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Vacuum UV Photolyses of Some Bichromophoric Alkenes Possessing Hydroxyl or Methoxycarbonyl Group

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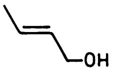
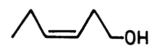
The direct photolyses at 185 nm of some naturally occurring and related bichromophoric alkenes possessing hydroxyl or methoxycarbonyl group at an allylic, homoallylic, or remote position gave the geometrical isomers as the major photoproducts detectable on gas chromatography. The isomerization yield was highly sensitive to the functional group introduced and its position; allylic alkenols gave poor yields, while both functionalization at a remote position and esterification of the hydroxyl group improve the photoisomerization yield.

The vacuum UV light has recently been used extensively in the investigation of the photochemistry of simple unsaturated compounds like alkenes and alkynes in solution phase.[1,2] With simple alkenes, a wide variety of novel singlet photobehavior *via* π,π^*, π, R(3s), and π,σ^* excited states has been reported to occur upon direct excitation in the vacuum UV, although the cis-trans photoisomerization, where accessible, is the dominant process in most cases.[1,2] On the other hand, much less effort has been done in order to reveal the effects of an additional functional group upon the fundamental photobehavior of simple alkenes, except for the works by Srinivasan[3] and by us.[4] The investigations on the photochemistry of bichromophoric alkenes not only afford insights into the nature of the excited double bond but also extend the scope and limitations of the vacuum UV photochemistry.

In this paper we report our results on the direct photolyses at 185 nm of bichromophoric alkenes possessing a hydroxyl or methoxycarbonyl group at an allylic, homoallylic, or remote position.[5] The bichromophoric alkenes examined in the present work are *trans*-2-buten-1-ol(**1t**), *cis*-3-hexen-1-ol or "leaf alcohol"[6] (**2c**), geraniol (**3t**), nerol (**3c**), methyl oleate (**4c**), methyl elaidate (**4t**), *cis*-3-hexenyl acetate (**5c**), and neryl acetate (**6c**). Most of these are naturally occurring products or their immediate derivatives, and, therefore, the present work will shed light on this relatively unexplored region of photochemistry/natural product chemistry.

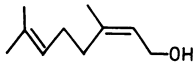


1t

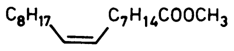


2c

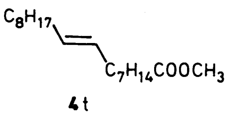
3t



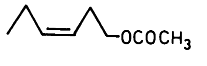
3c



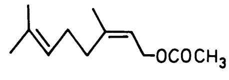
4c



4t



5c



6c

Another purpose of this paper is to test the suitability of water as a solvent for the vacuum UV photolysis by using water-soluble alkenols. The solvent available in the vacuum UV has long been restricted to the nonpolar, aprotic saturated hydrocarbons and even an alcohol such as methanol as a polar, protic solvent cannot be used due to the extinction coefficient of several handreds in this wavelength region,[7] whereas water is almost transparent at 185 nm.[7]

Results and Discussion

Photoisomerization. The direct irradiations of the bichromophoric alkenes **1**—**6** were performed at 185 nm in pentane and/or in water under a nitrogen atmosphere to give the geometrical isomers as the major photoproducts detected by GC analysis and the other valence isomers were not detected in significant yields. The isomerization yield varied drastically depending upon the functional group introduced and its position and also upon the solvent used. The isomerization yields at low and moderate conversions are listed in Table 1.

The direct photolyses of the allylic alcohols **1t**, **3t**, and **3c** in pentane afforded the corresponding geometrical isomers only in poor yields below 40%, while the homoallylic alcohol **2c** gave somewhat improved yield. The irradiation of **1t** or **2c** in water resulted merely in a similarly low or much reduced yield. From the mechanistic point of view, it is noted that no valence isomers other than cis-trans isomer were produced in significant yields and that the prolonged irradiations of **2c** in water led to the accumulated deposition of white precipitate, which was not characterized chemically due to the limited sample availability but is inferred to be water-insoluble polymeric

TABLE 1. DIRECT cis-trans PHOTOISOMERIZATION AT 185 NM OF SOME BICHROMOPHORIC ALKENES

Alkene (10 mM)	Solvent	Irradiation time/min	Conversion /%	Isomerization yield/%[a]
1t	Pentane	10	26	16
		20	36	20
	Water	10	14	24
		30	41	17
2c	Pentane	10	21	51
		20	40	41
	Water	10	30	18
		20	46	19
		60	86	6[b]
3t	Pentane	10	15	36
		20	27	34
3c	Pentane	10	15	27
		20	26	28
4c	Pentane	10	13	98
		20	27	79
4t	Pentane	10	18	91
		20	30	76
5c	Pentane	10	17	84
		20	29	72
6c	Pentane	10	12	28
		20	21	25

a) Chemical yield based on alkene consumed. b) Water-insoluble polymeric product was produced as white precipitate.

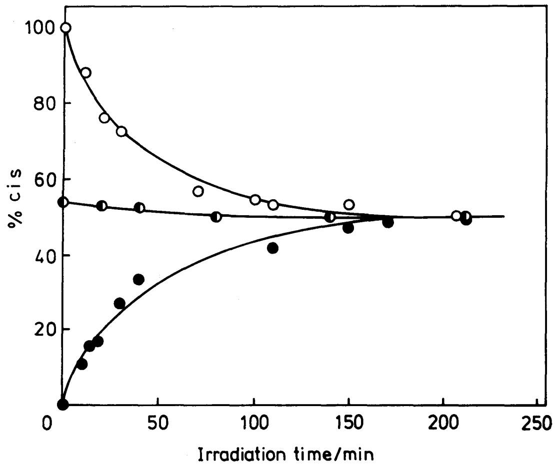


Fig. 1. Percent of the *cis*-isomer (**4c**) in **4** recovered on direct photolysis of **4** at 185 nm in pentane; initial composition: (○) 100% **4c**; (○) 54% **4c**; 46% **4t**; (●) 100% **4t**.

product. Above results suggest that the major process which occurred upon photolysis of the alkenols **1**—**3** is not the geometrical photoisomerization but the polymerization initiated probably by some radicals generated by the high-energy radiation in the vacuum UV. However, since analogous radical process which competes well with the cis-trans isomeization has not been reported in the photochemistry of simple acyclic alkenes,[1,2] this unexpected photobehavior must originate from the special electronic feature of the alkenols. The presence of oxygen atom at a weakly interactable, especially β, position may change the excitation profile of the alkenes significantly. The $\pi_{C=C}\rightarrow\sigma^*_{\pi CH_2}$ charge-transfer excitation is tentatively proposed as an electronic transition responsible for the radical formation,[3,8—10] since, in both semiempirical and *ab initio* calculations, the π atomic orbital ($\sigma_{\pi CH_2}$) of allylic CH_2 group has shown to mix readily with the π molecular orbital ($\pi_{C=C}$) of C=C bond. In particular, an oxygen atom β to C=C bond may lower the level of the σ^*_{π} orbital through further participation of its lone-pair electrons to the above mixing. The resulting electronic configuration with a reduced C–H bond order may facilitate the fission of the allylic C–H bond, giving rise to hydrogen and allylic radicals. The introduction of a hydroxyl group into an allylic position of alkene reduces the bond dissociation energy of the allylic C–H bond by 30—40 kJ mol^{-1}.[11] This may also facilitate the allylic bond fission in conjunction with the stabilization of the resulting allylic radical by the electron-donating hydroxyl group. The reason for much reduced isomerization yield upon photolysis of **2c** in water is not necessarily clear, but the nucleophilic trapping by water of π, 3s Rydberg excited state of alkene may consume the alkene affording addition products, *i.e.* diols,[12] as has been shown by Kropp *et al.* in the direct photolyses of tri- and tetrasubstituted alkenes at >200 nm,[1] and the possibility is not regorously ruled out that the use of a highly polar solvent may change the population of the excited states generated, which leads to different distribution of products.

In sharp contrast to the alkenols, methyl oleate **4c** and methyl elaidate **4t**, possessing a methoxycarbonyl group at a remote position, interconverted mutually in excellent yields upon direct irradiation, as is the case with simple alkenes.[1,2] Although the major reason for the facile isomerization in this particular case is probably the functionalization at a remote position in **4**, it is also expected that the methyoxycarbonyl group may improve the isomerization yield. Indeed *cis*-hexenyl acetate **5c** prepared by esterification of hexenol **2c** gave the trans-isomer **5t** in fairly improved yield as compared with **2c**. However this method is no longer applicable for the allylic alcohol. Neryl acetate **6c** isomerized photochemically only in low yields which are comparable with those for nerol **3c** itself. Thus the attempt to improve the photoisomerization yield by esterification is successful only for the alkenols possessing a hydroxyl group at a homoallylic or more remote position.

Photostationary State. Since the mutural photoisomerization between oleate **4c** and elaidate **4t** was highly efficient, the irradiation at 185 nm was prolonged up to 3 h in order to obtain the *cis/trans* ratio at the photostationary state, $(c/t)_{pss}$. As can be seen from Fig. 1, the prolonged irradiation of any given compositions of **4c** and **4t** afforded the identical ultimate value of 50% cis or $(c/t)_{pss}$ of 1.0. Since the reported molar extinction coefficients of **4c** and **4t** at

Table 2. Photostationary state *cis/trans* ratios on direct photoisomerizations at 185, 214, and 229 nm of methyl oleate **4c** and methyl elaidate **4t** in pentane

Excitation wavelength, nm	$(c/t)_{pss}$
185	1.0
214	1.2
229	0.43

185 nm are 12800 and 11600 $M^{-1}cm^{-1}$, respectively,[13] the decay ratio from the excited singlet (^1p) to **4c** an **4t**, k_{dc}/k_{dt}, is calculated, from the equation $(c/t)_{pss}=(\varepsilon_t/\varepsilon_c)(k_{dc}/k_{dt})$,[14] to be 1.1, which is reasonable for an acyclic alkene.

Similar prolonged irradiation of pentane solutions of a given mixture of **4** was run at 214 and 229 nm by using zinc and cadmium lamps, respectively. The photostationary states were attained at both wavelengths affording the $(c/t)_{pss}$ ratios listed in Table 2. The present $(c/t)_{pss}$ values obtained in the direct excitations of **4** at 185 and 214 nm are much higher than those reported for the semiconductor photosensitization, $(c/t)_{pss}$=0.20—0.44,[15,16] and for the triplet photosensitization, $(c/t)_{pss}$=0.21—0.74,[16] of the same compound, and therefore the direct photoisomerization merits synthetic application.

Experimental

General. Infrared spectra were obtained on a Jasco A-100 spectrometer. Mass spectra were recorded at 70 eV using a Hitachi RMU-6E instrument. ^{1}H NMR spectra were obtained on a Jeol JMX-60 sepctrometer in chloroform-*d* solution containing 1% tetramethylsilane as an internal standard. Gas chromatographic analyses of the photolyzates from **1**, **2**, **3**, **5**, and **6** were performed on a Yanaco G-180 or G-1800 instrument equipped with a System Instruments Chromatocorder 11 using columns of 20% PEG-20M (1.5 m) at 100 °C, 20% PEG-20M (1.5 m) at 120 °C, 20% PEG-20M (1.5 m) at 180 °C, 10% DEGS (3 m) at 120 °C, and 10% APL (65 cm) at 100 °C, respectively; the internal standards employed for pentane (water) solutions were cyclooctane (*t*-butyl alcohol), cyclooctane (*t*-butyl alcohol), dodecane, dodecane, and undecane, respectively. Liquid chromatographic analyses of the photolyzates from **4** were run on a Yanaco L-4000W instrument equipped with a Yanaco M-315 UV monitor, operated at 205 nm, and a Waters Data Module M730 using a 25 cm column of ODS-T with a water/methanol (2/98) eluent at a flow rate of 1.0 mL min^{-1}; the internal standard added after irradiation was *trans*-2-octene. Under the above conditions, the cis-trans isomers of **1—6** and the internal standard were seprated satisfactorily in each case.

Materials. Commercially available *trans*-2-buten-1-ol (**1t**), *cis*-3-hexen-1-ol (**2c**), geraniol (**3t**), and nerol (**3c**) (all from Tokyo Kasei) were fractionally distilled prior to use. Methyl oleate (**4c**) and methyl elaidate (**4t**) (both from Tokyo Kasei) were used without further purification.

cis-3-Hexenyl acetate (**5c**) and neryl acetate (**6c**) were prepared from the corresponding alcohols **2c** and **3c**. To a stirred mixture of **2c** or **3c** (0.07 mol) and *N,N*-dimethylaniline (0.07 mol) in dry ether (100 mL) was added dropwise acetyl choride (0.07 mol), and the mixture was heated to reflux for 2 h. The subsequent workup and fractional distillation gave the product **5c** or **6c** in 90—95% yield. **5c**: bp 105 °C/130 Torr[†]; MS *m/z* 142 (M^+); IR (neat) 3020, 2960, 2875, 1745, 1660, 1240, 1040 cm^{-1}; ^{1}H NMR δ=4.9—5.6 (m, 2H), 3.93 (t, 2H), 1.8—2.6 (m, 4H), 1.98 (s, 3H), 0.95 (t, 3H). **6c**: bp 115 °C/13 Torr; MS *m/z* 196 (M^+); IR (neat) 3025, 2970, 2930, 2850, 1740, 1675, 1235, 1030, 960, 830 cm^{-1}; ^{1}H NMR δ=4.8—5.5 (m, 2H), 4.47 (d, 2H), 2.0—2.2 (m, 7H), 1.67 (m, 9H).

Photolysis. A pentane or aqueous solution containing an alkene **1—6** (10 mM)[††] and an internal standard (2—3 mM) was charged in a Suprasil tubing (1 cm o.d.) and bubbled with nitrogen gas for 10 min at 0 °C. The solution was irradiated at room temperature by using a 30-W mercury resonance lamp made of Suprasil (Eikosha), the light path being flushed with nitrogen gas; the effective radiation in the present case is the 185 nm resonance line, since another intense resonance line at 254 nm is not absorbed by the alkenes **1—6**. The photolyses at 214 and 229 nm were conducted by using 16-W zinc and cadmium resonance lamps (Philips), respectively.

Identification. The photoproducts from **1t**, **2c**, **3**, **4**, **5c**, and **6c** were identified by the comparison of GC retention time of the product with that of the authentic specimen obtained commercially or prepared independently, using a couple of columns of different polarity. The authentic specimens of *trans*-3-hexen-1-ol (**2t**)(Nakarai), **3c**, **3t**, **4c**, **4t**, and geranyl acetate (**6t**)(Nakarai) were commercially available. *trans*-3-Hexenyl acetate (**5t**) was prepared from the corresponding alcohol **2t** according to the esterification procedure mentioned above. The pure specimen of *cis*-2-buten-1-ol (**1c**) was isolated from the photolyzate of **1t**. Preparative-scale irradiation of a pentane solution of **1t** (50 mM) were performed for 5 h with continuous bubbling of nitrogen gas and stirring in an immersion-well reactor (130 mL) using the same lamp. The solvent was distilled fractionally and the residue obtained was trap-to-trap distilled. The trap-distillate was subjected to preparative gas chromatography to give the pure product of **1c**. **1c**: IR (neat) 3350, 3030, 2930, 2880, 1660, 1035, 980, 900 cm^{-1}; ^{1}H NMR δ=5.57 (m, 2H), 4.17 (d, 2H), 2.5 (br, 1H), 1.67 (d, 3H). **5t**: IR (neat) 3030, 2960, 2930, 2870, 1740, 1660, 1240, 1040, 965, 900 cm^{-1}; ^{1}H NMR δ=5.2—5.5 (m, 2H), 3.99 (t, 2H), 1.8—2.5 (m, 4H), 2.00 (s, 3H), 0.95 (t, 3H).

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References

1) P. J. Kropp, *Org. Photochem.*, **4**, 1 (1979); *Molec. Photochem.*, **9**, 39 (1979).

2) Y. Inoue and T. Hakushi, *Kagaku to Kogyo (Science and Industry)*, **56**, 78, 116, 165 (1982).

3) R. Srinivasan, J. Studebaker, and K. H. Brown, *Tetrahedron Lett.*, 1955 (1979); R. Srinivasan, J. A. Ors, T.

[†] 1 Torr=133.322 Pa.

[††] 1 M=1 mol dm^{-3}.

Baum, L. S. White, and A. R. Rossi, *J. Am. Chem. Soc.*, **102**, 5297 (1980); R. Srinivasan, L. S. White, A. R. Rossi, and G. A. Epling, *ibid.*, **103**, 7299 (1981); W. J. Leigh and R. Srinivasan, *ibid.*, **104**, 4424 (1982); *ibid.*, **105**, 514 (1983).

4) Y. Inoue, N. Matsumoto, T. Hakushi, and R. Srinivasan, *J. Org. Chem.*, **46**, 2267 (1981).

5) Since typical absorption coefficients for simple alcohols and carboxylic esters are much smaller (by factors of 20—100) than those for simple alkenes (Ref. 8), more than 95% of the incident light is absorbed by the olefinic chromophore and the photoreaction is initiated by the excitation of a π electron. Indeed, no specific difference is seen between simple and bichromophoric alkenes at least above 205 nm, where only a tail of the major absorption band around 185 nm is observed.

6) For recent reviews on the biosynthesis and chemistry of leaf alcohol, see: A. Hatanaka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **61**, 180 (1983); *J. Synth. Org. Chem., Jpn*, **39**, 142 (1981).

7) M. B. Robin, "Higher Excited States of Polyatomic Molecules," Vol. 1, Academic, New York, 1974, p. 254.

8) Reference 7, Vol. 2, Chap. 4; and the references cited therein.

9) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.*, **44**, 1803 (1966); M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Weinwald, *ibid.*, **48**, 5037 (1968).

10) F. H. Watson, Jr., A. T. Armstrong, and S. P. McGlynn, *Theor. Chim. Acta*, **16**, 75 (1970); F. H. Watson, Jr. and S. P. McGlynn, *ibid.*, **21**, 309 (1971).

11) R. T. Sanderson, "Chemical Bonds and Bond Energy," Academic, New York, 1976, Chap. 10.

12) Under the GC conditions employed, these diols, even if produced, are absorbed on the column. No effort was done to detect the diols.

13) R. G. Binder, L. A. Goldblatt, and T. H. Applewhite, *J. Org. Chem.*, **30**, 2371 (1965).

14) Y. Inoue, S. Takamuku, and H. Sakurai, *J. Phys. Chem.*, **81**, 7 (1977).

15) K. Mizumoto, A. Kabumoto, C. Pac, and S. Yanagida, 25th Symposium on Photochemistry, Abstract, p. 257 (1984).

16) S. Yanagida, K. Mizumoto, A. Kabumoto, C. Pac, and K. Yoshino, 5th International Conference on Photochemical Conversion and Storage of Solar Energy, Abstract, p. 181 (1984).