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DIRECT PHOTOLYSIS AT 185 nm OF 1-ALKENES IN SOLUTION. MOLECULAR ELIMINATION OF TERMINAL HYDROGENS

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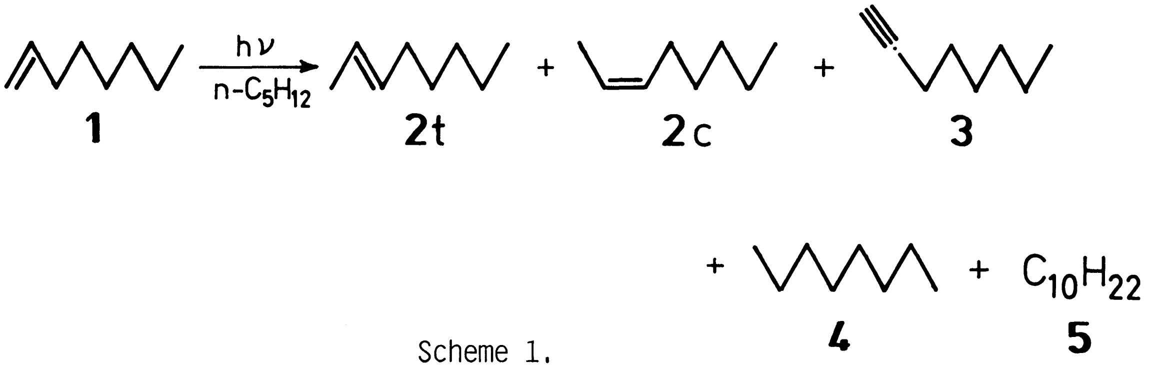
Direct irradiations at 185 nm of 1-octene and 2-methyl-1-pentene in pentane gave alkylidene carbenes through the molecular elimination of terminal hydrogens, as well as double-bond migration products via 1,3-shift of allylic hydrogen and radical-derived products.

Carrying just 2π, and some σ, electrons, the simple alkenes exhibit an unexpectedly wide variety of singlet photobehavior in solution upon direct excitation in the vacuum ultraviolet.[1-4)] They are: 1) cis-trans isomerization, 2) rearrangement to carbene, 3) 1,3-hydrogen shift, 4) hydrogen abstraction, and 5) ring-opening of cyclobutenes. The simultaneous occurrence of some of these reactions has been reported and, interestingly, the relative importance of individual path is evidently wavelength-dependent in the region of 185-228 nm, by which the assignment of the excited state responsible for each path is possible.[5)]

We wish now to report a novel photoreaction of simple terminal alkenes upon direct excitation at 185 nm in solution; this is also an additional example of the wavelength-dependent photochemistry of simple alkenes.

Direct photolyses of 1-octene (**1**) (10 mM) were carried out in pentane under a variety of conditions to give the cis-trans mixture of 2-octene (**2**) and 1-octyne (**3**) as the major photoproducts along with the radical-derived products, i.e. octane (**4**) and the dimers (**5**) of 2- and 3-pentyl radicals;[6)] see Scheme 1 and Table 1. The quantum yield of disappearance of **1** (Φ_{dis} =0.03) was one order of magnitude lower than that for 2-octene or 2,3-dimethyl-2-butene.[5)] This is probably due to the fact that the most favorable cis-trans isomerization process is degenerated and is just energy-wasting in this terminal alkene.

Of the photoreactions observed, the double bond-migration giving **2** and the



Scheme 1.

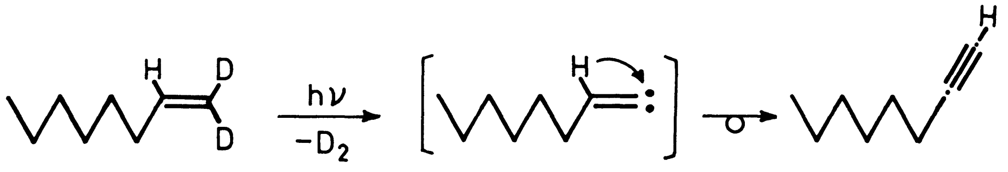
Table 1. Direct Photolyses of 1-Octene (**1**, 10 mM) in Pentane

Irradiation a)		Atmosphere	Conv.	Yield/ % b)					Product ratio
λ /nm	time /h		%	**2t**	**2c**	**3**	**4**	**5**	**3/2**
185	3	N_2	31	15	18	27	1.8	22	0.82
	3	O_2 c)	40	10	20	20	0.1	0.2	0.67
>200	20	N_2	23	5.0	3.4	0.7	1.9	3.0	0.08
>220	40	N_2	16	6.6	2.3	1.2	1.2	4.3	0.13

a) Light sources: 185 nm: a 30-W mercury resonance lamp made of Suprasil; >200 nm: a 300-W high pressure mercury arc without filter; >220 nm: a 300-W high pressure mercury arc fitted with a Vycor filter. b) Chemical yield based on the alkene consumed, determined by VPC on a PEG-300 column. c) Added as a radical scavenger.

hydrogen abstraction giving **4** and **5** have already been exemplified in the direct photolyses of various simple alkenes.1,2,5) However, there are few precedents of elimination of hydrogen molecule from an alkene in the solution-phase photochemistry7) except for the direct photolysis of liquid or solid ethylene,8) although, in the vapor phase, the direct or sensitized photolyses,9) γ-radiolysis,10) or infrared multi-photon decomposition11) of ethylene lead predominantly to the molecular elimination of hydrogen from 1,1- and/or 1,2-positions. In this context, it is interesting to reveal the elimination mechanism of the present case.

For this purpose, 1-octene-1,1-d_2 (**1**-d_2) was synthesized12) and its pentane solution (10 mM) was photolyzed at 185 nm in a preparative scale. The deuterium composition of the product 1-octyne was determined by GC-MS.13) As shown in Scheme 2, the product 1-octyne retained only 9 % deuterium, which is substantially below the original deuterium content of 77 % at the terminal carbon of **1**-d_2.14) This result clearly indicates that the two geminal hydrogens are eliminated predominantly at the terminal position. The elimination is inferred to be a molecular rather than successive atomic process, since a vinyl radical which would be produced by atomic elimination of hydrogen at 1-position has been shown to abstract hydrogen atom from the solvent regenerating the starting material rather than to further split off another terminal hydrogen to give 1-octyne.15) The finding14)



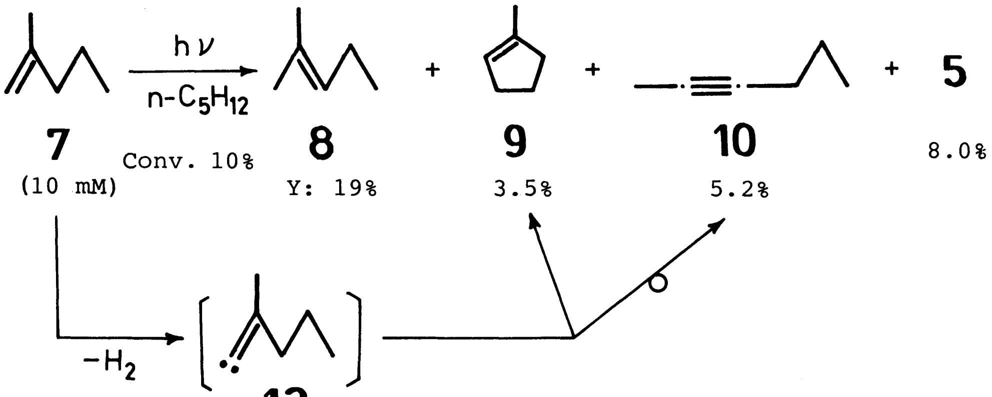
1-d_2 **6** **3**

d_2 61% d_1 9%
d_1 31% d_0 91%
d_0 8%

Scheme 2.

that any loss of deuterium was not observed in the recovered 1-octene-d$_2$ supports this elucidation. Also performed were the direct photolyses of pentane solution (10 mM) of 1-octene (**1**) and 1-octene-d$_2$(**1**-d$_2$) under the identical conditions in a merry-go-round apparatus. At the initial stages of the reaction, the deuterium isotope effects on the product yield, Φ_H/Φ_D, were 1.2-1.3 for **2**c+**2**t and 1.9 for **3**. The marked isotope effect upon the yield of hydrogen/deuterium elimination product **3** supports the involvement of terminal hydrogens in the elimination process, although the origin of the slight isotope effect upon the yield of **2** is not clear. The fact5,16) that the direct photolysis of 2-octene does not afford any trace of 2-octyne is additional support for the necessity of geminal vinyl hydrogens.

In order to survey the scope of this unique photoelimination of geminal hydrogens upon direct excitation in solution, the direct photolysis at 185 nm of 2-methyl-1-pentene (**7**), a 1,1-disubstituted ethylene, was performed in pentane under similar conditions. As shown in Scheme 3, 2-methyl-2-pentene (**8**), 1-methylcyclopentene (**9**), and 2-hexyne (**10**) were obtained in low yields;17) the quantum yields were again substantially low. The formation of **9** and **10** indicates the intervention of 2-pentylidene carbene **12** as their common precursor, since 3-heptylidene carbene generated thermally18) has been reported to undergo analogous reactions giving a self-insertion product, 1-ethyl-3-methylcyclopentene (**13**), and an alkyl-migration product, 3-octyne (**14**) in a comparable product ratio, i.e. **9**/**10** = 0.67 and **13**/**14** = 0.72. It is then shown that the molecular elimination of terminal hydrogens is not limited to a monosubstituted ethylene but is one of the major photoreactions of the electronically excited terminal alkenes.



Scheme 3.

As to the excited state involved in the hydrogen elimination process, the π-3s Rydberg excited state may be ruled out since the Rydberg band of 1-alkenes is not accessible with the excitation at >200 nm.19) The wavelength dependence of the product ratio **3**/**2** indicates that the elimination takes place via an excited state other than σ-π^* excited state which gives 1,3-hydrogen shift.5) It is concluded therefore that the hydrogen elimination is a low-efficiency reaction path of the π-π^* excited state, although the intervention of yet another excited state uncharacterized spectroscopically is not rigorously ruled out.

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5) Y. Inoue, T. Mukai, and T. Hakushi, Chem. Lett., 1983, 1665.
6) The starting material **1** and the products **2-4** are commercially available; for the identification of **5**, see Ref. 15. The absence of pentylcyclopropane and 1-methyl-2-butylcyclopropanes in the photolyzate was shown by VPC comparison with the authentic specimens prepared by the Simmons-Smith reactions of 1-heptene and 2-heptenes.
7) In a paper on the photolyses of γ,δ-unsaturated ketones, Leigh and Srinivasan have reported briefly without comments that the direct photolysis at 185 nm of **1** gives **3** in 18% yield along with unidentified isomers (54%); W.J. Leigh and R. Srinivasan, J. Am. Chem. Soc., 104, 4424(1982).
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12) The deuterated octene **1**-d$_2$ was prepared in the Wittig reaction of 1-heptanal with Ph$_3$PCD$_3$Br + BuLi in ether and the subsequent purification on VPC. The ^{1}H NMR specrum of **1**-d$_2$ shows that ca. 80% of the terminal hydrogens are replaced by deuterium, which is in good agreement with the deuterium content determined by mass spectrometry (Scheme 2).
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14) The deuterium distributions, d$_2$:d$_1$:d$_0$, in **1**-d$_2$ recovered and **2**c-d$_2$ produced were 60:31:9 and 64:28:8, respectively; no evident loss of deuterium was observed.
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16) The absence of 2-octyne in the photolyzate of 2-octene was checked again in this work.
17) The substrate **7** and the products **8** and **10** are commercially available. 1-Methylcyclopentene **9** was synthesized in the Grignard reaction of cyclopentanone with methylmagnesium iodide and the subsequent dehydration of the resulting 1-methylcyclopentanol.
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