studied in detail in search of the *trans*-isomer. Low-temperature irradiations and trapping experiments with acidic methanol have revealed that the primary process for the excited singlet and triplet states of cycloheptadiene is not direct disrotatory cyclization but geometrical isomerization to the highly strained *cis,trans*-isomer, which is detected spectroscopically, while no intermediacy of any transient species can be detected spectroscopically or trapped chemically in the photolyses of cycloheptatriene. The *cis,trans*-cycloheptadiene generated photochemically cyclizes thermally to bicyclo[3.2.0]hept-6-ene in neutral media or gives adducts, 3-methoxycycloheptene and 2-methoxynorcarane, in acidic methanol. The kinetic and thermodynamic parameters for the photochemical and the subsequent thermal processes are discussed.

Photochemical *cis–trans* isomerization is a convenient and versatile method for preparing highly strained *trans*-isomers of simple cycloalkenes.[2,3] In the photochemistry even of seven-membered ring cycloalkenes, a good deal of evidence has been presented that indicates unequivocally the existence of strained *trans*-isomers in the ground electronic state. The intervention of *trans*-cyclohexene has also been proposed in the photolyses of cyclohexene.[2a,3] Thus, the direct and sensitized photolyses of *cis*-cycloheptene both produce the highly strained *trans*-isomer, which is stable at 195 K and can be trapped by the subsequent addition of acidic methanol or diazomethane,[2a] while *trans*-cyclohexene has been postulated as a reactive intermediate giving rise to cyclodimers or a methanol adduct.[2c,3]

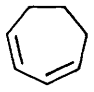
On the other hand, photochemical *cis–trans* isomerizations of medium-sized conjugated cycloalkadienes and cycloalkatrienes do not appear to be fully investigated as regards a search for the *trans*-isomers. Like *cis*-cyclo-octene, *cis,cis*-cyclo-octa-1,3-diene undergoes geometrical photoisomerization giving the *cis,trans*-isomer along with small amounts of a few valence isomers including the cyclization product.[4–6] By contrast, the smaller homologue *cis,cis*-cyclohepta-1,3-diene is known to photocyclize to give bicyclo[3.2.0]hept-6-ene in good yield,[7,8] and this process has been believed to proceed through a photochemical disrotatory ring-closure following the Woodward–Hoffmann rule.[9–11] Low-temperature experiments[1,12] have recently shown that the direct photolyses of cycloheptadiene in argon or organic matrices give an unstable intermediate, which is inferred to be the *cis,trans*-isomer on the basis of its i.r.[12] or u.v.[1] spectrum. However, there is no further evidence in support of the intervention of the *cis,trans*-isomer in the photocyclization process, and the chemical reactivities of this highly strained *cis,trans*-isomer are not known.

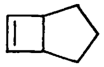
In this context, it is also interesting to study the photochemistry of cyclohepta-1,3,5-triene in detail. Upon direct irradiation, the cycloheptatriene affords similarly the cyclization product bicyclo[3.2.0]hepta-2,6-diene in good chemical yield,[7,13] although the otherwise invisible 1,7-sigmatropic hydrogen shift has been shown to occur concurrently by using 7-deuteriated cyclpheptatrienes.[14]

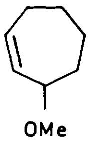
We report here the low-temperature photolyses of cycloheptadiene and cycloheptatriene as well as trapping experiments using acidic methanol to obtain definitive evidence for the strained *trans*-isomer as a reactive intermediate and also to reveal the subsequent chemical reactions of the *trans*-isomer. The results are discussed by comparison with the photochemistry of related cyclic olefins.

Results

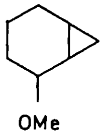
Cycloheptadiene.—Direct photolyses. Pentane and methanol solutions of *cis,cis*-cyclohepta-1,3-diene (**1*cc***) (10mM) were irradiated at 254 nm under a nitrogen atmosphere to give bicyclo[3.2.0]hept-6-ene (**2**) in excellent yields; see Table 1. The irradiations of (**1*cc***) in acidic methanol give additional new products, *i.e.* 3-methoxycycloheptene (**3**) and *endo*- and *exo*-2-methoxynorcaranes (**4n** and **x**),† the combined yields of which increased with increasing amount of sulphuric acid added to


(**1cc**)


(**2**)



(**3**)



(**4**)

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† The *endo*- and *exo*-isomers (**4n** and **x**) were not separated by g.l.c. under the conditions employed, but the *endo*:*exo* ratio of product (**4**) was determined to be 3:1 by n.m.r. spectrometry. This result is not unexpected, since the solvolyses of cyclohept-3-enyl brosylate or tosylate in acetic acid give *endo*- and *exo*-2-acetoxynorcarane in ratios of 3.5:1 or 4:1, respectively.[15]

Table 1. Direct and triphenylene-sensitized photolyses of 10mM-*cis,cis*-cyclohepta-1,3-diene (**1*cc***) in pentane and in neutral and acidic methanol[a,b]

					Yield (%)[c]		
Wavelength (nm)	Sensitizer (mM)	Solvent	H_2SO_4(M)	Conversion (%)	(**2**)	(**3**)	(**4**)
254[a]	None	Pentane	0	68	96	*d*	*d*
		Methanol	0	61	88	*d*	*d*
			0.047	57	84	3.2	3.2
			0.101	58	77	6.4	5.0
			0.194	65	71	10	7.0
			0.403	58	61	17	11
			0.601	60	53	22	13
			0.799	66	47	25	15
			1.00	66	41	28	17
>300[b]	Triphenylene	Pentane	0	11	88	*d*	*d*
	(0.5)	Methanol	0	17	89	*d*	*d*
			0.04	16	88	6.8	6.1
			0.20	17	75	17	12
			1.00	17	33	46	32

[a] Direct irradiations were performed at room temperature for 20 min in a merry-go-round apparatus using a 30 W mercury resonance lamp fitted with a Vycor filter. [b] Triplet sensitizations were conducted at room temperature for 10 min using a 300 W high-pressure mercury arc fitted with a Pyrex filter; some of the combined chemical yields exceed 100%, since the determination of the amount of (**1*cc***) consumed is somewhat less reliable at low conversions. [c] Chemical yield based on consumed (**1*cc***). [d] Formation not detected.

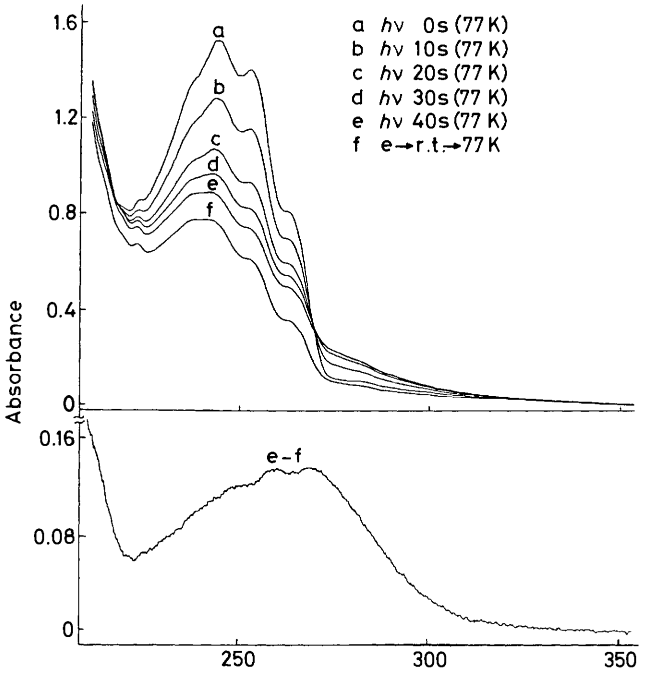


Figure 1. Spectral changes upon direct irradiation at 254 nm of 0.12mM-*cis,cis*-cyclohepta-1,3-diene (**1*cc***) in an isopentane–methylcyclohexane (3:1) matrix at 77 K and subsequent warming (upper traces), and the u.v. spectrum of *cis,trans*-cyclohepta-1,3-diene (**1*ct***) obtained by subtracting trace f from e (lower trace)

methanol at the expense of the cyclization product (**2**) (Table 1). Although the ratio of adducts, *i.e.* (**3**):(**4**), varied with the acid concentration employed, the dependence is accounted for in terms of the acid-catalysed isomerization of (**3**) into (**4**) described below.

Since high acid concentrations up to 1M were employed, the thermal reactions of the starting material (**1*cc***) and the product norcaranes (**4**) were examined under comparable conditions in the dark, as control experiments. The thermal reaction of (**1*cc***) at room temperature in acidic methanol containing 1M-sulphuric acid merely resulted in an extremely slow consumption of (**1*cc***) with a first-order rate constant of 7.1×10^{-7} s^{-1} or a lifetime of 16 days. In the mixture, the formation of (**3**) was detected by g.l.c., but its yield was *ca.* 6% based on (**1*cc***) consumed; the major process would be the formation of high molecular-weight products which cannot be detected on g.l.c. We may conclude therefore that the contribution of the thermal reaction of (**1*cc***) is negligible under our experimental conditions. In contrast, the reaction of (**4n**) in the same acidic methanol at 25 °C led to relatively fast consumption of (**4n**) (k_1 6.6×10^{-5} s^{-1}; τ 4.2 h), yielding (**3**) almost quantitatively (>95% yield). Thus the norcaranes (**4**) produced must be more or less transformed into (**3**) during the irradiation especially at the high acid concentrations, with the combined yields being kept unvaried.

In order to obtain further insights into the mechanism giving rise to the methanol adducts (**4**), the photolysis of (**1*cc***) was carried out in methan[^{2}H]ol containing 1M-[$^2H_2$]sulphuric acid. The product (**4**) separated from the photolysate by g.l.c. was subjected to the ^{1}H n.m.r. spectrometry to reveal predominant incorporation (89%) of one deuterium at the 7-*exo* position. The exact deuterium distribution in product (**3**) could not be determined owing to the overlapping signals of the methylene protons, but no deuterium is distributed at the 1-, 2-, or 3-position of (**3**).

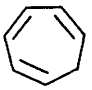
Sensitized photolyses. Triphenylene-sensitized photolyses of (**1*cc***) (10mM) were performed at >300 nm in pentane and in neutral and acidic methanol. As can be seen from Table 1, the same products as in direct photolyses were obtained in comparable yields, despite the different spin states involved.

Low-temperature irradiation. Since the above trapping experiments indicated the intervention of a reactive intermediate in the direct, as well as the sensitized, photolyses of (**1*cc***), the photoreaction was spectrophotometrically studied at low temperatures in search of a transient species, by using a transparent quartz Dewar vessel and a mercury resonance lamp.

The direct photolysis at 254 nm of (**1*cc***) (0.12mM) was performed in an isopentane–methylcyclohexane (3:1) matrix at 77 K and the spectral change was followed by the u.v. spectroscopy. As can be seen from traces a—e in Figure 1, upon irradiation the original absorption at 245 nm (ε 10 300 l mol^{-1} cm^{-1}) due to (**1*cc***) decreases gradually with an accompanying increase at *ca.* 275 nm, an isosbestic point being observed at 270 nm. Although the sample irradiated for 40 s (trace e) was stable at that temperature at least for 30 min in the dark, warming of this sample to room temperature followed by recooling to 77 K did not regenerate the original spectrum (trace e) but led to reduced absorption over the whole wavelength range giving trace f. Subtracting trace f from e gave the difference spectrum (e − f), which has a maximum at 275 nm and is ascribable to the unstable species which disappears upon warming. Prolonged irradiations up to 100 s resulted in slight deviation from the isosbestic point observed in the early stages of the photolysis (0—40 s).

Irradiation of the same solution at 195 K led again to a similar spectral change, *i.e.* a reduction at 245 nm and an increase at *ca.* 275 nm. However, the resulting spectrum, which is analogous in shape to trace c in Figure 1, was no longer stable at this temperature. A plot of optical density at 270 or 280 nm *versus* time gave an exponential decay, indicating unimolecular decay with a rate constant of 2.3×10^{-3} s^{-1} or a lifetime of 7.1 min at 195 K. Similar experiments were repeated in some polar solvents. The lifetimes obtained are listed in Table 2.

Cycloheptatriene.—Direct and sensitized photolyses. The direct photolyses at >300 nm of *cis,cis,cis*-cyclohepta-1,3,5-triene (**5*ccc***) in neutral solvents gave bicyclo[3.2.0]hepta-2,6-diene (**6**) in excellent yield; see Table 3. In sharp contrast to the cycloheptadiene case, irradiation in acidic methanol containing 1M-sulphuric acid merely afforded the cyclization product (**6**) in good yield without yielding any trace of addition products detectable by g.l.c.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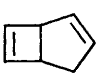
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Table 2. Lifetime of *cis,trans*-cyclohepta-1,3-diene (**1*ct***) in some solvents at 195 K[a]

Solvent	E_T/kcal mol^{-1} [b]	Lifetime (min)
Isopentane–methylcyclohexane(3:1)	30	7.1
Diethyl ether	34.6	7.5 ± 1.0
Tetrahydrofuran	37.4	7.8 ± 0.5
Methanol	55.5	6.5 ± 1.0

[a] (**1*cc***) (0.12mM) was irradiated at 254 nm for 1 min in a transparent quartz Dewar maintained at 195 K, and the unimolecular decay of the resulting transient spectrum was monitored photometrically. [b] Solvent polarity parameter, quoted in K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, 1963, **661**, 1; 1963, **669**, 95; 1 cal = 4.18 J.

Furthermore, the attempted photosensitization by benzophenone or triphenylene did not function well; the starting material disappeared only very slowly and the product yields were poor, as shown in Table 3.

Low-temperature irradiation. Although the above trapping experiment failed to reveal the intervention of any reactive intermediate, the photolysis of (**5*ccc***) was examined at low temperature. An isopentane–methylcyclohexane (3:1) matrix containing (**5*ccc***) (0.12mM) was photolysed at 77 K with 254 nm light and the spectral change was monitored as above. However, practically no change was observed in the spectrum of (**5*ccc***) even after 15 min irradiation under the optical conditions employed for (**1*cc***) (see Figure 2a).

On the other hand, the direct irradiation of (**5*ccc***) (0.4mM) in the same solvent at 195 K or room temperature led to the monotonous decrease in absorbance at 260 nm and then to the complete consumption of the starting material after 30 min, but did not show the appearance of a new peak at longer wavelengths (Figures 2b and c). Excitation at longer wavelength (>300 nm) gave the same result (Figure 2d).

Discussion

Detection and Trapping of cis,trans-*Cyclohepta*-1,3-*diene*.—The comparative irradiation of (**1*cc***) in neutral and acidic methanol containing varied amounts of sulphuric acid clearly indicates the intervention of a common precursor to the cyclization product (**2**) and the methanol adducts (**3**) and (**4**), since the combined yield of (**3**) and (**4**) increases with increasing acid concentration at the expense of that of (**2**), while the conversions are virtually unchanged with the acid concentration (Table 1). We may consequently postulate the intervention of the electronically excited singlet of (**1**) or the highly strained *cis-trans*-isomer (**1*ct***) as a reactive intermediate which gives exclusive cyclization in neutral media and competitive protonation in acid media. The former affords the cyclization product (**2**) *via* disrotatory ring closure allowed for the electronically excited state, whereas the latter yields (**2**) *via* a thermally allowed conrotatory process. Importantly, the triplet photosensitizations of (**1*cc***) with triphenylene gave quite analogous results. As shown in Table 1, the sensitization of (**1*cc***) in neutral methanol gave (**2**) in excellent yield, while the addition of acid led to decreased cyclization yields which were compensated by the combined yields of the adducts. The identical behaviour of the direct and triplet-sensitized photolyses of (**1*cc***) strongly supports the intervention of the *cis,trans*-isomer (**1*ct***), rather than the excited singlet or triplet state, as a common precursor to products (**2**)—(**4**).

The low-temperature irradiation of (**1*cc***) in a rigid matrix and the subsequent treatment provide the spectrum of the reactive intermediate most probably trapped by acidic methanol. Since the spectral change in Figure 1 shows an isosbestic point, the photochemical process involves almost quantitative transfor-

Table 3. Direct and sensitized photolyses of 10mM-*cis,cis,cis*-cyclohepta-1,3,5-triene (**5*ccc***) in pentene and in neutral and acidic methanol[a]

Solvent	H_2SO_4 (M)	Sensitizer (mM)	Irradiation time (h)	Conversion (%)	Yield of (**6**) (%)[b]
Pentane	0	None	1	20	88
	0	Benzophenone(5)	12	9.1	1
	0	Triphenylene(0.5)	12	1.5	*c*
Methanol	0	None	2	26	89
	1.0	None	2	30	72
	1.0	Benzophenone(2.5)	12	1.0	*d*

[a] Irradiations were conducted under nitrogen at room temperature using a 300 W high-pressure mercury arc fitted with a Pyrex filter (>300 nm) for the direct photolyses or with a solution filter containing 10mM-1-naphthol (>345 nm) for the sensitized photolyses. [b] Chemical yield based on consumed (**5*ccc***). [c] Formation detected, but yield not determined owing to the low conversion. [d] Formation not detected (<1% yield).

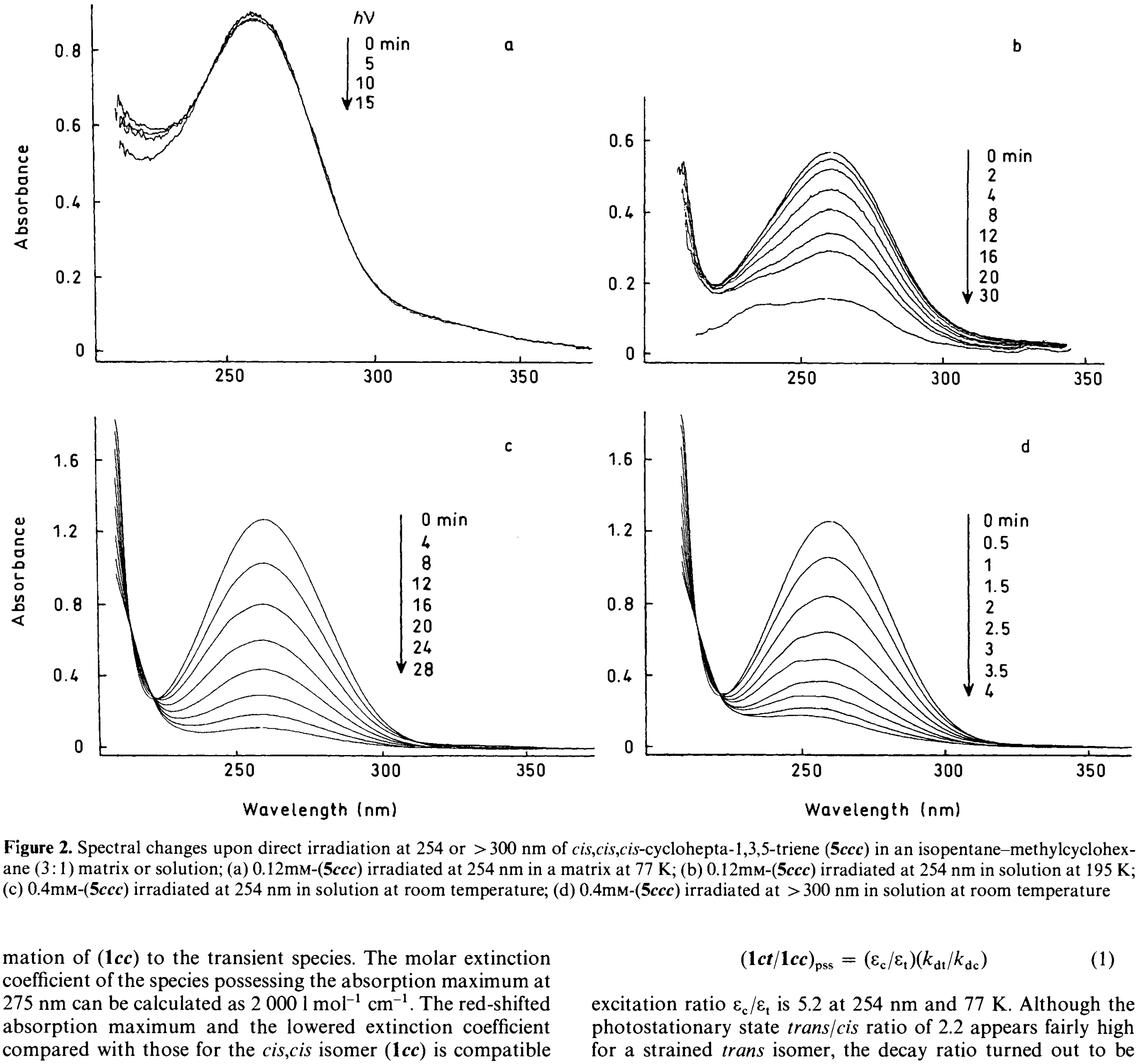


Figure 2. Spectral changes upon direct irradiation at 254 or > 300 nm of *cis,cis,cis*-cyclohepta-1,3,5-triene (**5*ccc***) in an isopentane–methylcyclohexane (3:1) matrix or solution; (a) 0.12mM-(**5*ccc***) irradiated at 254 nm in a matrix at 77 K; (b) 0.12mM-(**5*ccc***) irradiated at 254 nm in solution at 195 K; (c) 0.4mM-(**5*ccc***) irradiated at 254 nm in solution at room temperature; (d) 0.4mM-(**5*ccc***) irradiated at > 300 nm in solution at room temperature

mation of (**1*cc***) to the transient species. The molar extinction coefficient of the species possessing the absorption maximum at 275 nm can be calculated as 2 000 l mol^{-1} cm^{-1}. The red-shifted absorption maximum and the lowered extinction coefficient compared with those for the *cis,cis* isomer (**1*cc***) is compatible with the idea that the species observed is the *cis,trans*-isomer (**1*ct***) in view of the observations reported for some strained cycloalkenes.[16]

Quantitative analysis of the low-temperature irradiation provides further information about *cis–trans* photoisomerization of cycloheptadiene. Using the data in Figure 1 and those from extended irradiations, the corrected absorbances at 245 and 275 nm (A'_{245} and A_{275}), which are attributed to the *cis,cis* and *cis,trans* isomers respectively, are plotted as functions of irradiation time in Figure 3. Although the decrease in A'_{245} is nicely correlated with the increase in A_{275} at the initial stage, both values do not appear to reach plateaux upon prolonged irradiation, probably due to minimal direct photocyclization to (**2**). From the slopes at the initial and final stages, the approximate ratio of geometrical isomerization *versus* direct cyclization is 13:1, which interestingly coincides with that reported in the early stage of the direct photolysis at 248 nm of cyclo-octa-1,3-diene.[5]

As shown in Figure 4, the plot of A_{275}/A'_{245} gives the approximate photostationary state (**1*ct***)/(**1*cc***) ratio of 2.2. The decay ratio (k_{dt}/k_{dc}) from the excited singlet to (**1*cc***) and (**1*ct***) can be calculated as 0.42 from equation (1)[2d,17] where the

$$(\mathbf{1}ct/\mathbf{1}cc)_{pss} = (\varepsilon_c/\varepsilon_t)(k_{dt}/k_{dc}) \qquad (1)$$

excitation ratio $\varepsilon_c/\varepsilon_t$ is 5.2 at 254 nm and 77 K. Although the photostationary state *trans/cis* ratio of 2.2 appears fairly high for a strained *trans* isomer, the decay ratio turned out to be comparable with those for other strained cycloalkenes and cycloalkadienes as shown in Table 4.

The facile formation of the *cis,trans* isomer upon direct and sensitized photolyses indicates that the potential curves for the excited singlet and triplet states of cycloheptadiene are analogous to those of simple cycloalkenes notwithstanding the presence of the conjugating double bond. Thus the planar Franck–Condon singlet or triplet cycloheptadiene generated photochemically relaxes into the twisted excited state through rotation about one of the formal double bonds of the diene, which in turn decays to the ground state regenerating the *cis,cis* or *cis,trans* isomer.

Reactivity of cis,trans-*Cyclohepta*-1,3-*diene*.—The thermal behaviour of *cis,trans*-cyclohepta-1,3-diene (**1*ct***) generated photochemically is discussed in further detail. First, it should be noted that, unlike *trans*-cycloheptene,[2a] *cis,trans*-cycloheptadiene (**1*ct***) prepared at low temperature does not isomerize thermally to the *cis,cis* isomer (**1*cc***) but cyclizes exclusively to (**2**) upon warming. The availability of this facile cyclization process may rationalize the unexpectedly short lifetime of (**1*ct***) (7 min at 195 K) compared with that for *trans*-

cycloheptene (10 min at 274 K).[2a] It is also interesting that the lifetime of (**1*ct***) at 195 K is independent of the solvent polarity, as shown in Table 2. This indicates that the thermally allowed conrotatory cyclization of (**1*ct***) does not involve a polarized transition state.

The present cyclization may be compared with the thermal reaction of the next higher homologue, *cis,trans*-cyclo-octa-1,3-diene.[18] With one extra methylene in the ring, *cis,trans*-cyclo-octadiene is much more stable than (**1*ct***) and cyclizes fairly slowly to bicyclo[4.2.0]oct-7-ene with a rate constant of 3.7×10^{-5} s^{-1} at 70 °C (E_a 27.85 kcal mol^{-1}; log *A* 13.14),[18] while (**1*ct***) cyclizes with a ratio constant of 2.3×10^{-3} s^{-1} even at − 78 °C as demonstrated in the low-temperature experiment. Assuming the same pre-exponential factor, we can make a rough estimation of the energy of activation for the cyclization of (**1*ct***); E_a *ca.* 14 kcal mol^{-1}. This estimated energy of activation is somewhat smaller than that for the geometrical isomerization of *trans*-cycloheptene (E_a 17.4 kcal mol^{-1}) reported previously,[2a] which probably rationalizes the predominant thermal cyclization, rather than *trans–cis* isomerization, of (**1*ct***).

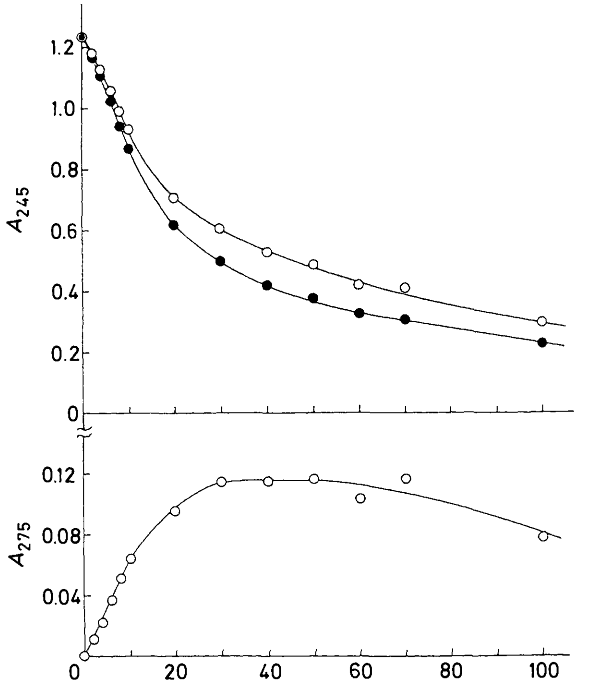


Figure 3. Plots of absorbances at 245 (top) and 275 nm (bottom) as a function of irradiation time in the direct photolysis of (**1*cc***) at 254 nm in a rigid matrix at 77 K; (○) original data from Figure 1 and extended irradiations; (●) corrected absorbance at 245 nm for the contribution of the *cis,trans*-isomer (**1*ct***)

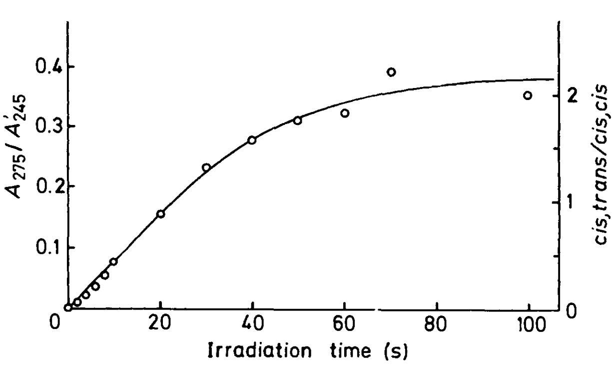


Figure 4. *cis,trans*/*cis,cis* Ratio of cyclohepta-1,3-diene, calculated from the corrected absorbances at 275 and 245 nm (Figure 3), as a function of irradiation time

In acidic methanol, rapid protonation to (**1*ct***), though a bimolecular process, competes with unimolecular cyclization, giving rise to the methanol adducts (**3**) and (**4**). Based on the labelling experiment in deuteriated methanol, the reaction mechanism shown in Scheme 1 is proposed. Protonation by route a leads to an allylic cation (**7**), which subsequently gives adduct (**3**). On the other hand, protonation by route b affords a homoallylic cation (**8**), which isomerizes to a cyclopropylmethyl cation (**9**)[15,19] and then gives adducts (**4n** and **x**) in 3:1 ratio. The predominant incorporation of a deuterium atom at the 7-*exo* position of adducts (**4**) obtained from photolysis in acidic methan[^{2}H]ol can be interpreted more reasonably in terms of a bridged homoallylic cation (**10**).

The relative rates of the competing cyclization and protonation processes are evaluated by quantitative analysis of the photoreaction in methanol of various acid concentrations, shown in Table 1. The photochemistry of (**1*cc***) is expressed by

$$(\mathbf{1}cc) \xrightarrow{h\nu} {}^1(\mathbf{1}cp) \quad (2)$$

$$^1(\mathbf{1}cp) \xrightarrow{k_{dc}} (\mathbf{1}cc) \quad (3)$$

$$\xrightarrow{k_{dt}} (\mathbf{1}ct) \quad (4)$$

$$(\mathbf{1}ct) \xrightarrow{k_{cy}} (\mathbf{2}) \quad (5)$$

$$\xrightarrow[\text{H}^+,\text{MeOH}]{k_{pr}} (\mathbf{3}) + (\mathbf{4}) \quad (6)$$

Scheme 2.

the sequence in Scheme 2 where ^{1}(**1*cp***) represents the perpendicular, excited singlet state of cycloheptadiene.

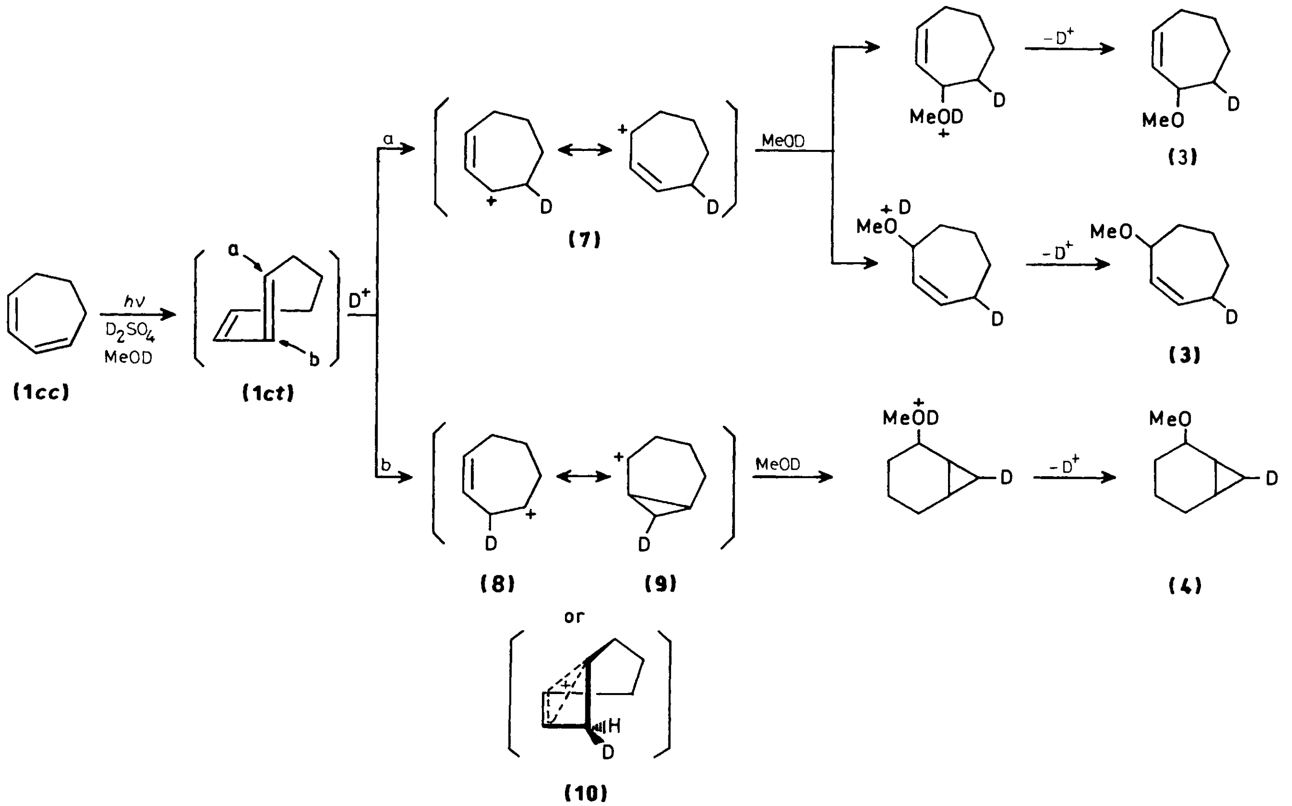
A steady-state treatment of sequence (2)–(6) leads to expression (7) for the reciprocal quantum yield of the adducts (**3**) and (**4**). According to equation (7), the reciprocal of the combined yield of (**3**) and (**4**) is plotted as a function of the reciprocal acid concentration to give the good straight line shown in Figure 5. From the slope and intercept, the ratio of the rate constants for cyclization and protonation, k_{cy}/k_{pr}, is calculated as 0.30 mol l^{-1}. A similar experiment on the trip-

$$1/\Phi_{(3)\,+\,(4)} = [(k_{dc} + k_{dt})/k_{dt}][1 + k_{cy}/(k_{pr}[\text{H}^+])] \quad (7)$$

Table 4. Photostationary state, excitation, and decay ratios for some cycloalkenes and cycloalkadienes

Compd.	Excitation	Temp. (K)	$(t/c)_{pss}$	$\varepsilon_c/\varepsilon_t$ or (k_{qc}/k_{qt})	k_{dt}/k_{dc}
Cycloheptene	Toluene-sens.[a]	195	0.07		
Cyclo-octene	Direct (185 nm)[b]	298	0.96	1.1	0.88
	Benzene-sens.[c]	298	0.20	0.35	0.5
Cyclohepta-1,3-diene	Direct (254 nm)[d]	77	2.2	5.2	0.42
Cyclo-octa-1,3-diene	Direct (248 nm)[e]	298	0.60		
	Propiophenone-sens.[f]	288	0.45		

[a] Ref. 2*a*. [b] Ref. 2*d*. [c] Ref. 17. [d] This work. [e] Ref. 5. [f] Ref. 4.



Scheme 1.

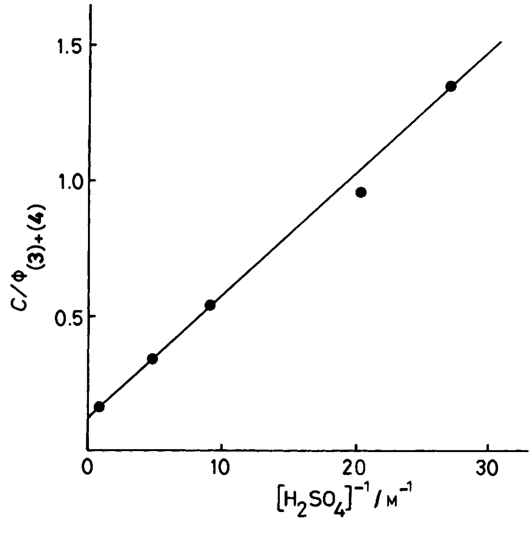


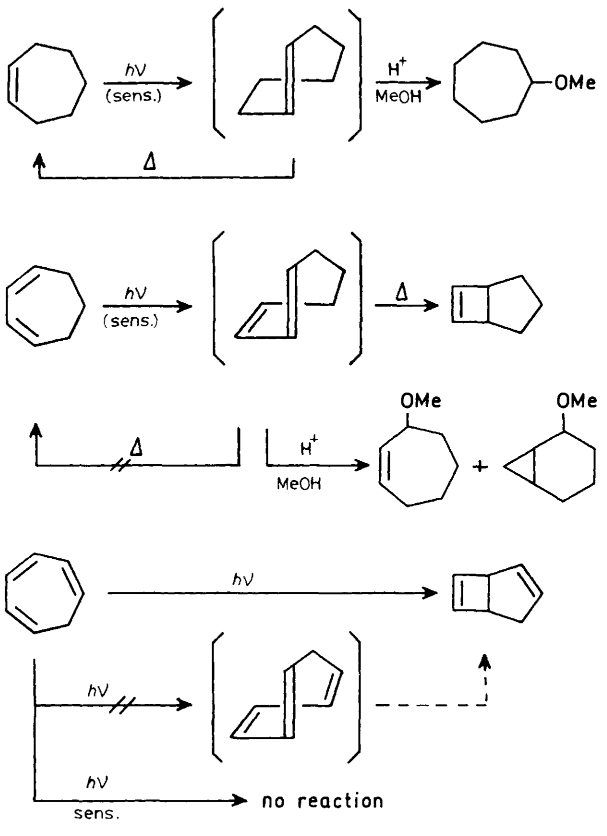
Figure 5. Reciprocal combined yield of (3) and (4) as a function of reciprocal acid concentration in the direct photolysis of (**1***cc*) at 254 nm in acidic methanol

let sensitization gave a similar k_{cy}/k_{pr} value of 0.27 mol l^{-1}, which again indicates the intervention of *cis,trans*-cycloheptadiene as a common intermediate in direct and sensitized photolyses. Thus bimolecular protonation can compete well with unimolecular cyclization at high acid concentration.

Cycloheptatriene.—In sharp contrast to the cycloheptadiene case, there is no indication of the intermediacy of a reactive species in the photochemistry of cyclohepta-1,3,5-triene (**5***ccc*). Although direct irradiation of (**5***ccc*) does afford predominantly the cyclization product (**6**), no intermediate is trapped chemically by the highly acidic methanol or detected spectroscopically in low-temperature irradiation. These results all indicate that, unlike cycloheptadiene, cycloheptatriene in the excited singlet state does not isomerize geometrically to the strained *cis,cis,trans* and/or *cis,trans,cis* isomer but undergoes photochemically allowed disrotatory cyclization directly giving bicycloheptadiene (**6**), probably along with a degenerate 1,7-sigmatropic hydrogen shift.[14] However, the photocyclization of (**5***ccc*) is deduced to be at least one order of magnitude less efficient than the geometrical isomerization of (**1***cc*) and appears to be comparable in yield with the direct photocyclization of (**1***cc*), since, under analogous optical conditions, absorbance due to (**5***ccc*) decreases quite slowly even in the fluid solution; compare Figures 1 and 2b,c. As shown in Figure 2a, this cyclization does not appear to proceed in appreciable yield in a rigid matrix at 77 K, which is attributable probably to the greater conformational change upon cyclization than that required in the geometrical photoisomerization of cycloheptadiene under the same matrix conditions. Furthermore, triplet sensitization also fails to demonstrate intervention of any species which is reactive to acidic methanol.

The failure of the excited singlet and triplet cycloheptatrienes to undergo geometrical isomerization may suggest that the potential curves for the conjugated triene no longer resemble those postulated for cycloheptene or cycloheptadiene and the rotation about the double bond does not mean relaxation in the excited states, although the increased rigidity of its framework would also be partly responsible.

Conclusions.—Possessing a common seven-membered ring, cycloheptene, cycloheptadiene, and cycloheptatriene exhibit distinctly different photochemical and subsequent thermal behaviour. Geometrical isomerization giving rise to a highly strained *trans* isomer is a major decay path for the singlet and



Scheme 3.

triplet excited states of cycloheptene and cycloheptadiene. Although both *trans* isomers are stable at sufficiently low temperatures and are trapped chemically, *cis,trans*-cycloheptadiene, unlike *trans*-cycloheptene, does not regenerate the *cis,cis*-isomer upon warming but cyclizes preferentially to bicycloheptene. Upon direct excitation, cycloheptatriene cyclizes directly to bicycloheptadiene without passing through a strained *trans*-isomer, while no appreciable reaction takes place upon triplet sensitization, where the concerted cyclization is not an allowed process. The lack of a *trans* isomer in the photochemistry of cycloheptatriene suggests that the conventional potential curve for simple alkenes is not applicable to the conjugated triene system.

Experimental

Materials.—Cycloheptadiene and cycloheptatriene (Nakarai) were purified by fractional distillation. The photosensitizers (Nakarai) were purified by repeated recrystallization from methanol. Pentane, isopentane, methylcyclohexane, cycloheptane, and cyclo-octane were stirred over sulphuric acid until the acid layer no longer turned yellow, washed with water, dried (K_3CO_3), and fractionally distilled. Methanol was fractionally distilled after refluxing overnight with magnesium turnings. Methan[^{2}H]ol (CEA), sulphuric acid (Nakarai, 'guarantee grade'), and [$^2H_2$]sulphuric acid (Merck) were used without further purification.

Analyses.—^{1}H N.m.r. spectra were measured in [^{2}H]chloroform on a Jeol PMX-60 or GX-400 spectrometer. I.r. spectra were recorded on a JASCO A-100 spectrometer. Mass spectra were recorded at 70 eV on a Hitachi RM-50GC instrument.

G.l.c. analyses were performed on a 1.5 m column of 10% Apiezon L grease; cycloheptane or cyclo-octane was used as internal standard. After irradiation, neutral mixtures were directly analysed by g.l.c. The acidic photolysate was poured into an excess of aqueous potassium carbonate solution and its pentane extract was subjected to g.l.c. analysis. The results were consistent with those from the direct injection onto a column of the acidic mixture, within experimental error.

Photolyses.—Most irradiations were carried out under nitrogen at 254 nm using quartz tubings and a 30 W mercury resonance lamp (Eikosha Co.) fitted with a Vycor filter as a light source. For irradiations at >300 nm, Pyrex tubings and a 300 W high-pressure mercury lamp (Eikosha) were employed. Kinetic studies were carried out in a merry-go-round apparatus at room temperature. Preparative-scale irradiations of (**1cc**) were conducted in a doughnut-shaped quartz vessel using a 30 W mercury resonance lamp.

Low-temperature irradiations and subsequent spectral monitoring were performed in a rigid matrix (isopentane–methylcyclohexane 3:1) at 77 K (liquid nitrogen) or in solution at 195 K (dry ice–methanol) using a quartz cell ($10 \times 10 \times 45$ mm) and a quartz Dewar vessel with transparent windows suitable for irradiation and monitoring.

Thermal Reactions.—Thermal reactions of (**1cc**) and *endo*-2-methoxynorcarane (**4n**) were performed in methanol containing 1M-sulphuric acid in stoppered flasks maintained at 25 °C or room temperature. Portions removed periodically from the bulk mixture were analysed as mentioned above to determine the conversions and product yields.

Product Identification.—Preparative-scale irradiation at 254 nm of (**1cc**) (0.14 g) in acidic methanol (10 ml, 1M-H_2SO_4) and the subsequent separation of the photolysate by preparative g.l.c. gave the methanol adducts (**3**) and (**4**). The products (**3**) and (**4**) showed the same g.l.c. retention times with those of the authentic specimens (**3**) and (**4n**) synthesized independently and the identical ^{1}H n.m.r. spectra (60 MHz) with those reported[20] for (**3**), (**4n** and **x**). The 400 MHz n.m.r. spectrum of isolated (**4**) showed that the adduct is a 3.0:1 mixture of *endo*- and *exo*-isomers (**4n** and **x**) as judged from the intensities of 7-*endo* protons* at δ 0.35 (t) and −0.04 (t) for (**4n** and **x**), respectively.

The irradiation of (**1cc**) (0.24 g) in methan[^{2}H]ol (10 ml, 1M-[$^2H_2$]SO_4) and the subsequent isolation by g.l.c. afforded the monodeuteriated adducts [^{2}H]-(**3**) and [^{2}H]-(**4**). The 400 MHz n.m.r. spectrum of the isolated [^{2}H]-(**4**) showed that the adduct is a 3.5:1 mixture of *endo* and *exo* isomers (**4n** and **x**), and that one deuterium atom is incorporated predominantly at the 7-*endo* position as judged from the intensity ratio of the 7-*endo* and 7-*exo* proton signals (8.3:1).

Authentic 3-methoxycycloheptene (**3**) was synthesized by methylation (NaH–CH_3I) of cyclohept-2-enol (50% yield), which was prepared from the singlet oxygenation (*h*ν–Methylene Blue–O_2) of cycloheptene followed by reduction of the product hydroperoxide with $NaBH_4$ (80% yield): $\nu_{max.}$ (neat) 2 850, 2 815, 1 650, 1 395, 1 105, and 680 cm; δ (60 MHz; CCl_4) 5.60—5.70 (m, 2H), 3.60—3.75 (m, 1H), 3.20 (s, 3H), and 1.10—2.25 (br, 8H); *m/z* (70 eV) 126.

endo-2-Methoxynorcarane (**4n**) was synthesized by Simmons–Smith reaction (Zn–Cu, CH_2I_2) of 2-methoxycyclohexene (64% yield), which was prepared by $LiAlH_4$ reduction of cyclohexen-2-one (60% yield) and the subsequent methylation with NaH and CH_3I (50% yield): $\nu_{max.}$ (neat) 3 000, 2 930, 1 440, 1 100, 1 020, and 730 cm^{-1}; δ (60 MHz; $CDCl_3$) 3.67 (m, 1H), 3.34 (s, 3H), 0.8—1.9 (m, 8H), and 0.19—0.70 (m, 2H); *m/z* (70 eV) 126.

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* The 7-*endo* proton of (**4n**) was assigned by comparing its chemical shift (δ 0.35) with that (δ 0.33) of *endo*-2-norcaranol.[21]

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