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The Photolysis of Ethoxycarbonylmethyltriphenylphosphonium Salts[1)]

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Irradiation of ethoxycarbonylmethyltriphenylphosphonium salts (IV) gave products expected to be derived from the homolytic fission of the P–CH_2CO_2Et or P–Ph bond. The rate of the product formation was dependent strongly on the anion species and on the solvent polarity; an oxidizable anion was effective for the photolysis and the less polar the solvent the faster the rate became. It was found through the measurement of the electrical conductance that the degree of electrolytic dissociation of IV was very low at the concentration employed in the photolysis. On the basis of these results, the photolysis of IV was confirmed to proceed through a direct charge transfer from an anion to a cation.

A fair number of works have been reported on the photochemistry of the compounds containing nitrogen or sulfur atoms.[2)] However, little attention has been paid to the photochemical behavior of organophosphorus compounds.[3)]

We found previously that the P–Ph bond was broken at the primary step of the photolysis of the phosphonium ylids,[4)] I and II, and that the mode of the bond fission of III depended on the wavelength of exciting light used.[5)] Now, we studied the photolysis of ethoxycarbonylmethyltriphenylphosphonium salts (IV).[6)] Although it has been reported that phosphonium salts are decomposed by ultraviolet irradiation.[7)] the mechanism is not yet established. In the present paper the effect of the anion species and solvent polarity on the rate of the product formation were examined in detail and the possibility of four different paths leading to the decomposition of IV was discussed. Further, we discussed briefly on the differences of the modes of the bond fission in the photolysis of I,[4)] IV, and ammonium[8)] and sulfonium salts.[9)]

$Ph_3P{=}CHCO_2Et$ (I), $Ph_3P{=}CHCOR$ R=Me or Ph (II),
$Ph_3P{=}CPh_2$ (III),
$Ph_3P^+CH_2CO_2Et\ X^-$
X=Cl, Br, I, BF_4, ClO_4, or NO_3 (IV).

Results

Acetonitrile solutions of IV (X=Cl, Br, or I) (3.5 mmol in 10 m*l*) in quartz tubes were degassed by three cycles of the freeze-pump-thaw method and irradiated with a high pressure mercury lamp for 150 hr. Triphenylphosphine (TPP), ethoxycarbonylmethyldiphenylphosphine (EDP), diphenyl, halobenzenes, diethyl succinate, ethyl phenylacetate, benzene, and ethyl acetate were detected by gas chromatographic analysis. The yields of the products are shown in Table 1.

$$\begin{aligned}Ph_3P^+CH_2CO_2Et\ X^- &\xrightarrow{h\nu} Ph_3P + Ph_2PCH_2CO_2Et\\ &+ Ph\text{-}Ph + PhX + EtO_2CCH_2CH_2CO_2Et\\ &+ PhCH_2CO_2Et + PhH + CH_3CO_2Et\end{aligned}$$
X=Cl, Br, or I

In order to see the effect of the nature of the anion species on the rate of the formation of the product, the quantum yields for the formation of TPP, EDP, benzene, and ethyl acetate (ϕ_{TPP}, ϕ_{EDP}, ϕ_{PhH}, and $\phi_{CH_3CO_2Et}$) from the phosphonium halides and tetrafluoroborate were determined at 253.7 nm using ferrioxalate actinometry.[10)] As shown in Table 2, ϕ_{TPP} and $\phi_{CH_3CO_2Et}$, or ϕ_{EDP} and ϕ_{PhH} were approximately

Table 1. Photolysis of IV in acetonitrile[a)]

X	Product yield (%)							
	TPP	EDP	PhX	$(EtO_2CCH_2\text{-})_2$	Ph-Ph	PhH	CH_3CO_2Et	$PhCH_2CO_2Et$
Cl	2.0	2.6	5.7	5.7	0.5	13.1	18	1.0
Br	10.6	2.6	0	7.1	2.4	6.3	35	0.5
I	6.9	0.9	6.0	0.1	0.2	6.0	49	0.1

a) IV (3.5 mmol) in 10 m*l* of acetonitrile.

[1)] A preliminary report of this work has been published: Y. Nagao, K. Shima, and H. Sakurai, *Tetrahedron Lett.*, **1971**, 1101.

[2)] A. Schönberg, G. O. Schenck, and O-A. Neumller, "Preparative Organic Photochemistry," Springer-Verlag, Berlin (1968), pp. 48, 105, 242, 434.

[3)] R. S. Davidson, "Organophosphorus Chemistry," S. Trippett (Senior Reporter), The Chemical Society, London, Vol. 1, (1970) p. 246 and Vol. 2, (1971) p. 221.

[4)] Y. Nagao, K. Shima, and H. Sakurai, *Kogyo Kagaku Zasshi*, **72**, 236 (1969).

[5)] Y. Nagao, K. Shima, and H. Sakurai, *Tetrahedron Lett.*, **1970**, 2221.

[6)] H. J. Bestmann, "Newer Methods of Preparative Organic Chemistry," Vol. 5, ed. by W. Foerst, Academic Press, New York (1968), p. 2.

[7)] C. E. Griffin and M. L. Kaufman, *Tetrahedron Lett.*, **1965**, 773.

[8)] a) J. W. Knapczyk and W. E. MacEwen, *J. Org. Chem.*, **35**, 2539 (1970). b) A. L. Maycock and G. A. Berchtold, *ibid.*, 2532 (1970). c) T. Laird and H. Williams, *Chem. Commun.*, **1969**, 561 and *J. Chem. Soc., C*, **1971**, 1863.

[9)] T. D. Walsh and R. C. Long, *J. Amer. Chem. Soc.*, **89**, 3943 (1967). b) C. Pac and H. Sakurai, *Chem. Commun.*, **1969**, 20.

[10)] The yields of these four products were increased linearly with the irradiation time and the determination was done within such irradiation time as the linearity was held.

Table 2. Quantum yields for the formation of the products[a]

X	TPP	EDP	CH_3CO_2Et	PhH
Cl	0.04	0.005	0.008	0.005
Br	0.04	0.001	0.03	0.001
BF_4	0.05	0.002	0.04	0.002
I	0.0004	0	0.13	0.02

a) Acetonitrile solution (0.5 M). Low pressure mercury lamp.

equal for each salt except in the case of the iodide, where ϕ_{TPP} and ϕ_{EDP} were extremely low. It is noteworthy that both ϕ_{PhH} and $\phi_{CH_3CO_2Et}$ were increased in the order, chloride<bromide<tetrafluoroborate<iodide.

The photochemical stability of IV ($X=NO_3$, Cl, Br, BF_4, or I) was estimated from the amount of the recovered salt after the photolysis. The results are shown in Table 3. The rate of the photodecomposition of IV was increased with the change of the anion in the order, $NO_3^- < Cl^- < Br^- < BF_3^- < I^-$. This order was essentially the same as obtained in the quantum yields measurements. Thus, the photolysis of IV in acetonitrile solution was found to be very sensitive to the nature of the anion species.

The effect of the solvent polarity on the rate of the product formation was examined in the photolysis of the bromide. The data shown in Table 4 indicate that with decreasing solvent polarity the yields of TPP and EDP were increased and the yield ratio TPP/EDP was decreased. These tendencies might suggest that a direct relation exists between solvent polarity and the rate of the product formation. More definitive evidence indicating the relation was obtained when the photolysis was carried out in benzene–ethanol mixed solvent in quartz tube. As shown in Fig. 1, the yields of TPP and EDP were increased linearly with the increase in the ratio of benzene to ethanol. Similar results as shown in Fig. 1 were also obtained when the photolysis was done in Pyrex tube.[11] This result indicates that the absorption of the light by benzene does not contribute to the acceleration of the rate of the formation of phosphines (that is, benzene does not sensitize the photodecomposition of IV). Thus, it was found that the rate of the product formation was sensitive to the solvent polarity and less polar solvents were effective for the photolysis.

Table 3. The relative reactivity of the salts

X	NO_3	Cl	Br	BF_4	I
Conversion[a] (%)	12	18	24	33	45
Relative reactivity	1.0	1.5	2.0	2.8	3.7

a) Calculated from the amount of the recovered salts.

Table 4. Photolysis of IV (X=Br) in various solvents[a]

Solvent	Yield (%)		TPP/EDP	Relative rate	E_T value[b] (kcal/mol)
	TPP	EDP			
MeOH	0.4	0	—	0.2	55.5
EtOH	6.1	0.38	16	1.2	51.9
i-PrOH	6.3	0.38	18	1.2	48.6
MeCN	4.9	0.38	14	1.0	46.0
DMF	10.3	0.94	11	2.1	43.8
EtOH-PhH (1 : 4)	7.8	1.25	7	1.7	—

a) IV (1.6 mmol) in 4 m*l* of appropriate solvent.

b) This value represents the polarity of the solvent; K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963).

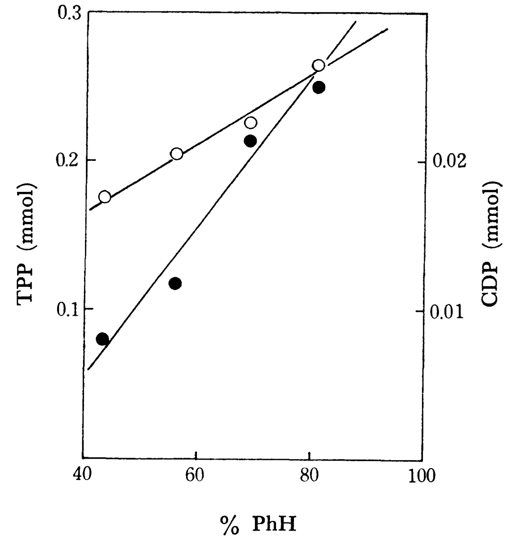

Fig. 1. Photolysis of IV in PhH-EtOH mixed solvent. IV (1.6 mmol) in 4 m*l* of solvent.
○: TPP, ●: EDP

As it was suggested through the examination of the solvent effect that the degree of the interaction between an anion and a cation in a solution may be an important factor in the photolysis of IV, the degree of the electrolytic dissociation of IV were determined through the measurements of electrical conductances of the acetonitrile solutions of IV. The degree of dissociation ($\alpha=\Lambda/\Lambda_\infty$) at 0.32 M (this concentration is close to that at which the photolysis was done; 0.37 M) was calculated to be 0.24 for the bromide and 0.26 for the iodide. Under such circumstances an appreciable interaction between an anion and a cation may be possible.

Table 5 shows the effects of the additives on the yields of the products in the photolysis of the bromide. The addition of iodine strongly inhibited the formation of all the products. Lithium nitrate also showed the inhibition. Oxygen and phenyl iodide enhanced the rate of the photodecomposition of IV.

Discussion

Four different paths are possible for the photochemical decomposition of the ionic compounds, RY^+X^-.

$$X^- \xrightarrow{h\nu} X\cdot + e^-$$

$$RY^+ + e^- \longrightarrow R\cdot + Y \qquad (A)$$

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[11] Since a Pyrex tube eliminates wavelengths below 280 nm, benzene does not absorb the light energy in this case.

TABLE 5. PHOTOLYSIS OF IV IN THE PRESENCE OF THE ADDITIVES[a)]

X	Additive	Product yield (%)					
		PhH	CH_3CO_2Et	$(EtO_2CCH_2-)_2$	$PhCH_2CO_2Et$	Ph-Ph	H^+
NO_3	none	0.25	0.38	0	0	0	nd[b)]
ClO_4	none	0	0.12	0	0	0	3.1
Br	none	0.9	17.2	2.3	0.2	0.1	33.8
Br	$LiNO_3$	0.9	10.4	4.1	0.3	0	2.5
Br	PhI	4.6	44.1	1.4	0.1	0.1	32.5
Br	O_2	2.1	38.4	3.3	0.3	0.1	50.6
Br	I_2	0.1	3.3	0	0	0	nd[b)]

a) IV (1.6 mmol) in 4 m*l* of acetonitrile. b) Not determined.

$$RY^+ \xrightarrow{h\nu} R\cdot + Y^+\cdot \qquad (B)$$

$$RY^+ \xrightarrow{h\nu} R^+ + Y \qquad (C)$$

$$RY^+X^- \xrightarrow{h\nu} R\cdot + Y + X\cdot \qquad (D)$$

A solvated electron is involved in Path A. Path B involves a homolytic cleavage of a bond to produce a cation radical. Path C involves a heterolytic bond cleavage to produce a carbonium ion. Both Path B and Path C predict no anion dependency. Path D represents a direct charge transfer reaction under the interaction between an anion and a cation.

All the products shown in Table 1 can be expected to be derived from radical reactions because the rates of their formation were retarded markedly by the addition of iodine, a radical scavenger (Table 5). Path C (a heterolytic bond cleavage) can be ruled out on the basis that phenetole could not be detected at all when the photolysis was carried out in ethanol.

Tables 2, 3, and 5 show that the photochemical reactivity of IV depends strongly on the anion species. The quantum yields of the products (Table 2) and the rate of the photodecomposition of IV (Table 3) were increased with the change of the anion in the order, ClO_4^-, $NO_3^- < Cl^- < Br^- < BF_4^- < I^-$. An oxidizable anion was shown to be more effective except for BF_4^-.[12)] This result indicates that Path A and/or Path D may be operative in the photolysis. However, Path A can be safely ruled out on the basis that any anion does not absorb the light above 250 nm,[13)] and that a Brønsted acid which is a good scavenger of the solvated electron[14)] is generated during each overall reaction (Table 5). Consequently, Path D may be most likely among the four paths.

The observation that no more than 30% of IV is ionized in solution at the concentration employed in the photolysis may be a further support for the direct charge transfer mechanism (Path D) because at such a low degree of dissociation the electron transfer from an anion to a cation should be easy. Further, as shown in Table 6, an absorption band which may be due to the charge transfer was observed at 245 nm in the UV spectrum of the iodide.[15)]

The solvent effect on the rates of the formation of the phosphines can also be explained well by the charge transfer mechanism. That is, the degree of dissociation of IV in benzene–ethanol mixed solvent may be decreased with increasing proportion of benzene to ethanol. As a result, an anion may transfer an electron to a cation more easily at high concentration of benzene. TPP and EDP may be obtained in better yields under these conditions. It may be reasonable to explain the solvent effect in this way since the degree of dissociation of $Ph_4P^+I^-$ in solution has been reported to be increased with increasing solvent polarity in the order, $MeCN < MeOH < H_2O$.[16)] It is not yet clarified why the ratio TPP/EDP was decreased with solvent polarity in this experiment.

As shown in Table 5, the addition of lithium nitrate retarded the photodecomposition. This may be due to that the charge transfer became difficult as a result of an increase in ionic strength of the medium. The acceleration of the reaction by the addition of oxygen may be accounted for by the oxidative decomposition of the phosphonium salts. Such accelerative effect of oxygen has been observed also in the pyrolysis of I in cyclohexene, producing triphenylphosphine oxide instead of TPP.[17)] Formation of neither TPP nor EDP could be detected in the photolysis of the nitrate or perchlorate. This may be due to the interaction of oxygen atoms in a nitrate or perchlorate anion with the resulting phosphines. Further, the observation that ϕ_{TPP} and ϕ_{EDP} were very low for the iodide may be attributable to the formation of the diiodophosphorane (Ph_2PRI_2) by the reaction of TPP or EDP with an iodine molecule, which is formed by the dimerization of iodine atoms.

$$2I\cdot \rightarrow I_2$$

$$Ph_2PR + I_2 \rightarrow Ph_2PRI_2, \quad R = Ph \text{ or } CH_2CO_2Et$$

[12)] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York (1966), p. 268.

[13)] a) Ref. 9, p. 269. b) H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953).

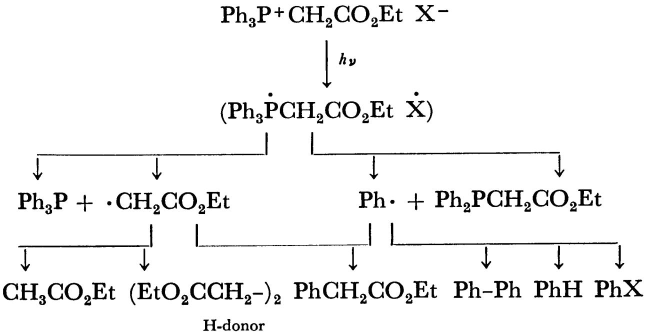
[14)] L. E. Orgel, *Quart. Rev.*, **8**, 422 (1954).

[15)] The assignment of the band should be reasonable since it has been reported that the absorption bands at 233 nm in the UV spectra of tris-*p*-tolylalkylphosphonium iodides are attributable to the charge transfer: M. A. A. Beg and Samiuzzaman, *Tetrahedron*, **24**, 191 (1968).

[16)] A. Honiger and H. Schindlbauer, *Ber. Bunsenges. Phys. Chem.*, **69**, 138 (1965).

[17)] Y. Nagao, K. Shima, and H. Sakurai, This Bulletin, **43**, 1885 (1970).

On the basis of the above discussion, we can conclude that the photolysis of IV proceeds through the charge transfer from an anion to a cation. The processes shown in Scheme 1 may account for the observations in the photolysis of IV.



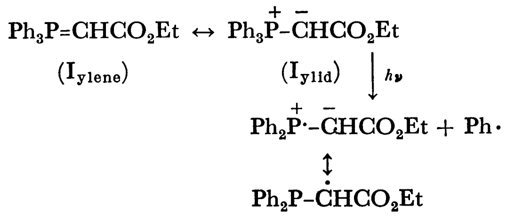
Scheme 1.

In this scheme, the phosphoranyl radical ($Ph_3\dot{P}CH_2CO_2Et$)[18] formed by one electron transfer decomposes mainly to TPP and an ethoxycarbonylmethyl radical, and partly to EDP and a phenyl radical. Radicals such as Cl· or Br· may abstract hydrogen atoms from solvent molecules, yielding hydrogen halides.

The photolysis of the tetrafluoroborate is the only one case where the charge transfer mechanism may not be operative. That is, the tetrafluoroborate was photolyzed more easily than the bromide although a tetrafluoroborate ion is less oxidizable than a bromide ion. Probably Path B, a direct cation excitation mechanism, may be important in this case.

Now, as the photolysis of IV has been confirmed to proceed through the charge transfer mechanism, we have compared the results with those of the photolysis of I and sulfonium and ammonium salts.

Owing to the important contribution of the ylid structure,[19] the compound I would have a positively charged phosphorus atom in its ground state. However, the mode of the photodecomposition of I differs significantly from that of IV. In the photolysis of I, a homolytic fission of a P-Ph bond may take place in the first stage by the direct absorption of light at a triphenylphosphinyl moiety. The charge transfer mechanism may not be important in this case.[20] On the other hand, a homolytic fission of a $P-CH_2CO_2Et$ bond took place preferentially through the electron transfer from the counter-anion to the associated acceptor cation in the photolysis of IV.



The charge transfer mechanism has also been proposed to take place in the direct[8a] and acetone sensitized photolysis[8b] of trimethylphenylammonium salts. However, a less stable radical (a phenyl radical) has been formed exclusively in these photolyses. In contrast, a more stable radical (an ethoxycarbonylmethyl radical) was produced preferentially in the photolysis of IV. Such a difference may arise from whether the *d* orbitals of the phosphorus or the nitrogen atom can participate or not in the photodecomposition. In the photolysis of IV, the phosphoranyl radical may be formed as an intermediate by the participation of the *d* orbitals of the phosphorus atom after the charge transfer. It is, thus, reasonable that a more stable ethoxycarbonylmethyl radical is produced preferentially from this intermediate. On the other hand, the energy level of the *d* orbitals of the nitrogen atom is so high that the *d* orbitals cannot participate in the photolysis of the ammonium salts. Possibly the direct electron transfer from an anion to the lowest antibonding orbital of the phenyl group of the cation might result in the exclusive cleavage of the N–Ph bond.

The photolysis of triarylsulfonium salts in alcohol[9] has been reported to involve both a charge transfer

TABLE 6. PREPARATION AND PROPERTIES OF PHOSPHONIUM SALTS

X	Cl[a]	Br	I	NO$_3$	ClO$_4$	BF$_4$
Mp (°C)	87—88	158	161—163	137	160—162	139—140
(lit, mp)	(87—88)	(158)	—	—	—	—
Literature	21	22	—	—	—	—
Method	A	A	A	B	B	B
UV λ_{max}^{EtOH} (nm)	267	267	245 268	267	268	267
$\varepsilon \times 10^{-3}$	3.85	3.38	9.78 3.96	3.29	3.23	3.40
			C H	C H	C H	C H
Anal. Found	—	—	55.82 4.70	64.29 5.60	58.68 5.05	68.65 5.87
Calcd	—	—	55.48 4.66	64.22 5.39	58.87 4.94	69.68 5.85

a) This compound was obtained as a dihydrate, and dehydrated with phosphorus pentoxide.

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[18] J. I. G. Cadogan, "Advances in Free Radical Chemistry," Vol. 2, ed. by G. H. Williams, Academic Press, New York (1967), p. 220.

[19] Z. Yoshida, "Quantum Organic Chemistry," ed. by S. Nagakura, K. Fukui, and Z. Yoshida, Kagaku Dojin, Kyoto (1966), p. 231.

[20] In the UV spectrum of III, an absorption band, being attributable to the charge transfer, has been observed at 432 nm. The photolysis of III using light above 320 nm may proceed through the charge transfer.[5]

[21] W. J. Considine, *J. Org. Chem.*, **27**, 647 (1962).

[22] O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).

(Path D) and a direct excitation of a cation yielding an aryl radical and a sulfinium cation radical (Path B). It has been considered that triarylsulfur radicals (sulfur analogs of phosphoranyl radicals) are formed by the participation of the *d* orbitals of the sulfur atom as the intermediate in the charge transfer process. Although the photolysis of dimethylphenacylsulfonium salts[9b,c] has been found to form a phenacyl radical (more stable than a methyl radical), the *d* orbitals may not participate in this system since this reaction proceeds through the direct cation excitation mechanism (Path B) only.

Experimental

All melting points are uncorrected. UV spectra were recorded on a Hitachi 124 Spectrophotometer. Gas chromatographic analysis were performed on a Shimadzu Gas Chromatograph, GC-3AF (carrier gas; N_2).

Preparation of Phosphonium Salts. Phosphonium salts were prepared by the following two methods, A and B.

Method A: A solution of 0.06 mol of TPP in 30 m*l* of benzene was treated with a solution containing an equivalent amount of ethyl α-haloacetate in 30 m*l* of benzene. The salt was filtered, washed with benzene, dried, and recrystallized from methylene chloride-ether.

Method B: A solution of 0.01 mol of AgX ($X=ClO_4$, NO_3 or BF_4) in water was added dropwise with stirring to a solution containing an equivalent amount of phosphonium bromide in methanol and the mixture was washed with methanol, and the filtrate and washing were combined and concentrated to a residue that was recrystallized from methylene chloride-ether.

Melting points and the UV spectral data of the salts are shown in Table 6.

Ethoxycarbonylmethyldiphenylphosphine (EDP). This compound was prepared by the method of Issleib and Thomas.[23] Hydrolysis of this compound gave carboxymethyldiphenylphosphine, mp 121—122°C (lit,[23] mp 120—121°C).

Photochemical Studies. A solution of 3.5 mmol of IV (X=Cl, Br, or I) in 10 m*l* of acetonitrile was placed in a quartz tube and degassed by three cycles of the freeze-pump-thaw method. The solution was irradiated with a quartz Eikosha PIH 350-W water-cooled, high pressure mercury lamp for 150 hr. After the irradiation the tube was opened and the contents were analyzed directly by gas chromatography. Four different columns were used in order to separate the peaks of the products: (1) a 1-m 15% SE-30 column for TPP and EDP, (2) a 3-m 25% DEGS column for most of the volatile components, (3) a 3-m 25% Silicone-DC column for halobenzenes, and (4) a 3-m 25% PEG column for benzene and ethyl acetate. Cyclohexane, α-methyl naphthalene and ethyl succinate were used as the internal standards in determining product yields.

Kinetic Experiments. Solutions containing 1.6 mmol of IV and equimolar amounts of the appropriate additives in the appropriate anhydrous solvents (4 m*l*) were degassed in quartz or Pyrex tubes and irradiated with the same high pressure mercury lamp as used above. Samples in quartz tubes were irradiated for 45 min. Within such irradiation time the yields of the products increased linearly. Samples in Pyrex tubes needed longer irradiation. The amounts of unreacted salts were found by adding ether to the reaction mixture slowly. The crystals formed were filtered, washed with ether, dried, and weighed. The concentrations of Brønsted acids were determined by titrating the reaction mixture with 0.1 N potassium hydroxide solution.

Quantum yields were measured by use of a 4 ml of quartz spectrophotometric cell. Acetonitrile solutions of IV (0.5 M) were degassed and irradiated at 253.7 nm. Potassium ferrioxalate was used as an actinometer. The yields of the products were determined by gas chromatography.

The Measurement of the Electrical Conductance. Resistances were measured with a Yokokawa On-Ichi-Go Impedencemeter at a frequency of 1000 Hz. An oscilloscope, Yokokawa OL-51C, and an oscillator, Matsushita VP-706 were used. The cell constant was $0.393\ cm^{-1}$.

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[23] K. Issleib and G. Thomas, *Chem. Ber.*, **93**, 803 (1960).