

Sensitised Photolysis of *cis*-Cyclo-octene Vapour ¹

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The mercury-sensitised photolysis of *cis*-cyclo-octene (1c) gave octa-1,7-diene and three bicyclo-octanes as the major products. The reaction is interpreted in terms of three intramolecular hydrogen transfers, *i.e.* [1,2], [1,4], and [1,5] shifts. The most important primary process is the [1,5] hydrogen shift through a six-membered transition state resulting in a cyclic 1,4-diradical intermediate. The 1,4-diradical thus formed undergoes competitive cyclisation and β -cleavage, thus providing an analogy with the Norrish type II reaction of carbonyl compounds. The kinetics of the reaction indicate that the precursor to hydrogen abstraction is a vibrationally excited π,π^* triplet of (1c). With benzene as sensitiser only the products formed by a [1,5] hydrogen shift are observed (together with formation of *trans*-cyclo-octene) and this is consistent with a ready type II-like reaction.

A NUMBER of studies of photolysis of alkenes in the vapour phase sensitised by mercury, benzene, *etc.* have been reported. It is generally agreed that the triplet state of open-chain alkenes undergoes allylic C-C and C-H bond cleavage in addition to *cis-trans*-isomerisation upon mercury photosensitisation in the vapour phase.² With cycloalkenes, where *cis-trans*-isomerisation *via* triplet species is geometrically difficult, only allylic fission takes place.³ Since allylic fission is not observed in liquid-phase photolysis, the peculiar reactivity of triplet alkenes in the vapour phase is believed to arise from vibrational excitation of the triplet species. The vibrationally excited triplet of alkenes has also been reported to undergo molecular rearrangement to cyclopropane derivatives *via* an intramolecular [1,2] shift of the allylic hydrogen.^{4,5} We now report novel behaviour of the vibrationally excited triplet of *cis*-cyclo-octene (1c).

EXPERIMENTAL

Materials.—*cis*-Cyclo-octene (1c). Commercially available cyclo-octene was purified by preparative g.l.c. on poly-

¹ Preliminary report, S. Takamuku, K. Moritsugu, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1971, **44**, 2562.

² (a) J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, ch. 2; (b) H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, 1963, **1**, 209.

ethylene glycol-6000 (PEG) to a purity of 99.5%. The product contained a small amount (0.5%) of cyclo-octane but was free from the *trans*-isomer (1t).

[5,6-²H₂]cis-Cyclo-octene. To a stirred solution containing cyclo-octa-1,5-diene (25 g, 0.23 mol) in CCl₄ (150 cm³) at -10° was added dropwise bromine (33.3 g, 0.21 mol) in CCl₄ (50 cm³). On removal of the solvent and the excess of diene, an oily residue was obtained which when fractionated under reduced pressure gave 5,6-dibromocyclo-octene (27 g, 44%), b.p. 91—95° at 1.0 mmHg, (CCl₄) δ 5.7br (2 H, s), 4.65br (2 H, s), and 1.8—3.0 (8 H, m). Reduction of the dibromide (25.0 g, 0.093 mol) was conducted with a mixture of LiAlD₄ (1.0 g, 0.024 mol; Merck) and LiD (2.5 g, 0.31 mol; Merck) in tetrahydrofuran under reflux. Basic work-up⁶ gave a mixture (7.1 g), b.p. 140—150° at 760 mmHg, composed mainly of [5,6-²H₂]cyclo-octene (27%) and cyclo-octa-1,5-diene (65%). Separation by preparative g.l.c. on a PEG column afforded the labelled cyclo-octene containing 1.1% bicyclo[5.1.0]octane (3), 0.2% cyclo-octane, and 0.05% bicyclo[3.3.0]octane (5). The i.r. spectrum of the

³ (a) G. R. De Maré, O. P. Strausz, and H. E. Gunning, *Canad. J. Chem.*, 1965, **43**, 1329; (b) G. R. De Maré, *Bull. Soc. chim. belges*, 1972, **81**, 459.

⁴ R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, 1962, **37**, 543.

⁵ Y. Inoue, M. Kadohira, S. Takamuku, and H. Sakurai, *Tetrahedron Letters*, 1974, 459.

⁶ J. E. Johnson, R. H. Blizzard, and H. W. Carhart, *J. Amer. Chem. Soc.*, 1948, **70**, 3664.

deuteriated compound showed an absorption at $2\ 180\text{ cm}^{-1}$ attributable to C-D stretching. The isotopic purity (98.9%) was confirmed by n.m.r. and mass spectrometry.

Quantitative Photolyses.—All experiments were carried out at room temperature and under static conditions. Mercury photosensitisation in the vapour phase was conducted using cylindrical quartz cells, 5 cm long and 5 cm in diameter, and a conventional vacuum system. A mercury-free vacuum system and similar cylindrical cells were used for benzene photosensitisation in the vapour phase. Both sensitisations were performed using a spiral array of 30 W low-pressure mercury lamps fitted with a Toshiba UV-25 filter which removes the 184.9 nm resonance line of mercury. The lamps were allowed to warm up for at least 30 min before each run in order to reach a stable operating condition. A control run revealed that no detectable reaction occurred in the absence of u.v. irradiation. The quantum yield (ϕ) for mercury sensitisation was determined by propane actinometry at 300 Torr, where $\phi(\text{H}_2)$ was taken as unity.⁷ The absorption of the incident radiation was incomplete in the cell and appropriate corrections were made in the determination of the quantum yields.

After each run, products were trapped in a capillary at -196° . The non-condensable products were analysed and measured by a combination of Toepler pump gas burette, and Pd chamber. The condensables were analysed by g.l.c. on a 6 m column of 20% β,β' -oxydipropionitrile (ODPN) on Celite at 70° . All products, which can be separated cleanly from each other under these conditions, had retention times identical with those of authentic specimens on g.l.c. employing ODPN, PEG, and dinonyl phthalate columns. Analysis of dimeric products from the mercury sensitisation was performed by g.l.c. on a 1.5 m FFAP column on Celite at 150° . The molecular weights of the dimers were measured using a Hitachi RMS-4 g.l.c.-mass spectrometer combination.

Preparative Photolyses.—The preparative scale mercury-sensitised photolysis of (1c) was carried out at its b.p. at atmospheric pressure. A cylindrical quartz cell, 20 cm long and 2 cm in diameter, was mounted vertically along the axis of a helical array of 30 W low-pressure mercury lamps. The lower end of the cell, where an externally heated tray containing mercury (ca. 1 g) was interposed, was connected to a flask in which (1c) (70 g), with hydroquinone (1 g) as an inhibitor, was placed. The top end of the cell was attached to a reflux condenser. On heating the contents of the flask, the vapour of the substrate and mercury ascended the cell, condensed at the cold surface at the top, and dropped back into the flask. The heat from the lamp prevents any condensation on the wall of the cell. After irradiation for 80 h, the contents of the flask were fractionated through a spinning band column to give a fraction (18.6 g), b.p. $120\text{--}145^\circ$ at 760 mmHg. Isolation of the products was performed by preparative g.l.c. on PEG. The n.m.r. and mass spectra of the products agreed exactly with those of authentic specimens which were either commercial (octa-1,7-diene) or independently synthesised.

Independent Synthesis of Authentic Specimens.—Bicyclo[5.1.0]octane (3) was prepared by a Simmons-Smith reaction

* The product reported as cyclo-octane in ref. 1 was identified as (3) by g.l.c.

⁷ K. Yang, *J. Amer. Chem. Soc.*, 1967, **89**, 3941.

⁸ E. LeGoff, *J. Org. Chem.*, 1964, **29**, 2048.

⁹ W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, 1962, **27**, 1910.

of cycloheptene with dibromomethane in the presence of zinc-copper couple according to the procedure described by LeGoff.⁸

Bicyclo[4.2.0]octane (4) was synthesised by photocyclisation of cyclo-octa-1,3-diene to bicyclo[4.2.0]oct-7-ene⁹ and subsequent hydrogenation of the bicyclo-octene to (4) over platinum.

Bicyclo[3.3.0]octane (5) was synthesised by potassium catalysed cyclisation of cyclo-octa-1,3-diene to bicyclo[3.3.0]oct-2-ene¹⁰ and subsequent hydrogenation over platinum.

trans-Cyclo-octene (1t) was prepared by a three-step process starting from (1c). The procedure consisted of performic acid oxidation of (1c) to *trans*-cyclo-octane-1,2-diol,¹¹ followed by condensation with benzaldehyde to give the acetal, and subsequent treatment with *n*-butyl-lithium¹² to give (1t).

RESULTS

Mercury-sensitised Photolysis.—The major products of the mercury photosensitisation of (1c) were hydrogen, ethylene, hexa-1,5-diene, octa-1,7-diene (2), bicyclo[5.1.0]octane (3),* bicyclo[4.2.0]octane (4), bicyclo[3.3.0]octane (5), and *trans*-cyclo-octene (1t). The quantum yields of the products are shown in Table 1. The yield of hexadiene equals that of ethylene. Although a search was made for cyclo-octane and dimeric C_{16} compounds which are familiar radical products in mercury photosensitisation of alkenes,^{2,3} these were not observed in significant yields ($\phi < 0.02$). G.l.c.-mass spectrometric analysis showed that the dimeric products were composed of $\text{C}_{16}\text{H}_{26}$, $\text{C}_{16}\text{H}_{28}$, and $\text{C}_{16}\text{H}_{30}$, which may correspond to bicyclo-octenyl, cyclo-octylcyclo-octene, and bicyclo-octyl, respectively. The fragmentation pattern of the mass spectra suggested the absence of cyclic dimers with a cyclobutane ring.

The product distribution for a short reaction time (1 min) was in good agreement with the results shown in Table 1 thus indicating that these are the primary photoproducts.

An experiment was performed with a small amount of nitric oxide added as a radical scavenger since radical-induced reactions caused by excited mercury atoms are well known in mercury photosensitisation of hydrocarbons.² As is shown in Table 1, the yields of the major photoproducts were not affected by the addition of nitric oxide.

The effect of pressure on the product yields was examined up to 150 Torr by adding carbon dioxide as an inert gas since the range available was limited by the low vapour pressure (ca. 6 Torr) of the substrate at room temperature. The effect of the pressure on suppressing product yields is evident from the data in Figure 1.

Since the formation of (4) and (5) was considered to involve hydrogen transfer at the 5- and 6-position of (1c), $[\text{5,6-}^2\text{H}_2]$ cyclo-octene was synthesised and subjected to mercury sensitisation in order to examine isotope effects on the reaction. The reaction was carried out under comparable conditions, and afforded similar results except for somewhat different distribution of the products, as shown in Table 2. Detectable decreases in deuterium content were not observed by mass spectrometry of the products (2)—(5)

¹⁰ P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, 1965, **30**, 3006.

¹¹ A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Amer. Chem. Soc.*, 1952, **74**, 5884.

¹² J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Comm.*, 1968, 1593.

and (1*t*). Mass spectrometric analysis also revealed that at least 80% of the hexadiene produced contains *two* deuterium atoms, suggesting predominant elimination of [²H₀]ethylene.

The study of the effect of pressure was repeated for the mercury sensitisation of the deuteriated cyclo-octene with added carbon dioxide under comparable conditions, since deuteriation at the 5- and 6-position of (1*c*) is expected to affect the rate of hydrogen transfer. As shown in Figure 2,

using a mercury-free vacuum system. As shown in Table 1, benzene sensitisation of (1*c*) afforded mainly (1*t*) along with (2), (4), and trace amounts of ethylene and hexa-1,5-diene. It is noteworthy that except for (1*t*) benzene sensitisation gave only two of the isomeric products obtained by mercury sensitisation.

Liquid-phase photolysis of (1*c*) was attempted with benzene or xylene as a sensitizer to give (1*t*) as sole product in

TABLE 1
Sensitised photolysis of (1*c*)

Sensitiser	<i>p</i> /Torr		Exposure time/min	Products							
	(1 <i>c</i>)	NO		(2)	(3)	(4)	(5)	(1 <i>t</i>)	Hexadiene	C ₂ H ₄	H ₂
Mercury ^a	4.5	0	3.0	0.181	0.049	0.128	0.025	0.075	0.017	0.019	0.017
	4.5	0.5	3.0	0.191	0.049	0.129	0.025	0.074	0.018	<i>c</i>	<i>c</i>
Benzene ^b	5.0	0	15.0	0.010	<i>d</i>	0.006	<i>d</i>	0.107	0.001	<i>c</i>	<i>d</i>

^a Yields shown as ϕ . ^b 5 Torr benzene added as sensitiser. Yields shown in μmol . ^c Not determined. ^d Not detected.

TABLE 2
Mercury photosensitisation of (1*c*) and its [5,6-²H₂] isomer

Compound	<i>p</i> /Torr	Exposure time/min	Products (μmol) ^a						
			(2)	(3)	(4)	(5)	(1 <i>t</i>)	Hexadiene	C ₂ H ₄
(1 <i>c</i>)	4.0	4.0	0.812	0.311	0.578	0.109	0.538	0.013	0.013
[5,6- ² H ₂]- (1 <i>c</i>)	4.0	4.0	0.744	0.401	0.541	0.092	0.666	0.009	0.010

^a Average of four independent runs.

the product yields decrease with increasing pressure as in the case of (1*c*) except for greater reduction of the yields of (2) and (4).

In a separate experiment, mercury photosensitisation of *trans*-cyclo-octene (1*t*) under similar conditions gave analogous products, *i.e.* hydrogen, ethylene, hexa-1,5-diene, (2)—(5), and (1*c*) with a different distribution of products. A control run, however, revealed that the substrate suffers isomerisation to a limited extent (*ca.* 3%) to the *cis*-isomer in the absence of irradiation. *trans-cis*-Isomerisation in the dark may be caused by any active sites on the glass surface of the vacuum system. Therefore, some uncertainty

agreement with the literature.¹³ Analysis by g.l.c. showed the absence of peaks corresponding to isomers (2)—(5).

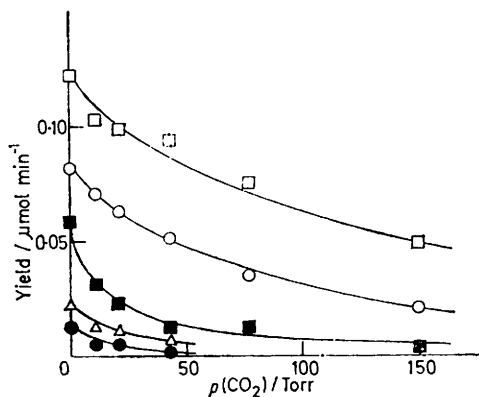


FIGURE 1 Product yield as a function of added CO₂ pressure in the mercury sensitisation of (1*c*). The pressure of the substrate is 3.0 Torr: (2), □; (3), ■; (4), ○; (5), △; (1*t*), ●.

in the determination of the yield of (1*t*) is unavoidable in the photolysis of (1*c*).

Benzene-sensitised Photolysis.—Vapour-phase photolysis of (1*c*) was examined with benzene vapour as sensitiser

¹³ J. S. Swenton, *J. Org. Chem.*, 1969, **34**, 3219.

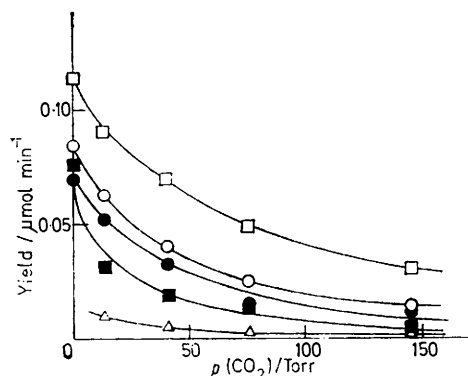
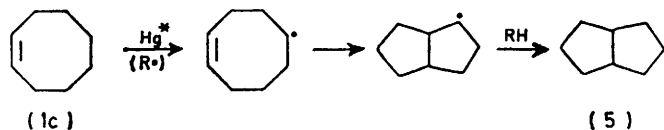


FIGURE 2 Product yield as a function of added CO₂ pressure in the mercury sensitisation of [5,6-²H₂]- (1*c*). The pressure of the substrate is 3.0 Torr: (2), □; (3), ■; (4), ○; (5), △; (1*t*), ●.

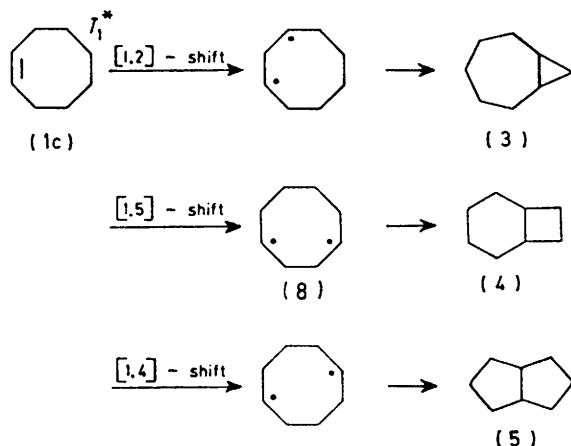
DISCUSSION

It is generally accepted that a primary process between an excited mercury atom (6^3P_1) and an alkene molecule leads to a vibrationally excited triplet state of the alkene.^{2,3} In the present system, the pressure dependence of the product yields and the lack of inhibition by nitric oxide indicated the formation of a vibrationally excited cyclo-octene triplet; this is inconsistent with the accepted view on alkene photochemistry. The cyclo-octene triplet thus formed underwent unique isomerisation reactions to give three bicyclo-octanes (3)—(5) in contrast to other alkene triplets generated by mercury photosensitisation, which have hitherto been reported

to undergo allylic C-H and/or C-C bond cleavage.^{2,3} The lack of inhibition by nitric oxide indicates that the formation of the bicyclo-octanes cannot be explained in terms of a radical-initiated cyclisation as exemplified for

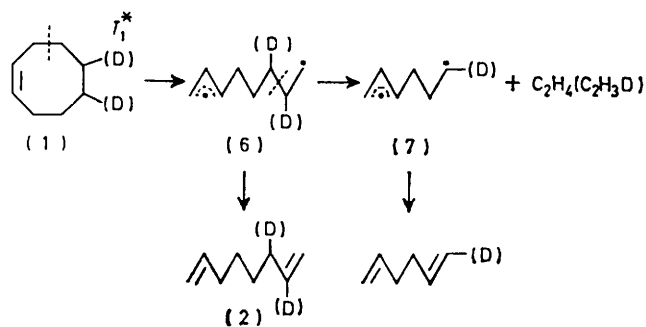


bicyclo[3.3.0]octane. Bicyclo[5.1.0]octane (3) is probably formed *via* a [1,2] shift of an allylic hydrogen atom as in the formation of bicyclo[4.1.0]heptane in the photolysis of cycloheptene.⁵ The mechanism of formation of the other bicyclo-octanes also involves intramolecular hydrogen-transfer processes followed by closure of the resulting cyclic diradicals (Scheme 1).[†]



SCHEME 1

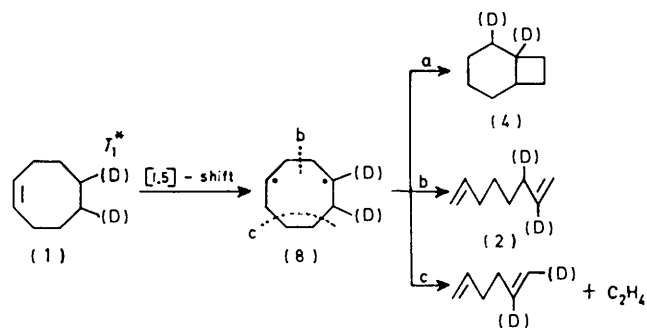
On the other hand, the α,ω -dienes might result from intramolecular disproportionation of the allylic diradicals (6) and (7) produced by the familiar allylic C-C cleavage (Scheme 2).



SCHEME 2

[†] A complex of (1c) with excited mercury may be postulated as the precursor of transannular hydrogen abstraction. It was reported that saturated hydrocarbons form mercury complexes which show new u.v. emissions in the region 250–280 nm. Unsaturated hydrocarbons, however, do not show new u.v. emissions and are considered not to form such complexes (O. P. Strausz, J. M. Campbell, S. De Pauli, H. S. Sandhu, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1972, **95**, 732). The formation of (2) and (4) in benzene sensitisation also suggests that a vibrationally excited triplet of (1c) is more probable than a mercury complex as precursor.

There are, however, some mechanistic ambiguities in the formation of the α,ω -dienes, since it cannot be reasonably explained why allylic diradicals such as (6) and (7) undergo intramolecular disproportionation preferentially to form α,ω -dienes without giving the more stable conjugated 1,3-dienes. Furthermore, it is difficult



SCHEME 3

to rule out the possibility that the diradical (7) cyclises to cyclohexene and/or vinylcyclobutane.[‡]

As an alternative mechanism for the formation of α,ω -dienes, the intervention of the cyclic 1,4-diradical (8), which was proposed as a precursor of (4) may be considered (Scheme 3). β -Cleavage of such a 1,4-diradical is a well known reaction.¹⁴ The most remarkable feature of the mechanism is that the resulting dienes should be exclusively terminal. If the cyclic diradical (8) undergoes elimination of ethylene yielding an equimolar amount of hexa-1,5-diene (path c in Scheme 3), the allylic diradical (6) in Scheme 2 may also be ruled out as the precursor of the decomposition products. Since the position from which ethylene molecule is eliminated in (1c) is different in the intermediates (6) and (8), the two mechanisms are clearly distinguishable by the deuterium labelling at the 5- and 6-position of (1c) as illustrated in Schemes 2 and 3. Photolysis of [5,6-²H₂]cis-cyclo-octene gave hexadiene, for which mass spectrometric analysis revealed the presence of >80% [²H₂]hexa-1,5-diene.[§] We conclude that most of the ethylene is attributable to molecular elimination from (8), and this may be considered as evidence in support of path b in Scheme 3 for the formation of (2), which is more reasonable than Scheme 2.

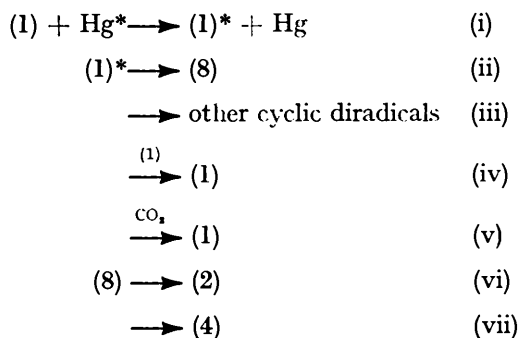
However, it remains unanswered whether the formation of the octadiene (2) *via* the allylic diradical (6) is thoroughly ruled out. One might suppose that the octadiene was attributable to both the allylic diradical (Scheme 2) and the cyclic biradical (Scheme 3). A study of the kinetics of the photolysis of (1c) and the [5,6-²H₂]isomer will provide further evidence on the mechanisms

[‡] Actually a diradical similar to (7) postulated in the photolysis of cyclohexene vapour^{3a} cyclises to vinylcyclobutane. We could not observe any formation of cyclohexene and vinylcyclobutane in the photolysis of (1c).

[§] The deuterium distribution in the resulting [²H₂]hexadiene could not be confirmed.

¹⁴ (a) C. D. Gutsche and J. W. Baum, *J. Amer. Chem. Soc.*, 1968, **90**, 5862; (b) E. J. Corey and E. Block, *J. Org. Chem.*, 1969, **34**, 1233.

of formation of the octadiene. Deuterium substitution at the 5- and 6-positions of (1c) is expected to cause a marked decrease in the rate of hydrogen transfer from these positions and, therefore, in the rate of the formation of bicyclo[4.2.0]octane. On the other hand, the rate of formation of the octadiene formed *via* the allylic diradical would not be affected by deuterium labelling, since the rate-determining step is probably fission of the allylic C-C bond. Therefore, if some octadiene was formed *via* the allylic diradical, a smaller isotope effect would be observed in the formation of octadiene compared with that of bicyclo[4.2.0]octane. The sequence (i)–(vii) is proposed for the formation of (2) and (4), the small amount of decomposition of (1)* and quenching of excited mercury by CO₂ being neglected. 'Other cyclic



diradicals' include the cyclic 1,3- and 1,5-species shown in Scheme 1; the asterisk represents the excited triplet state.

A steady-state treatment of sequence (i)–(vii) results in equation (viii) for the reciprocal of quantum yield

$$1/\phi_{(8)} = 1 + k_{\text{iii}}/k_{\text{ii}} + k_{\text{iv}}[(1)]/k_{\text{ii}} + k_{\text{v}}[\text{CO}_2]/k_{\text{ii}} \quad \text{(viii)}$$

$$1/\phi_{(2)} = (1 + k_{\text{vii}}/k_{\text{vi}})(1/\phi_{(8)}) \quad \text{(ix)}$$

$$1/\phi_{(4)} = (1 + k_{\text{vii}}/k_{\text{vii}})(1/\phi_{(8)}) \quad \text{(x)}$$

of the diradical (8) *versus* CO₂ pressure, and (ix) and (x) for those of (2) and (4). In Figures 3(a) and (b), the reciprocals of yields of (2) and (4) from photolysis of (1c) and the [5,6-²H₂]isomer are plotted against CO₂ pressure and good linear relations are obtained. Assuming that the value $k_{\text{vi}}/k_{\text{vii}}$ for both (1c) and the [5,6-²H₂]isomer to be identical, the isotope effect on the rate of process (ii), denoted by ' $k_{\text{H}}/k_{\text{D}}$ ',† is estimated from the slopes of both equations (ix) and (x). From Figures 3(a) and (b) the value of ' $k_{\text{H}}/k_{\text{D}}$ ' for the formation of (2) is 1.67 and for (4) is 1.70; these values are in good agreement. Despite the negligible difference in the quantum yield ($\phi_{\text{H}}/\phi_{\text{D}}$ in Table 3), the rates of formation of (2) and (4) decreased to a similar extent upon deuteri-

† In this work, only half the hydrogens at the 5- and 6-positions of (1c) were replaced by deuterium. The term ' $k_{\text{H}}/k_{\text{D}}$ ' means k_{H} for (1c)/ k_{H} for the labelled isomer.

‡ A recent report of Hornback on the photolysis of 1,4-diphenylpent-4-en-1-ol presents another example of a hydrocarbon analogue of a Norrish type II photocleavage (J. M. Hornback, *J. Amer. Chem. Soc.*, 1974, **96**, 6773). However, to the best of our knowledge there is no other example of a type II reaction of such a simple alkene as (1c).

ation, which is inconsistent with a mechanism involving intramolecular hydrogen transfer. This supports the presence of diradical (8) as a common intermediate for

TABLE 3

Isotope effects on the quantum yield and the rate constant in the photolysis of (1c) and its [5,6-²H₂] isomer

Product	$\phi_{\text{H}}/\phi_{\text{D}}$ *	' $k_{\text{H}}/k_{\text{D}}$ '
(2)	1.09	1.67
(4)	1.07	1.70

* Calculated from the value shown in Table 2.

(2) and (4) and in consequence indicates the absence of the allylic diradical (6).

Since the products (2), (4), and hexadiene are formed *via* (8), the most important primary process in the mercury sensitisation of (1c) is considered to be a transannular

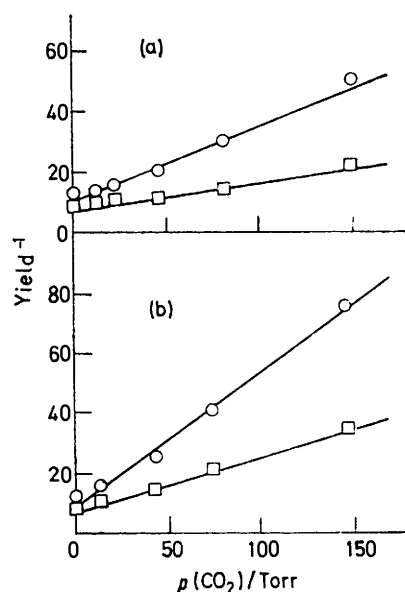


FIGURE 3 Reciprocal of yield *versus* added CO₂ pressure in the mercury sensitisation of (a) (1c) and (b) [5,6-²H₂]- (1c): (2), □; (4), ○

[1,5] hydrogen shift which occurs through a six-membered transition state whose quantum yield calculated from those of (2), (4), and hexadiene is 0.33 (Table 1). Bicyclo[3.3.0]octane (5) formed from a [1,4] hydrogen shift *via* an unfavourable five-membered transition state is only a minor product. Intramolecular hydrogen abstraction in the six-membered transition state, followed by competitive cyclisation and β -cleavage of the resulting 1,4-biradical, corresponds to the well known γ -hydrogen abstraction observed in the photolysis of carbonyl compounds.¹⁵ This may be the first reported case in which a π,π^* triplet of a simple alkene undergoes a Norrish type II reaction.‡ The sensitised photolysis of (1c) in solution afforded only (1t), and the intermediate in the photoisomerisation is believed to be the *vibrationally relaxed* π,π^* triplet which never gives bicyclo-octanes.

¹⁵ See for example, P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.

On the other hand, it is considered that the π,π^* triplet generated in mercury sensitisation is in a *vibrationally excited* state and is much more slowly deactivated by collision in the vapour phase. Vibrational excitation in the triplet state enhances the rate of the novel hydrogen abstraction reaction.

Although it is suggested that the excess vibrational energy of the triplet plays a significant role in mercury sensitisation, its effect on the reactivity of the triplet remains unclear.

Benzene sensitisation in the vapour phase¹⁶ is expected to give a triplet having lower vibrational energy whose reactivity is of interest. Photolysis of (1c) in the presence of benzene vapour gave mainly (1t) together with (2), (4), and trace amounts of hexadiene and ethylene. The formation of (1t) suggests the intermediacy of the cyclo-octene triplet resulting from the energy transfer from the

benzene triplet. This cyclo-octene triplet afforded only two of the isomeric products obtained by mercury sensitisation. These products, (2) and (4), are also considered to arise from the Norrish type II-like reaction proposed in Scheme 3. The other possible hydrogen shifts, *i.e.* [1,4] and [1,2], which occurred in mercury sensitisation, were not observed. This result is explained on the basis that only the energetically favoured path, the [1,5] shift, takes place, since the triplet formed in benzene sensitisation has less vibrational energy than that from mercury sensitisation by the difference in the triplet energy of the sensitisers, 84 and 113 kcal mol⁻¹, respectively.

[5/1299 Received, 1st July, 1975]

¹⁶ For intermolecular triplet energy transfer from benzene to alkenes, see M. W. Schmidt and E. K. C. Lee, *J. Amer. Chem. Soc.*, 1970, **92**, 3579.