0.5, 0.09; 1, 0.10; 2.5, 0.08; 4, 0.09.

p*K* Measurements. Our general procedures have been described extensively.[1] For some of the lower pK_a values higher concentrations were used, e.g., 0.01 M for II in water. We further note that the Debye–Hückel corrections for II, III, and in particular IV are large due to the higher charge numbers involved. Thus, with IV in 75E the corrections for the two concentrations are 0.727 and 0.858. Even in this extreme case the derived thermodynamic values, 6.544 and 6.537, respectively, come close together.

^{1}H NMR Spectra. Dilute solutions (1 mg of sample/mL of solvent) in D_2O were measured on a Nicolet NT-200 apparatus at 20 ± 2 °C. The following coupling constants (in hertz) were obtained by iterative analysis (LAOCOON-8). Tyrosine: pD = 0.1 (DCl), 7.48, 5.55, −14.65; pD = 6.5, 7.81, 5.12, −14.67; pD = 12.9 (NaOD), 7.53, 5.10, −13.71. The vicinal constants agree well with those from ref 17. *N,N,N*-Trimethyltyrosine: pD = 0.1, 12.02, 4.10, −12.77; pD = 6.5, 12.00, 3.67, −12.51; pD = 12.9, 11.62, 3.73, −12.71; in 4 M NaCl, 12.02, 3.75, −12.66.

Geometries. Distances were obtained by using the standard geometries of ref 1.

Acknowledgment. We thank Dr. J. A. Peters from this laboratory for taking the NMR spectra.

Registry No. I, 81158-75-0; II, 81158-76-1; II $2ClO_4^-$, 81158-77-2; III, 60728-23-6; IV, 81158-78-3; IV $2K^+$, 22038-37-5; V, 81158-79-4; VIII, 81158-80-7; IX, 81158-81-8; X, 81158-82-9; 3-NMe_2-5-$NMe_3^+C_6H_4COOH$ I^-, 81158-83-0; 3-NMe_2-5-$NMe_3^+C_6H_4COOMe$ I^-, 81158-84-1; ethyl 3,5-diaminobenzoate, 1949-51-5; tripotassium 3,5-disulfonatobenzoate, 81177-88-0; potassium 3-nitro-5-sulfonatobenzoic acid, 81177-80-2; L-tyrosine, 60-18-4; *N,N,N*-trimethyltyrosine, 81158-85-2.

Photochemistry of Vinyl Halides. Vinyl Cation from Photolysis of 1,1-Diaryl-2-halopropenes

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Received April 21, 1981

Irradiation of 1,1-diaryl-2-halopropenes in methanol gave 1,1-diarylpropenes, 1,1-diarylallenes, 1,2-diaryl-1-methoxypropenes, and 9-methoxy-10-methylphenanthrenes. The propenes are derived from vinyl radicals which are generated by homolytic fission of the carbon–halogen bonds. The allenes, the methoxypropenes, and the phenanthrenes are derived from ionic intermediates. When the aryl substituents are more electron rich and the halogen atoms had higher electron affinity, the amounts of products from the ionic intermediates increased. These results suggest that vinyl cations are generated by electron transfer in the radical pairs. The vinyl cations gave the allenes by deprotonation or changed to more stabilized vinyl cations by a 1,2-aryl shift. The phenanthrenes were formed from the methoxypropenes which were obtained by nucleophilic attack of the solvent, methanol, on the rearranged vinyl cations. When the photolysis was carried out in THF which is subject to hydrogen abstraction, the yield of the radical product, i.e., propene, increased. However, the photolysis in ethylene glycol or in methanol at −70 °C elicited a decrease in the yield of the radical products. Sensitized irradiation of 2-bromo-1,1-diarylpropenes with benzophenone or acetophenone resulted in no reaction, and this suggested that the photolysis occurred via the excited singlet state.

There are several examples of photolysis of organic halides which give ionic intermediates. In all these cases, e.g., benzyl,[1] norbornyl,[2] and adamantyl[2] halides, the halogen atom is bonded to an sp^3-hybridized carbon.

However, until recently there has never been any apparent evidence that photolysis of vinyl halides in which the halogen atom is bonded to an sp^2-hybridized carbon gives a vinyl cation. It is generally known that photolysis of vinyl halides leads to a cis–trans isomerization of the double bond or to homolytic fission of the carbon–halogen bond with a consequent formation of products from the derived radical intermediate.[3]

Recently we reported that photolysis of β,β-bis(methoxyphenyl)vinyl bromides in benzene gave bis(methoxyphenyl)acetylenes. We suggested that an intermediate vinyl cation was formed by an internal electron transfer in the radical pair which was formed in the homolytic fission of the carbon–halogen bond.[4] McNeely and Kropp found that photolysis of alicyclic vinyl halides gave solvent-incorporated products which were interpreted as resulting from intermediate vinyl cations.[5] Sket and Zupan also proposed a similar mechanism for the photolysis of 1,1-diphenyl-2-haloethylenes.[6]

The photolysis of 1,1-diaryl-2-halopropenes is a very suitable reaction for a detailed mechanistic study of vinyl cation formation for several reasons. (a) Both radical and ionic products are formed and their ratios have mechanistic significance. (b) The 1,1-diaryl-2-halopropenes do not give solvolysis products by initial heterolytic carbon–halogen bond cleavage under the conditions of the photolysis experiment. (c) Whereas, in the case of photolysis of 1,1-diaryl-2-haloethylenes,[4] a possible formation of vinylidene carbenes cannot be excluded, such intermediates cannot be formed with 1,1-diaryl-2-halopropenes. (d) Structural variation in the β substituent and the halogen atom (Cl, Br, and I) as well as change in the solvent and the temperature can be used as mechanistic tools.

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(1) (a) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915. (b) Ivanov, V. B.; Ivanov, V. L.; Kuzmin, M. G. *Mol. Photochem.*, 1974, *6*, 125. (c) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105. (d) Appleton, D. C.; Brocklenhurst, B.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Chem. Commun.* **1977**, 108. (e) Hyömüki, J.; Koskioallio, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 321. (f) Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951. (g) Slocum, G. H.; Kaufmann, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 4625.

(2) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135.

(3) Sammes, P. G. "Chemistry of The Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

(4) Suzuki, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.*, **1976**, 180.

(5) McNeely, S. A.; Kropp, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 4319.

(6) Sket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 752.

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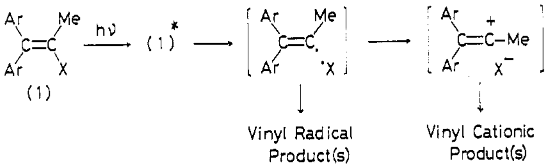
Table I. Products from the Photolysis of the Vinyl Halides 1

		conditions				products				
						yield,[a] %				
compd	X	solvent	temp, °C	time, h	% conv	2	3	8	4	substituents
1a	Cl	MeOH	5	4.3	72	15	28	13	18	R_1 = OMe, R_2 = H
	Cl	MeOH	5	6	82	12	23		19	
	Br	MeOH	5	1	61	30	20	10	9	
	Br	MeOH	5	3	84	29	16		15	
	Br	MeOH	−70	4.5	65	18	46	11	9	
	Br	MeOH	−70	12	87	16	39	5	12	
	Br	$HOCH_2CH_2OH$	15	6	93	3	26		11	R_1 = OCH_2CH_2OH, R_2 = H
	I	MeOH	5	0.4	92	47	31		trace	R_1 = OMe, R_2 = H
	I	MeOH	5	0.75	100	46	26		2	
	I	MeOH	5	1.5	100	39	22		2	
	I	c-C_6H_{12}	10	0.5	86	53				
	I	$HOCH_2CH_2OH$	15	0.67	96	3	44		1	R_1 = OCH_2CH_2OH, R_2 = H
1b	Cl	MeOH	5	4	87	6	11		52	R_1 = OMe, R_2 = OMe
	Br	MeOH	5	2	86	19	10		36	
	Br	THF	5	4	79	31	24	10		R_1 = H, R_2 = OMe
	I	MeOH	5	0.33	65	49	16	9	6	R_1 = OMe, R_2 = OMe

[a] Based on the consumed vinyl halide 1.

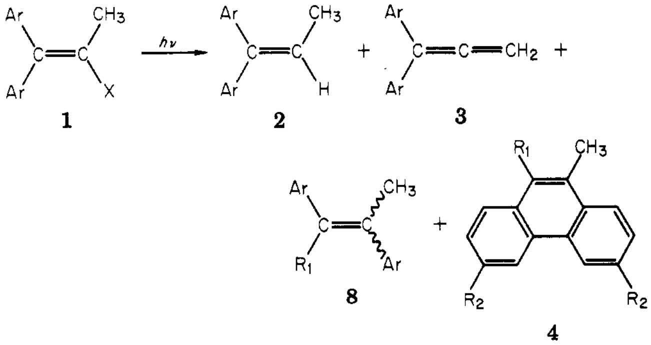
We report now that the photolysis of the 1,1-diaryl-2-halopropenes is consistent with a reaction involving initial homolysis to the radical pair followed by an electron transfer mechanism (eq 1). The initially formed β,β-diaryl-α-methylvinyl cation undergoes deprotonation, 1,2-aryl shift, and capture by the solvent. These are well-known reactions in vinyl cation chemistry.[7]



(1)

Results

When 1,1-diaryl-2-halopropene (1) was irradiated in various solvents by using a 100-W high-pressure mercury lamp, the products obtained were 1,1-diarylpropene (2), 1,1-diarylallene (3), 1,2-diarylpropene (8), and 9-methylphenanthrene derivative 4 (eq 2), whose yields were determined by NMR spectroscopy with an internal standard.



(2)

Irradiation of the vinyl halides 1 in methanol gave 2, 3, 8, and 4. The products 8 and 4 are those trapped by methanol nucleophilically. A longer irradiation time resulted in the formation of 2–4, suggesting that 4 was formed by the stilbene-like photocyclization of 8. The nucleophilically trapped products 8 and 4 are those that accompany 1,2-aryl migration.

Irradiation of the vinyl bromide **1a** (X = Br) in methanol-*O-d* for 5.5 h gave the same products, **2a**–**4a**, and the reduced product **2a** had only 2% of incorporation of deuterium.

The type of halogen atom affected the product distributions. The vinyl chloride afforded a smaller amount of **2** and larger amounts of **8** and **4**. When the halogen atom was Br or I, the amount of **2** increased, and the amounts of **8** and **4** decreased. In the case of the vinyl iodide, the reduced product **2** was formed in the highest yield compared with those for other vinyl halides. The formation of **3** was mostly dependent on the reaction conditions rather than the halogen atom.

Irradiation time and conversion did not change the product distribution significantly except in the case of **8**.

Irradiation of the vinyl bromide **1a** (X = Br) in methanol at −70 °C gave **2a** in smaller yield than the irradiation at 5 °C. The photolyses at −70 °C were carried out by using external irradiation. Other photolysis experiments were carried out by internal irradiation using an immersion-type photoreactor.

Irradiation of the vinyl bromide **1a** (X = Br) and iodide **1a** (X = I) in ethylene glycol showed a drastic decrease in the yield of **2a**. In contrast, irradiation of **1a** (X = I) in cyclohexane gave **2a** only and did not give **3a**, **8a**, and **4a** at all.

When 1,1-bis(*p*-methoxyphenyl)-2-halopropene (**1b**) was irradiated, the products were **2b**, **3b**, **8b**, and **4b**, similarly to the case for the vinyl halide **1a**. Similar results were obtained; i.e., the vinyl chloride **1b** (X = Cl) gave the lowest yields of **2b** and the highest yields of methanol-incorporated products **8b** and **4b**, and the vinyl iodide results **1b** (X = I) were the reverse of those for the vinyl chloride **1b** (X = Cl). In these cases aryl-rearranged products were formed in higher yields than in the case of the vinyl halide **1a**, suggesting this to be due to the larger migration aptitude of the *p*-methoxyphenyl group as compared to phenyl group.[8]

Irradiation in THF gave a larger amount of **2**, and the β-aryl-rearranged **8** was formed along with **3**.

The photolyses of 1,1-diaryl-2-halopropenes (**1**) are summarized in Table I.

The sensitized irradiation of 2-bromo-1,1-diphenylpropene (**1a**, X = Br) was carried out in methanol by using

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(7) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.

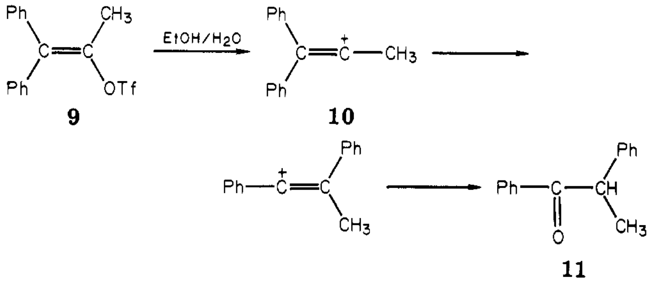
(8) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; p 284.

benzophenone or acetophenone as a triplet sensitizer through a Pyrex filter with a high-pressure mercury lamp. It was found, however, that the reaction did not take place, and the vinyl bromide **1a** (X = Br) was recovered unchanged. Also, the sensitized irradiation of 2-bromo-1,1-bis(*p*-methoxyphenyl)propene (**1b**, X = Br) with benzophenone resulted in no reaction.

Discussion

In aryl-substituted vinyl halide the double bond is conjugated with the aromatic ring, resulting in λ_{max} in the ultraviolet region and excitation by light emitted from the mercury lamp. No differences between the halogen atoms in the vinyl halides **1** and between the vinyl halides **1** and the corresponding propenes **2** were observed in the electronic spectra and extinction coefficients, and both the vinyl halides **1** and the corresponding propenes **2** exhibit absorption maxima at about 245 nm (log ϵ ~4) (Table II). Consequently, it is assumed that the excitation of the aryl-substituted vinyl halides is due to a $\pi \rightarrow \pi^*$ transition.

Formation of Radical and Ionic Products. It is well-known that the photolysis of vinyl halides leads to the formation of vinyl radicals by the homolytic fission of the carbon–halogen bond.[3] The reduction product, i.e., the propene **2**, is apparently formed by hydrogen abstraction from the solvent by the vinyl radical. Irradiation in methanol-*O-d* shows that the hydrogen atom comes from C–H of methanol.[9] On the other hand, the phenanthrene **4** is necessarily formed by a series of reactions involving a 1,2-aryl shift, followed by nucleophilic attack of solvent on the intermediate, and stilbene-like photocyclization. In addition, α-methoxy-α'-methylstilbene (**8**), which was a precursor of the phenanthrene **4**, was formed on shorter irradiation. Since vinyl radicals do not undergo 1,2-aryl shift across the double bond,[10] the observation of 1,2-aryl shift and nucleophilic displacement implies the intervention of a cationic intermediate, which in this system is the vinyl cation **6**. The vinyl cation **6a** was also generated by the solvolysis of the corresponding vinyl triflate **9** by Imhoff et al.[11] (eq 3). The product was mainly the rearranged ketone **11**. The similarity of the products in both reactions corroborates the intermediacy of the vinyl cation in the photolysis of vinyl halides. The formation of the allene **3** by the deprotonation of the vinyl cation **6** is supported by the following facts. (a) Photolysis of the vinyl halides **1a** (X = Br and I) in cyclohexane gave only the radical product, i.e., the propene **2a**, but none of the allene **3a**, suggesting that **3a** is not derived from the vinyl radical **5**. (b) When the vinyl bromide **1a** (X = Br) was irradiated in the presence of cupric acetate the radical product **2a** could not be detected, whereas the amounts of **3a** increased along with that of the other ionic products.[12] These results are consistent with the conclusion that the allene **3** is derived from the vinyl cation **6**.



9 10 11

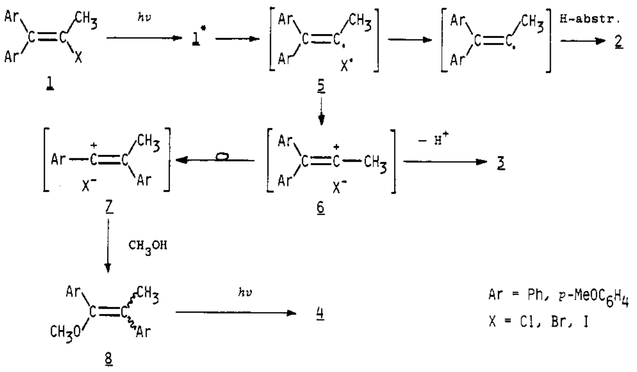
(3)

Table II. Ultraviolet Spectral Data for Vinyl Halides 1 and Propenes 2

compd	solvent	λ_{max}, nm (log ϵ)
2a	EtOH	235 (3.87), 248 (3.94)[a]
1a, X = Cl	MeOH	242 (4.12)[b]
1a, X = Br	MeOH	222 (sh, 4.18), 243 (4.01)[b]
1a, X = I	EtOH	232 (4.16), 248 (sh, 4.02)
2b	EtOH	245 (4.33), 260 (4.25)[c]
1b, X = Cl	cyclohexane	246 (4.25), 268 (sh, 4.02)
1b, X = Br	cyclohexane	245 (4.25), 270 (sh, 4.03)
1b, X = I	cyclohexane	245 (4.37), 275 (sh, 4.06)

[a] Djerassi, C.; Shamma, M.; Kan, T. Y. *J. Am. Chem. Soc.* **1958**, *80*, 4723. [b] Beltrame, P.; Carrá, S.; Macchi, P.; Simonetta, M. *J. Chem. Soc.* **1964**, 4386. [c] Miquel, J. F.; Wahlstam, H.; Olsson, K.; Sundbed, B. *J. Med. Chem Chem.* **1963**, *6*, 774.

Scheme I



The competition between the ionic and the radical routes is shown in Scheme I. Irradiation gives the photoexcited vinyl halide (**1***), which leads to the radical pair **5** by cleavage of the carbon–halogen bond. An internal electron transfer in **5** gives the α-methylvinyl cation **6**. Deprotonation of 6 gives the allene **3**, whereas migration of a β-aryl group across the double bond of **6** gives the more stabilized α-arylvinyl cation **7**. 1,2-Diaryl-1-methoxypropene (**8**) is formed by nucleophilic attack of the methanol on **7**. Photoreaction of **8** gives rise to stilbene-like cyclization to the phenanthrene derivative **4**. The propene **2** is formed by competitive hydrogen abstraction from the solvent by the free vinyl radical, which can be trapped by a cupric salt added to the reaction system.[12] Consequently, the ratio of the rates of the reactions via ionic and radical intermediates is equivalent to the product ratio, ([3] + [8] + [4])/[2], which is independent of the irradiation time or conversion as seen from Table III.

The product ratios in the photolysis of the vinyl halides **1** are given in Table III.

The sensitized irradiation of the vinyl bromides **1a** and **1b** (X = Br) with benzophenone or acetophenone resulted in no reaction. This suggests that photolysis occurs from S_1 of the vinyl bromide **1**.

Electron Transfer Mechanism for the Formation of Vinyl Cation. There are two possible routes for the formation of vinyl cations from vinyl halides. One is a single-step process involving the heterolytic fission of the carbon–halogen bond (eq 4), which is observed in the solvolysis of vinyl halides.[7] In this case the reaction is

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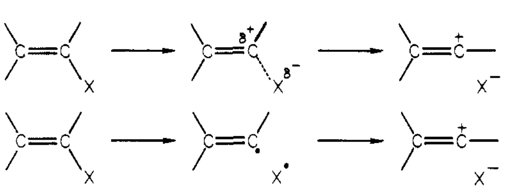
[9] Only a small amount of incorporation of deuterium is considered to be derived from D–Br which is generated by the reaction of methanol-*O-d* with the vinyl cation 7.

[10] Haynes, J. K., Jr.; Kampmeier, J. A. *J. Org. Chem.* **1972**, *37*, 4167.

[11] Imhoff, M. A.; Summerville, R. H.; Schleyer, P. v. R.; Martinez, A. G.; Hanack, M.; Dueber, T. E.; Stang, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 3802.

[12] Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1978**, 1223.



(4)

(5)

faster in more polar solvents, and the leaving group effect follows the order I > Br > Cl. The other route is a two-step process, involving first a homolytic fission of the carbon–halogen bond and then an electron-transfer step (eq 5). In this mechanism (eq 5) the effect of the solvent polarity should be smaller for the reaction rate than that in the single-step process of eq 4, if the rate-determining step is a homolytic fission of the carbon–halogen bond in the case of the photolysis of organic halides. Since a high electron affinity of halogen atom will favor an electron-transfer process, the rates of the second step should follow the order Cl > Br > I.

In the photolysis of the aryl-substituted vinyl halides it was found that the highest ratio of ionic to radical products was obtained when the aryl group was substituted by a *p*-methoxyphenyl group and when the halogen atom was chlorine. The ([3] + [8] + [4])/[2] ratios follow the orders Ar = *p*-$MeOC_6H_4$ > Ph and X = Cl > Br > I.[13] However, the overall yield for a constant irradiation time decreases in the order X = Cl > Br > I (Table III).[14] The overall yields are determined in the slow step of the carbon–halogen bond cleavage which is easier when the halogen atom is a heavier atom. These results agree with the electron-transfer mechanism. The ratio of products, however, is determined by the competing reaction routes of the radical pair **5**. In the internal electron transfer in **5** the vinyl radical acts as the electron donor and the halogen atom as the electron acceptor. The electron transfer is easier from a donor with a low ionization potential and to an acceptor with a high electron affinity. Consequently, the more electron-rich the vinyl radical and the higher the electron affinity of the halogen atom, the easier the electron-transfer steps are. In an analogous system, the styrene derivatives, it was found that the ionization potentials of styrene and *p*-methoxystyrene are 8.47 and 7.92 eV, respectively.[15] The electron affinities of iodine, bromine, and chlorine atoms are 75.7, 82.0, and 87.3 kcal/mol, respectively.[16] Accordingly, the vinyl radical pair where the vinyl part is substituted by the electron-rich *p*-methoxyphenyl group and the halogen has the highest electronegativity is involved in the fastest electron-transfer process.[17]

The competing hydrogen-abstraction process should be only slightly affected by the nature of X· in **5**, since only the free radical which escapes from the solvent cage is involved in hydrogen abstraction. This has been confirmed by the photolysis of vinyl bromides in the presence of cupric acetate, where a vinyl radical pair within a cage undergoes an electron-transfer process to give a vinyl cation, while the free radical which escapes from the cage is trapped by the copper(II) salt.[12] The competing hydrogen-abstraction process also should be only slightly affected by the difference of the *para* substituent on the β-aryl group, since the substituent effects in radical reactions are smaller than ionic reactions,[18] and, in addition, in this case the substituent is present at the para position on the β-aryl group. Consequently, in this case the ([3] + [8] + [4])/[2] ratios are governed by the ease of electron transfer in the radical pair **5**.

Photolysis of vinyl halides in ethylene glycol gave a significant decrease in the product ratios of radical to ionic products. When the vinyl bromide and iodide **1a** (X = Br and I) were irradiated in ethylene glycol, the radical product **2a** was obtained only in 3% yield. This result is interpreted as being associated with the viscosity of the solvent, since the *Z* value, which is the solvent polarity parameter for ethylene glycol (85.1 kcal/mol), is nearly equal to that for methanol (83.6 kcal/mol),[19] and the polarity effect on the ease of an electron transfer should be nearly equal under similar conditions. However, ethylene glycol has a high viscosity (26.9 cP, 15 °C) compared with that for methanol (0.55 cP, 26 °C),[20] resulting in a lower extent of dissociation of the radical pair from the solvent cage. The competing internal electron transfer in the radical pair becomes more significant with a consequent increase in the yield of the ionic products. It is also suggested that the propene **2** comes from the free radical which escaped from the solvent cage.

Photolysis of the vinyl bromide **1a** (X = Br) in methanol at −70 °C also gave a decrease in the yield of radical product **2a**. The increase in viscosity[21] may be partially responsible for this behavior, but a temperature effect, which was observed in the photolysis of 1-halocyclohexene,[5] may also be important.

Compared with methanol, THF is more easily subject to hydrogen abstraction by radical species.[22] The amount of radical product should, therefore, increase when a vinyl bromide is irradiated in THF. Indeed, on irradiation of **1b** (X = Br) in THF the yield of the propene **2b** increased from 19% to 31%.

Experimental Section

Melting points are uncorrected. NMR spectra were taken with JEOL JNM-MH-60 and Hitachi R-24B spectrometers. Mass spectra were obtained with a JEOL JMS-07 spectrometer. Ultraviolet spectra were recorded on a Shimadzu UV-200S spectrometer, and IR spectra were obtained with a Shimadzu IR-400 spectrometer.

Materials. 2-Bromo-1,1-diphenylpropene (**1a**, X = Br) was prepared by bromination of 1,1-diphenylpropene (**2a**).[23]

In the preparation of 2-chloro-1,1-diphenylpropene (**1a**, X = Cl) the following modification of the literature procedure[23] was adopted. After chlorination of the propene **2a** (3.88 g) in acetic acid (200 mL) the solvent was evaporated, and the crude product was subjected to column chromatography on alumina. Elution with benzene gave an oil, which was assigned as 1,2-dichloro-1,1-diphenylpropane by its NMR spectrum: NMR (CCl_4) δ 1.41 (d, *J* = 7 Hz, 3 H, CH_3), 5.01 (q, *J* = 7 Hz, 1 H, CH), 7.00–7.73

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[13] McNeely and Kropp[5] reported that photolysis of 1-halocyclohexenes gave radical products and ionic products, and the iodide yielded higher amounts of ionic products compared with those for the bromide.

[14] The following facts are enough for the qualitative discussion on the efficiency. (a) The vinyl halides have similar electronic spectra and extinction coefficients. (b) The photolysis for the comparison of the efficiency was done under the same reaction conditions.

[15] Hatano, M.; Tamura, N.; Kambara, S. *Kogyo Kagaku Zasshi* **1967**, *70*, 2012.

[16] Pauling, L. "The Nature of The Chemical Bond"; 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 510.

[17] From the result that more π-electron-rich vinyl halides give greater amounts of ionic products, it is reasonable to consider that an electron transfer takes place from the π-electron system in the vinyl radical to the halogen atom.

[18] Kosower, E. M. "An Introduction to Physical Organic Chemistry"; Wiley: New York, 1968; p 45.

[19] Reference 18, p 301.

[20] Riddick, J. A.; Bunger, W. B. "Techniques of Chemistry, Vol. II, Organic Solvents", 3rd ed.; Weissberger, A., Ed., Wiley-Interscience: New York, 1970.

[21] The calculated value is 1.96 cP (at −70 °C) by the following equation: $T = 0.24316\Phi + 279.01 - 4498.9/\Phi$; $\Phi = 1/\eta$.[20]

[22] Russell, G. A. "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, Chapter 7.

[23] Beltrame, P.; Carrà, S.; Macchi, P.; Simonetta, M. *J. Chem. Soc.* **1946**, 4386.

Table III. Product Ratios in the Photolysis of the Vinyl Halides 1 in Methanol and Ethylene Glycol

vinyl halide	X	solvent	time, h	conv, %	product ratio, %				([3] + [8] + [4])/[2][a]
					2	**3**	**8**	**4**	
1a	Cl	MeOH	4.3	72	20	38	18	24	3.9
	Cl	MeOH	6	82	22	43		35	3.5
	Br	MeOH	1	61	43	29	15	13	1.3
	Br	MeOH	3	84	48	27		25	1.1
	Br	MeOH[b]	4.5	65	21	55	13	11	3.7
	Br	MeOH[b]	12	87	22	54	7	17	3.5
	Br	$HOCH_2CH_2OH$	6	93	7.5	65		27.5	12.3
	I	MeOH	0.4	92	60	40			0.66
	I	MeOH	0.75	100	62	35		3	0.61
	I	MeOH	1.5	100	62	35		3	0.61
	I	$HOCH_2CH_2OH$	0.67	96	6	92		2	15.0
1b	Cl	MeOH	4	87	9	16		75	10.5
	Br	MeOH	2	86	29.2	15.4		55.4	2.4
	I	MeOH	0.33	65	61	20	11	8	0.63

[a] Ratios of ionic products to radical product. [b] Irradiation at −70 °C.

(m, 10 H, Ar H). This dichloride was dissolved in acetic acid (300 mL), and the solution was refluxed for 2 h. The reaction mixture was poured into water, extracted with ether, washed with water and saturated sodium chloride, and dried over anhydrous sodium sulfate. After evaporation of the solvent, recrystallization from ethanol gave 2-chloro-1,1-diphenylpropene (**1a**, X = Cl): 1.50 g; mp 36–37 °C (lit.[23] mp 39 °C); NMR (CCl_4) δ 2.20 (s, 3 H, CH_3), 7.00–7.36 (m, 10 H, Ar H).

2-Bromo-1,1-bis(*p*-methoxyphenyl)propene (**1b**, X = Br) was prepared by bromination of 1,1-bis(*p*-methoxyphenyl)propene (**2b**).[24]

2-Chloro-1,1-bis(*p*-methoxyphenyl)propene (**1b**, X = Cl) was prepared similarly. After chlorination of the propene **2b** (5.00 g) in acetic acid (200 mL), the solvent was evaporated, and the crude reaction mixture was chromatographed over alumina. Elution with benzene gave the vinyl chloride **1b** (X = Cl), which was recrystallized from ethanol: 2.24 g; mp 64–65 °C; NMR (CCl_4) δ 2.23 (s, 3 H, CH_3), 3.78 (s, 6 H, OCH_3), 6.78–7.32 (m, 8 H, Ar H). Anal. Calcd for $C_{17}H_{17}O_2Cl$: C, 70.71; H, 5.93. Found: C, 70.66; H, 5.99.

2-Iodo-1,1-diphenylpropene (**1a**, X = I) and 2-iodo-1,1-bis(*p*-methoxyphenyl)propene (**1b**, X = I) were prepared by the reaction of the corresponding vinyl magnesium bromides with iodine.

The vinyl bromide **1a** (X = Br; 2.74 g, 10 mmol) was converted to the Grignard reagent by reaction with magnesium (0.29 g, 12 mmol) in 15 mL of dry THF. Addition of methyl iodide is necessary to initiate the reaction. After the mixture was refluxed for 2 h, the THF solution of iodine was added until the solution became brown. The reaction mixture was then hydrolyzed with 2 N hydrochloric acid (6 mL), and the product was extracted with ether. The ethereal solution was washed with water and saturated sodium chloride and dried over anhydrous sodium sulfate, and after evaporation of the solvent the residual oil was purified by column chromatography on silica gel. The vinyl iodide **1a** (X = I) was obtained as an oil: 1.68 g (51%); NMR (CCl_4) δ 2.60 (s, 3 H, CH_3), 7.17 (s, 10 H, Ar H). Anal. Calcd for $C_{15}H_{13}I$: C, 56.27; H, 4.09. Found: C, 56.49; H, 4.14.

In the same manner, the vinyl iodide **1b** (X = I) was obtained as an oil: 65% yield; NMR (CCl_4) δ 2.60 (s, 3 H, CH_3), 3.70 (s, 6 H, OCH_3), 6.57–7.07 (m, 8 H, Ar H). Anal. Calcd for $C_{17}H_{17}O_2I$: C, 53.70; H, 4.51. Found: C, 53.94; H, 4.55.

Photolysis of 1,1-Diphenyl-2-halopropenes (1a, X = I, Br, and Cl) in Methanol. A solution of the vinyl halide **1a** (2 mmol) in methanol (200 mL) containing pyridine (0.2 mL) was irradiated under nitrogen atmosphere at 5 °C by using a high-pressure mercury lamp (100 W). The solvent was removed under reduced pressure, and the residue was chromatographed over alumina. Elution with 20% benzene–hexane gave the starting material **1a**, the propene **2a**, and the allene **3a**. The propene **2a** was identified by comparison with an authentic sample:[25] NMR (CCl_4) δ 1.67 (d, J = 7 Hz, 3 H, CH_3), 6.05 (q, J = 7 Hz, 1 H, CH), 6.87–7.30 (m, 10 H, Ar H). The allene **3a** was identified on the basis of its spectral data [NMR ($CDCl_3$) δ 5.23 (s, CH_2); IR 1935 cm^{-1} (C=C=C)] which are in accord with those of the literature:[26] NMR δ 5.18 (CH_2); IR 1935 cm^{-1} (C=C=C). Elution with 50% benzene–hexane gave the phenanthrene **4a**: mp 48–50 °C; picrate, mp 135.5–137.5 °C; NMR ($CDCl_3$) δ 2.65 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 7.48–8.72 (m, 8 H, Ar H); UV (cyclohexane) λ_{max} 223 nm (log ϵ 4.21), 248 (sh, 4.26), 255 (4.71), 271 (4.21), 278 (4.06), 288 (3.95), 300 (4.01), 322 (2.43), 337 (2.73), 353 (2.81); mass spectrum, m/e 222 (M^+). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.75; H, 6.41.

In the case of the shorter irradiation (*E*)- and (*Z*)-1-methoxyphenyl-1,2-diphenylpropenes (**8a**) were formed, which were identical with those obtained by the photolysis of **1a** (X = Br) in the presence of cupric acetate.[12] (*E*)-**8a**: NMR (CCl_4) δ 2.08 (s, 3 H, CH_3), 3.29 (s, 3 H, OCH_3), 6.82 (s, 5 H, Ar H), 6.88 (s, 5 H, Ar H); UV (cyclohexane) λ_{max} 271 nm (ϵ ~7020). (*Z*)-**8a**: NMR (CCl_4) δ 1.91 (s, 3 H, CH_3), 3.13 (s, 3 H, OCH_3), 6.90–7.35 (m, 10 H, Ar H); UV (cyclohexane) λ_{max} 266 nm (ϵ ~12000); mp 53–55 °C.

Photolysis of 1,1-Bis(*p*-methoxyphenyl)-2-halopropenes (1b, X = I, Br, and Cl) in Methanol. A solution of the vinyl halide **1b** (2 mmol) in methanol (200 mL) containing pyridine (0.2 mL) was irradiated in a manner similar to that described above for **1a**. The solvent was removed under reduced pressure, and the residue was chromatographed over alumina. Elution with 20% benzene–hexane gave a material which crystallized on being allowed to stand overnight. Recrystallization from ethanol gave a pure compound (mp 97–100 °C) which was assigned as the propene **2b** by comparison with an authentic sample.[25] The NMR spectrum of the mother liquor showed the presence of the allene **3b** [NMR ($CDCl_3$) δ 5.20 (s, CH_2); IR 1936 cm^{-1} (C=C=C)] and the propene **2b**. Elution with 50% benzene–hexane gave the phenanthrene **4b**: mp 85–86 °C; picrate, mp 157–158 °C; NMR ($CDCl_3$) δ 2.58 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 3.97 (s, 6 H, OCH_3), 7.12–7.43 (m, 2 H, Ar H), 7.83–8.21 (m, 4 H, Ar H); (cyclohexane) λ_{max} 235 nm (sh, log ϵ 4.50), 250 (4.63), 257 (4.61), 282 (sh, 4.25), 289 (4.33), 308 (4.05), 338 (2.98), 356 (3.23), 373 (3.32); mass spectrum, m/e 282 (M^+). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.40; H, 6.36.

In the case of the vinyl iodide **1b** (X = I), (*E*)- and (*Z*)-1-methoxy-1,2-bis(*p*-methoxyphenyl)propenes (**8b**) were formed as shown by the NMR spectrum in $CDCl_3$. (*E*)-**8b**: δ 2.10 (s, CH_3); 3.34 (s, OCH_3). (*Z*)-**8b**: δ 1.89 (s, CH_3); 3.08 (s, OCH_3). These vinyl ethers **8b** were confirmed by acid-catalyzed hydrolysis to the ketone, α-methylanisoin:[27] NMR ($CDCl_3$) δ 1.47 (d, J = 7 Hz, 3 H, CH_3), 3.71 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 4.55 (q, J = 7 Hz, 1 H, CH), 6.67–7.94 (m, 8 H, Ar H); IR 1670 cm^{-1} (C=O).

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Photolysis of 2-Iodo-1,1-diphenylpropene (1a, X = I) in Cyclohexane. A solution of the vinyl iodide **1a** (X = I, 1 mmol) in cyclohexane (100 mL) was irradiated in the presence of zinc powder (10 mmol) under a nitrogen atmosphere at 10 °C by using a high-pressure mercury lamp (100 W) for 70 min. The solvent was removed under reduced pressure, and the residue was chromatographed over alumina. The only product was the propene **2a**, which was identified by comparison with an authentic sample.[25] Its yield was 53%, as determined by NMR with *p*-*tert*-butylbenzoic acid as an internal standard.

Photolysis of 2-Bromo-1,1-bis(*p*-methoxyphenyl)propene (1b, X = Br) in THF. A solution of the vinyl bromide **1b** (X = Br, 2 mmol) in THF (200 mL) containing pyridine (0.2 mL) was irradiated in a manner similar to that described for **1a** for 4 h. The solvent was removed under reduced pressure, and the residue was chromatographed over alumina. Elution with 40% benzene–hexane gave the starting material (**1b**, X = Br), the propene **2b**, and the allene **3b**. Elution with benzene gave 1,2-bis(*p*-methoxyphenyl)propene (**12**): mp 124 °C; NMR ($CDCl_3$) δ 2.23 (d, J = 1.2 Hz, 3 H, CH_3), 3.80 (s, 6 H, OCH_3), 6.67–7.50 (m, 9 H, CH and Ar H); UV (EtOH) λ_{max} 287 nm (log ϵ 4.01); mass spectrum, *m/e* 254 (M^+).[28]

Photolysis of 1,1-Diphenyl-2-halopropenes (1a, X = Br and I) in Ethylene Glycol. A solution of the vinyl halide **1a** (1 mmol) in ethylene glycol (100 mL) containing pyridine (0.1 mL) was irradiated in a similar manner. The reaction mixture was poured into water (500 mL) and extracted with ether. The ethereal solution was washed with water and saturated sodium chloride and dried over anhydrous sodium sulfate. The crude photoproducts were obtained by the removal of the ether and chromatographed over alumina. Elution with 40–80% benzene–hexane gave the starting material **1a**, the propene **2a**, and the allene **3a**. Elution with 50% ether–benzene gave 9-(2-hydroxyethoxy)-10-methylphenanthrene (**13**) which was isolated as the picrate: mp 106–107 °C; NMR ($CDCl_3$) δ 2.59 (s, 3 H, CH_3), 2.58 (br s, 1 H, OH), 3.98 (s, 4 H, CH_2CH_2), 6.96–8.58 (m, 8 H, Ar H); mass spectrum, 252 (M^+). Anal. Calcd for $C_{23}H_{19}O_9N_3$ (picrate): C, 57.38; H, 3.98; N, 8.73. Found (picrate): C, 57.14; H, 4.00; N, 8.77.

Photolysis of 2-Bromo-1,1-diphenylpropene (1a, X = Br) in Methanol at −70 °C. A solution of the vinyl bromide **1a** (X = Br, 141 mg) in methanol (25 mL) containing pyridine (0.05 mL) was placed in a quartz tube and irradiated for 4.5 h under a nitrogen atmosphere at −70 °C by using a high-pressure mercury lamp (100 W). The solvent was removed under reduced pressure, and the residue was chromatographed over alumina in order to remove the pyridinium salt. The photoproducts which were eluted with benzene were analyzed by recording their NMR spectra. The identified products were the propene **2a**, the allene **3a**, the phenanthrene **4a**, and (*E*)- and (*Z*)-1-methoxy-1,2-diphenylpropenes (**8a**).

Photolysis of 2-Bromo-1,1-diphenylpropene (1a, X = Br) in Methanol-*O*-*d*. A solution of the vinyl bromide **1a** (X = Br, 144 mg) in methanol-*O*-*d* (10 mL) containing pyridine (0.05 mL) was placed in a quartz tube and irradiated for 5.5 h under conditions similar to those for the photolysis in methanol at 5 °C. After workup of the reaction mixture, the NMR spectrum showed the same products: the propene **2a**, the allene **3a**, and the phenanthrene **4a**. The mass spectral analysis of the propene **2a**, which was separated by column chromatography on alumina, indicated only 2% of incorporation of deuterium.

Sensitized Irradiation of 1,1-Diaryl-2-bromopropene (1a or 1b, X = Br) in Methanol. A solution of the vinyl bromide **1a** (X = Br, 1 mmol) in methanol (100 mL) containing pyridine (0.1 mL) was similarly irradiated in the presence of benzophenone (10 mmol) with a Pyrex filter for 3 h. After the workup of the reaction mixture, the vinyl bromide **1a** (X = Br) was recovered unchanged. Similar irradiation of the vinyl bromide **1a** (X = Br) with acetophenone and the vinyl bromide **1b** (X = Br) with benzophenone and a Pyrex filter, respectively, gave no products, and the starting material was recovered unchanged.

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Registry No. 1a (X = Cl), 781-34-0; **1a** (X = Br), 781-32-8; **1a** (X = I), 81360-97-6; **1b** (X = Cl), 81360-98-7; **1b** (X = Br), 39179-87-8; **1b** (X = I), 81360-99-8; **2a**, 778-66-5; **2b**, 4663-13-2.

Further Studies on the Synthesis of Thienamycin: a Facile and Stereoselective Synthesis of a Bicyclic β-Keto Ester by 1,3-Dipolar Cycloaddition

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A potential compound, ethyl 6-[(1R*)-1-hydroxyethyl]-3,7-dioxo-1-azabicyclo[3.2.0]heptane-2-carboxylate (**18**), for the synthesis of thienamycin (**1**), was stereoselectively prepared by 1,3-dipolar cycloaddition of the nitrone (**12**) and benzyl crotonate as a key reaction.

The carbapenem antibiotics have become an increasingly interesting class of naturally occurring substances with regards to both biology and synthesis. Thienamycin (**1**) is a novel member of this family of compounds, isolated from *Streptomyces cattleya*[1] and fully characterized by spectroscopic and X-ray technique.[2] The first synthesis of **1** has been reported by Merck group,[3] and modified syntheses have also been published by them.[4-8] Recently we have developed[9-11] a stereoselective synthesis of **1** by

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