Intramolecular Hydrogen Abstraction of the Vibrationally Excited Triplet State of Simple Alkenes

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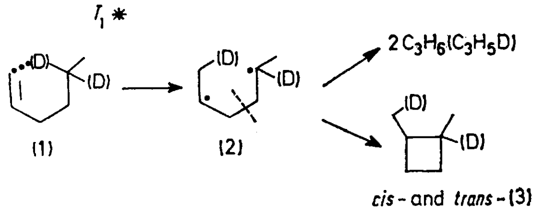
Summary The vibrationally excited triplet generated in the mercury photosensitisation of hex-1-ene and *cis*-oct-2-ene underwent intramolecular hydrogen abstraction *via* a six-membered transition state and subsequent β-cleavage and recombination of the resulting 1,4-biradical.

The Norrish type II photocleavage of carbonyl compounds containing a γ-hydrogen atom has been studied extensively, whereas studies of the photochemistry of alkenes have been mainly concerned with *cis–trans* isomerisation, cycloaddition, polar addition, and allylic bond fission. Although recent reports[1] on the photolysis of a few arylalkenes demonstrated that hydrogen abstraction by excited-state C=C double bonds does occur, intramolecular hydrogen abstraction is less well known in the photochemistry of simple alkenes. We report our studies on the sensitised photolyses of hex-1-ene (**1**) and *cis*-oct-2-ene, *cis*-(**4**), in the vapour phase, which provide evidence for the existence of an olefinic type II reaction of simple alkenes.†



Products resulting from the mercury photosensitisation of hex-1-ene (**1**) (99·9%) vapour are shown in Table 1. Of these products we assume that n-hexane is produced *via* the well known radical reaction initiated by excited mercury atoms because of the complete suppression of its formation upon addition of the radical scavenger nitric oxide (see Table 1). Although the formation of propene might be interpreted in terms of the familiar allylic C–C bond cleavage and disproportionation of the resulting radicals,

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† Although Majer *et al.* have already reported the molecular rearrangement of pent-1-ene to methylcyclobutane on mercury photosensitisation, the detailed mechanism and the nature of the intermediate involved were not fully clarified; J. R. Majer, J. F. T. Pinkard, and J. C. Robb, *Trans. Faraday Soc.*, 1964, **60**, 1247.

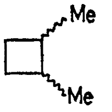
Table 1

Mercury photosensitisation of hex-1-ene (**1**)[a]

		Product/μmol					
Compound	Pressure /Torr	Propene	*cis*-(**3**)	*trans*-(**3**)	Methyl-cyclopentane	Cyclohexane	n-Hexane
(**1**)	10	2·64	0·22	0·33	0·05	0·02	0·02
(**1**)	30	1·66	0·14	0·20	0·03	0·012	0·02
(**1**)	51	1·04	0·11	0·14	0·02	0·008	0·02
(**1**)+NO[b]	10	2·64	0·19	0·30	0·04	0·02	c
[$^2H_2$]-(**1**)	10	1·38	0·12	0·18	0·05	0·03	d

[a] A cylindrical quartz cell, 5 × 5 cm diam., was used with a 30 W low-pressure mercury lamp fitted with a Toshiba UV-25 filter which removes the 184·9 nm-resonance line of mercury; exposure time 5 min. [b] NO (1 Torr) was added. [c] Not detected. [d] Amount not determined.

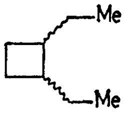
the effect of nitric oxide indicates that products other than n-hexane are not formed *via* any free-radical processes. The mercury sensitisation of [5,5-$^2H_2$]hex-1-ene,‡ [$^2H_2$]-(**1**), (99·9%) under comparable conditions provided definitive evidence for intramolecular hydrogen abstraction *via* a cyclic, six-membered transition state and subsequent β-cleavage of the resulting 1,4-biradical (**2**); in the photolysis of [$^2H_2$]-(**1**), the yields of propene and the cyclobutanes *cis*- and *trans*-(**3**) were reduced substantially, by a similar extent, to that from non-deuteriated (**1**) ($\phi_H/\phi_D = 1·9 \pm 0·1$), and $> 88\%$ of the resulting propene from [$^2H_2$]-(**1**) was shown to be C_3H_5D by mass spectrometry. The other cyclic products, methylcyclopentane and cyclohexane, are also interpreted as arising from hydrogen abstraction *via* unfavoured transition states.



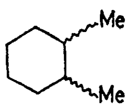
(3)

Me[CH$_2$]$_4$CH=CHMe

(4)



(5)



(6)

Table 2

Mercury photosensitisation of *cis*-oct-2-ene[a]

Pressure/Torr		Product/μmol					
cis-(**4**)	NO	But-1-ene	*trans*-(**5**)	*cis*-(**5**)[b] *trans*-(**6**)[b]	*cis*-(**6**)	*trans*-(**4**)	n-Octane
10	0	0·111	0·011	0·013	0·004	0·594	0·007
10	1·0	0·094	0·009	0·010	0·003	0·467	c

[a] The apparatus used is identical to that in Table 1. [b] The combined yields of *cis*-(**5**) and *trans*-(**6**) are shown because of incomplete separation on g.l.c. [c] Not detected.

A pressure dependence study of the photolysis and the generally accepted view on mercury photosensitisation of alkenes[2] indicate that the intermediate in the reaction is the vibrationally excited triplet state of hexene. Since intramolecular hydrogen abstraction of such a simple alkene has not been reported in liquid-phase photolysis, vibrational activation in the triplet state is considered to play a significant role in this novel reactivity which is characteristic of a 'hot triplet.'

cis-Oct-2-ene, *cis*-(**4**), (99·1%) vapour was also subjected to mercury photosensitisation giving but-1-ene and the cyclic *cis*- and *trans*-(**5**), and *cis*- and *trans*-(**6**), along with the *trans*-isomer of (**4**) (Table 2). The formation of (**5**) and (**6**) is inferred to be a result of intramolecular hydrogen abstraction by the excited-state C=C double bond of *cis*-(**4**) and recombination of the resulting 1,4- and 1,6-biradicals. Since significant amounts of but-2-ene and n-butane were not formed, the familiar allylic bond fission is ruled out and, consequently, the formation of but-1-ene was attributable to β-cleavage of the intermediate 1,4-biradical. Results of experiments with added nitric oxide also support these conclusions.

It is thus confirmed that, as with the n,π^* excited state of carbonyl compounds, the vibrationally excited triplet of simple alkenes undergoes intramolecular hydrogen abstraction *via* a six-membered transition state.

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‡ [$^2H_2$]-(**1**) was prepared by reduction ($LiAlD_4$) of hex-5-en-2-one to [2-^2H]hex-5-en-2-ol, followed by esterification with toluene-*p*-sulphonyl chloride to the tosylate and subsequent reduction with $LiAlD_4$ to give [$^2H_2$]-(**1**) (isotopic purity 98·7% by mass spectrometry).

[1] H. M. Rosenberg and P. Serve, *J. Amer. Chem. Soc.*, 1970, **92**, 4746; J. M. Hornback, *ibid.*, 1974, **96**, 6773.
[2] J. G. Calvert and J. N. Pitts, Jr., 'Photochemistry,' Wiley, New York, 1966, ch. 2.