WAVELENGTH-DEPENDENT PHOTOCHEMISTRY OF
# 2,3-DIMETHYL-2-BUTENE AND 2-OCTENE IN SOLUTION[1]

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Direct irradiations of the title compounds were performed at 185, >200, >220, and 228 nm in hydrocarbon solvents. The evident wavelength dependence of the product distributions observed is of importance in specifying the excited state involved in the forma- tion of each photoproduct, and suggests that more than two excited singlet states of an alkene undergo distinctly different photore- actions rather than suffer mutual conversions between the states.

In contrast with the well-documented wavelength-dependent photochemistry of aromatics, carbonyl and thiocarbonyl compounds, and bichromophoric alkenes,[2,3] the photochemistry of most monoolefins, though studied extensively,[4-6] is still believed to be independent of excitation wavelength at least in solution,[2a,4,7] and in the absence of interacting chromophores.[3] We now present a couple of examples of evident wavelength dependence of product distribution in the solution- phase direct photolyses of simple alkenes which indicate the involvement of higher excited singlet state(s).

Direct irradiations of 2,3-dimethyl-2-butene(1) were carried out in solution under a variety of conditions to give the products shown in Scheme 1 and Table 1.

Scheme 1.
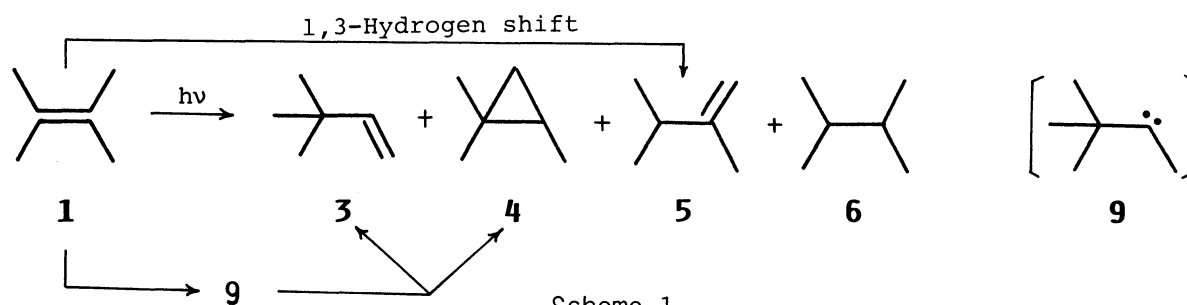
Although the major products **3-5** are the same as those reported previously in the photolysis of **1** with a full mercury arc(>200 nm),[4] important is the finding that the product composition varies drastically with excitation wavelength. As exci- tation wavelength increases from 185 to 228 nm, the yields of the rearrangement products **3** and **4** increase at the expense of the double bond-migration product **5**, as indicated by the product ratio (**3+4**)/**5**. This result does not immediately mean the involvement of a higher excited state. A number of analogous observations had been revealed to originate from spurious wavelength effects attributable to:

Table 1. Direct Photolyses of 2,3-Dimethyl-2-butene (1)

Irradiation [a]		Alkene concn/M	Solvent	Atmosphere [b]	Conv. %	Yield / % [c]			
λ /nm	Time /h					3	4	5	6
185	0.5	0.01	Pentane	N_2	23	2.6	3.9	38	d)
						(Φ: 0.016	0.023	0.23) e)	
			Cyclohexane	N_2	27	5.9	9.6	60	1.7
				O_2	27	6.6	11.0	66	f)
>200	3	0.01	Pentane	N_2	26	21	30	13	d)
						(17	24	18) g)	
>220	19	0.01	Pentane	N_2	27	20	30	7	d)
228	7	0.01	Pentane	N_2	33	15	22	5.7	d)
254	20	0.01-1.0	Pentane	N_2	No Reaction				

a) Light sources: 185 nm: a 30-W mercury resonance lamp made of Suprasil (the 254 nm resonance line is not eliminated); >200 nm: a 300-W high-pressure mercury arc without filter; >220 nm: a 300-W high-pressure mercury arc with a Vycor filter; 228 nm: a 300-W high-pressure mercury arc with a solution filter (K_2CrO_4: 7.0 x 10^{-4}M; Na_2CO_3: 4.7 x 10^{-3}M in H_2O); 254 nm: a 30-W mercury resonance lamp with a Vycor filter. b) Following treatment was made prior to irradiation: N_2: nitrogen bubbled; O_2: oxygen bubbled. c) Chemical yield based on consumed alkene, determined by VPC on an ODPN column. d) Yield not determined due to the partial overlap with solvent peak on VPC. e) Quantum yield, determined by the cyclooctene actinometry (Ref. 5a). f) Formation not detected (yield<0.5%). g) Result under similar conditions, reported by Kropp(Ref. 4).

(a) the independent excitation of structural or conformational isomers, (b) the excitation of ground state complexes, or (c) the secondary reaction of photoproducts.[2a] Of these, the first two possibilities may readily be ruled out in our present case. The further reactions of initial photoproducts would sound plausible, especially for the 185 nm irradiation. However, no evidence for the selective decomposition of any of the photoproducts 3-5 was obtained upon direct irradiations at 185 nm of pure 3-5.[8]

Although the above discussion is based on the reaction mechanism (Scheme 1) proposed by Kropp,[4] there may be yet another possibility especially in the photolysis at 185 nm that the hydrogen abstraction by an excited double bond and the subsequent disproportionation between the resulting radicals give the double bond-migration product 5 along with the saturated product 6. As shown in Table 1, the addition of oxygen, however, merely scavenged the reduction product 6 without affecting the yields of the isomeric products 3-5. The effect of temperature was also examined upon photolysis at >200 nm only to give a slight change in the product distribution; the ratios of 3 : 4 : 5 were 1:1.3:0.71 at 16 °C and 1:1.2:0.86 at -78 °C. We conclude therefore that the present wavelength dependence really originates from the participation of a higher excited state, and that the rearrangement products 3 and 4 and the double bond-migration product 5 are produced independently via different excited states of 1.

Similar wavelength dependence of product composition was found in the direct photolysis of cis-2-octene (**2c**). As can be seen from Table 2, the irradiations at >200 and >220 nm give the trans-isomer **2t** exclusively, whereas at 185 nm significant amounts of the double bond-migration products, i.e. 1-octene (**7**) and cis- and trans-3-octenes (**8c** and **8t**), are produced at the expense of the cis-trans isomerization product **2t**. Since the irradiation of **2c** at 185 nm in the presence of oxygen did not affect the product ratio, the increased yields of **7** and **8** at 185 nm can not be attributed to radical reactions and therefore the change in the product ratio is considered to originate from the true wavelength effect.

We now have two examples of the true wavelength-dependent photochemistry of simple alkenes to be rationalized. The present phenomena may arise from the involvement of either a hot, i.e. vibrationally activated, lowest singlet $(S_1^{\ddagger})$ or a thermally-populated upper singlet (S_2). However the result of the low temperature irradiation excludes the hot S_1 and thermally-populated S_2 hypotheses. The next question is which state is actually involved in each photochemical process. Quite significantly, Hirayama and Lipsky[9] have reported that the fluorescence quantum yield from excited 2,3-dimethyl-2-butene **1** is dependent upon excitation wavelength in the range of 185-229 nm, as shown in Table 3. They attributed the origin of this weak fluorescence to the π,3s Rydberg state for several reasons.[9] The fluorescence quantum yield reported exactly parallels the trend of the combined yield of **3** and **4**. This is the most convincing evidence for the proposal that not a zwitterionic π,π^*[10] but a radical-cationic π,3s Rydberg excited state[4,6] gives rise to the carbene **9**. This assignment is also consistent with the absorption bands of **1**; excitation at >200 nm leads predominantly to a π→3s Rydberg transition, while that at 185 nm to π→π^*.[11]

The reverse wavelength dependence of the yield of double bond-migration product **5**, on the other hand, indicates that an excited state other than π,3s must be responsible for the 1,3-shift of

Table 2. Direct Photolyses of cis-2-Octene (**2c**)[a]

Irradiation		Atmosphere	Conv. %	Yield /%[b]	
λ /nm	Time /h			**2t**	**7 + 8**[c]
185	0.3	N_2	20	81	15
				(Φ: 0.39	0.07)[d]
		O_2	20	80	14
>200	0.5	N_2	25	90	e)
>220	1.0	N_2	32	91	e)

a) Pentane solutions (0.01 M); for experimental conditions, see Table 1. b) Chemical yield based on consumed alkene, determined by VPC on a PEG-300 column. c) Combined yields are shown due to incomplete separation on VPC; (**7 + 8t**) : **8c**= ca. 4 : 1. d) Quantum yield. e) Yield<1%.

Table 3. Wavelength Dependence of Product Ratio and Fluorescence Quantum Yield of **1**

Irrad.	Product ratio[a]	Excit.	$\Phi_f \times 10^4$ [b]
λ / nm	(**3 + 4**)/ **5**	λ / nm	
185	0.17	185	0.43
>200	3.9	214	1.5
228	6.5	229	2.4

a) This work. b) Fluorescence quantum yield determined with a 0.42 M pentane solution of **1**; data quoted from Ref. 9.

hydrogen.   The same sort of opposite wavelength effect is seen between the cis-trans isomerization and 1,3-hydrogen shift processes of cis-2-octene **2c**.   Since it is widely accepted that the cis-trans photoisomerization of alkenes proceeds via a π,π^* excited state, the π,π^* singlet is also ruled out as a candidate for the precursor of the 1,3-shift of allylic hydrogen.   The $\pi,3p$[11] and π,σ^* excited singlets remain at hand.   However, since the π,σ^* excitation is located at the lowest in energy[12] and the $\pi,3p$ excitation is parity forbidden,[11] we suggest that yet another excited state is responsible for the 1,3-shift of hydrogen.[13]

References

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