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Photolysis of (Arylmethyl)triphenylphosphonium Salts. Substituent, Counterion, and Solvent Effects on Reaction Products

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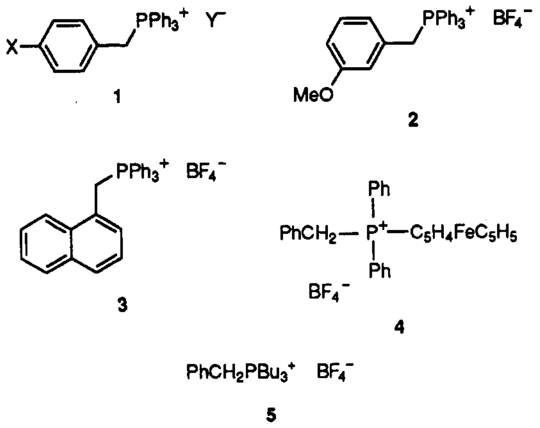
Quaternary (arylmethyl)phosphonium salts of the general formula $ArCH_2–PR_3^+Y^-$ (Ar = substituted phenyl or 1-naphthyl; R = phenyl, ferrocenyl, or butyl; Y^- = BF_4^- or halide) have been photolyzed in acetonitrile or in methanol. Photolysis involved the cleavage of the $P–CH_2$ bond and the products derived from both, the arylmethyl radical and the carbocation, were formed. The proportion of the radical- and carbocation-derived products was determined as a function of substituents in group Ar, of groups R, counterions Y^-, and the solvent. For the nonoxidizable counterion (BF_4^-), the proposed mechanism of the reaction involves initial homolysis, followed by the escape of the radical products from a solvent cage, or by the electron transfer from carbon to phosphorus, yielding the corresponding arylmethyl carbocation. The latter can either react with the solvent to form the observed carbocation-derived product or can undergo recombination with the tertiary phosphine formed to yield the starting phosphonium ion. Some indication of the "inverted substituent effect" resulting from the inhibition of single electron transfer from an easily oxidized radical was obtained. For the oxidizable counterions (halides), an additional pathway is suggested, that involves electron transfer from the anion, yielding the arylmethyl radical and the phosphine, thus decreasing the ionic/radical products ratio.

While the photochemistry of phosphine chalcogenides,[1] as well as of phosphonic systems[2] has been extensively studied, photolytic cleavage of quaternary phosphonium ions has received much less attention. Photolysis of benzyltriphenylphosphonium chloride was investigated almost 30 years ago,[3] and the reaction products were interpreted only in terms of the radical pathways following the initial electron transfer from Cl^- to the phosphorus atom. More recently, Breslin and Saeva[4] studied the photochemistry of some Group V onium salts and proposed a mechanism accounting for the in-cage and out-of-cage products of the initially formed cation-radical/radical pair. For the phosphonium substrate ((4-cyanobenzyl)triphenylphosphonium tetrafluoroborate) the product of the out-of cage radical coupling (bibenzyl derivative) was reported as the only non-phosphorus compound, while the arsonium analogue yielded both the radical coupling product and the product indicating the intermediacy of the 4-cyanobenzyl carbocation. Recent laser flash photolysis studies[5] demonstrated competitive formation of the carbocation and radical species directly from a phosphonium precursor, with the relative yields of radical *vs* cation varying considerably with the solvent composition.

As a first part of our studies on the photochemistry of phosphonium derivatives, we have investigated the photolysis (254 and 300 nm) of a series of (arylmethyl)triphenylphosphonium salts and found that the reaction products depend strongly on the substituents in the arylmethyl group, on the counterion, and on the reaction medium. In some cases the PPh_3^+ group of the substrate was replaced by the PBu_3^+ or the PPh_2Fc^+ (Fc = ferrocenyl) group, in order to evaluate additionally the effect of difference in the nucleophilicity of the corresponding tertiary phosphine on the photolysis products. Structural (and medium) variables were then correlated with the composition of the reaction products, resulting from the homolytic and ionic cleavage of a phosphonium substrate.

Scheme I[a]



[a] **1a**, X = H; **1b**, X = Me; **1c**, X = Bu^t; **1d**, X = OMe; **1e**, X = F; **1f**, X = Cl; **1g**, X = CN; **1h**, X = NO_2. For anions Y^-; see Tables I and II.

Results

The quaternary phosphonium ions used in the photolysis experiments are shown in Scheme I.

Tetrafluoroborate and chloride (in case of **1a** and **1g** also other halides) ions were selected as examples of nonoxidizable and oxidizable counterions Y^-. Acetonitrile and methanol were used as solvents of greatly different

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[●] Abstract published in *Advance ACS Abstracts*, September 1, 1993.

[1] Dankowski, M. *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley: Chichester, 1992; Chapter 4.

[2] Suzuki, N.; Kawai, T.; Inoue, S.; Sano, N.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1421. Shi, M.; Okamoto, Y.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 453. Okamoto, Y.; Kokubu, I.; Takamuku, S. *Phosphorus, Sulfur, and Silicon* **1990**, *48*, 63. Shi, M.; Yamamoto, K.; Okamoto, Y.; Takamuku, S. *Phosphorus, Sulfur, and Silicon* **1991**, *60*, 1.

[3] Griffin, C. E.; Kaufman, M. L. *Tetrahedron Lett.* **1965**, 773.

[4] Breslin, D. T.; Saeva, F. D. *J. Org. Chem.* **1988**, *53*, 713.

[5] Alonso, E. O.; Johnston, L. J.; Scaiano, J. C.; Toscano, V. G. *Can. J. Chem.* **1992**, *70*, 1784.

0022-3263/93/1958-5643$04.00/0

nucleophilicity.[6] Photolysis products were identified and semiquantitatively determined by NMR (^1H and ^{31}P) spectroscopy, while GC (using authentic samples as standards) or GC/MS (when standards were not available) were used for quantitative determinations. All substrates reacted easily at room temperature and 3 (**1**–**3**) or 24 (**4**, **5**) h of irradiation was usually sufficient to achieve full conversion. The only exception was **1h**, in which the substituent itself represents the chromophoric center and which did not undergo any noticeable change after more than 24 h of irradiation.

(Arylmethyl)triphenylphosphonium Salts 1–3. Photolysis in Acetonitrile. Common products of the photolysis of substrates **1**–**3** are shown in eq 1; in all cases

$$ArCH_2{-}PPh_3^+\ Y^- \xrightarrow{h\nu,\ CH_3CN} PhH + \underset{\mathbf{6}}{Ar{-}CH_3} + \underset{\mathbf{7}}{ArCH_2CH_2CN} + \underset{\mathbf{8}}{(ArCH_2)_2} + \underset{\mathbf{9}}{ArCH_2NHC(O)CH_3}$$
$$+ Ph_3PO + Ph_2P(O)H + Ph_4P^+\ Y^- + Ph_3PO{\cdot}BF_3 + HY \quad (\text{when } Y^- = BF_4^-) \qquad (1)$$

the NMR and GC analysis indicated the formation of only negligible quantities of other products.[7] Although reactions were always carried out until all substrate had disappeared, the complete mass balance could not be achieved upon evaporation of the solvent because of the partial loss of the most volatile products (benzene, toluene, *p*-xylene, HF, BF_3). In order to achieve quantitative determination of all products, the irradiated solutions were analyzed directly by GC using internal standards of known concentration. The total yields determined in that way varied from quantitative to medium (50–60%), but the proportions of the individual products were well reproducible and did not depend on the total yield. The observed variations in total yields resulted from the fact that the relative GC detector response factors may vary slightly from run to run. Products **6**, **7**, and **8** were taken as derived from the homolytic cleavage of substrates yielding arylmethyl radicals (abstraction of hydrogen atom from the solvent,[8] coupling with the cyanomethyl radical, and dimerization, respectively),[9] while **9** resulted from the reaction of arylmethyl carbocations with acetonitrile, followed by hydrolysis.[4] The formation of diphenylphosphine oxide and tetraphenylphosphonium ion, as well as of benzene, indicated some cleavage of the phosphorus–phenyl bond. No evidence was however found for CH_2–Ar bond cleavage; for example, GC analysis of the product of photolysis of **1d** ($Y^- = Cl^-$; 3.5 h) showed no trace of anisole. Since we were mostly interested in the mechanism of the cleavage of the phosphorus–benzyl carbon bond, the proportions of products **6**–**9** were determined quantitatively and will be discussed in detail. Table I lists the composition of the non-phosphorus products of the P–CH_2 bond fission, together with the oxidation potentials of the corresponding arylmethyl radicals. The proportion of the individual products did not depend on the degree of conversion (irradiation time in the range of 15–120 min) or on the initial concentration of the substrate (c_o in the range of 10–40 mg/5 mL). No rearranged products resulting from the migration of the $ArCH_2$ moiety to the phenyl ring, reported before for the arsonium ions,[4] could be detected.[10-12] It can be seen, however, from Table I, that the composition of the product depends on the salt's counterion (BF_4^- *vs* halide). In addition, as demonstrated for **1a** and **1d**, photolysis yielded different results when carried out in the presence of diphenylferrocenylphosphine (Table I, footnote c).

Table I. Products (Non-Phosphorus) of the P–CH_2 Bond Cleavage in the Photolysis of Substrates 1–3 in Acetonitrile at 30 °C

	products[a]					
substrate	6	7	8	9	other	$E_{1/2}^{ox}$ [b]
1a, $Y^- = BF_4^-$	9.4	8.4	3.4	78.8		0.73
c	2.0	4.4	16.6	34.2	33.9 ($ArCH_2$*p*-tol), 8.9 ($ArCH_2PPh_2Fc^+$)	
$Y^- = Cl^-$	14.8	11.1	18.4	53.7	2.0 (Ar_2CH_2)	
$Y^- = Br^-$	54.7	5.7	1.3	37.0	1.3 (Ar_2CH_2)	
$Y^- = I^-$	56.2		25.1	9.3	0.3 (Ar_2CH_2) 9.1 ($ArCH_2I$)	
1b, $Y^- = BF_4^-$	13.1		3.3	83.5		0.51
1c, $Y^- = BF_4^-$	14.8			85.2		0.57[d]
1d, $Y^- = BF_4^-$	78.1		13.9	8.0		0.26
c	1.6		35.2	trace	63.2 ($ArCH_2PPh_2Fc^+$)	
$Y^- = Cl^-$	23.3		54.8	2.8	19.1 ($ArCH_2Cl$)	
1e, $Y^- = BF_4^-$	6.2	2.4	4.3	87.1		0.73
$Y^- = Cl^-$	10.4		20.0	64.0	5.5 ($ArCH_2Cl$)	
1f, $Y^- = BF_4^-$	9.7		4.3	86.0		0.80
$Y^- = Cl^-$	6.9		22.4	78.5	7.9 ($ArCH_2Cl$)	
1g, $Y^- = BF_4^-$	65.9		32.6	0.51		1.08
$Y^- = Cl^-$	16.9	10.1	49.0	24.0		
$Y^- = Br^-$	78.7	0.7	11.3	9.3		
2, $Y^- = BF_4^-$	78.7		8.9	12.3		0.79[d]
3, $Y^- = BF_4^-$	38.5		15.6	45.9		0.47[e]
4, $Y^- = BF_4^-$	37.0		34.0	15.0	14.0 (PhCHO)	
5, $Y^- = BF_4^-$ [f]	15.0	51.0	34.0	trace		

[a] Relative yield (%), determined by GC, GC/MS, and ^1H NMR spectroscopy. [b] Electrochemical potential (in V, in MeCN); unless otherwise stated, taken from ref 10. [c] The photolysis carried out in the presence of 1 mol equiv of Ph_2PFc. [d] Estimated from the $E_{1/2}^{ox}$ *vs* σ^+ plot. [e] Taken from ref 11. [f] Major phosphorus-containing products are Bu_3P (62%) and Bu_3PO (38%).

Photolysis in Methanol. Equation 2 shows the products of photolysis in methanol. As before, products **6** and **8** were taken as a measure of the homolytic pathway (solvent incorporated product, analogous to **7** was not observed in methanol), while ethers **10** were formed by the reaction of the arylmethyl carbocation with the nucleophilic solvent. The total yields, determined as described above, were usually higher than in acetonitrile (quantitative to 70–80%); any other products but those

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[6] Solvent nucleophilicity parameter (*N*) for acetonitrile and for methanol differ by 2.12 units of *N*: Peterson, P. E. In *Nucleophilicity*, Harris, J. M., McManus, S. P., Ed.; American Chemical Society: Washington, D.C.,1987; Chapter 21.

[7] For example, crude product of the photolysis of **1e** was examined directly by ^{19}F NMR spectroscopy. Only the signals corresponding to products **6**-**9** were observed. Similarly, for **1d** only three signals of the OCH_3 group (in **6**, **8**, and **9**) were observed in the ^1H NMR spectrum.

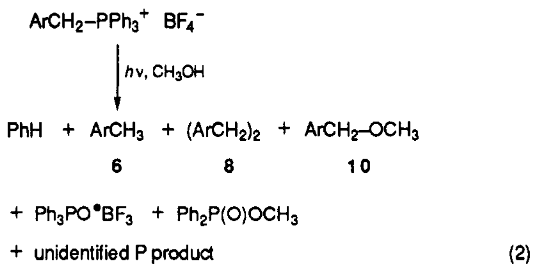
[8] As the referee pointed out, hydrogen abstraction from MeCN by a benzyl radical should be endothermic and slow. Products **7** have been, however, identified unambiguously by GC/MS. Formation of large quantities of toluene in the photolysis of quaternary benzylammonium ions in MeCN or in alcohols has been reported before. Ratcliff, M. A.; Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 3112. Appleton, D. C.; Bull, D. C.; Givens, R. S.; Lillis, V.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc. Perkin Trans. 2* **1980**, 77.

[9] In quenching experiments (solutions saturated with O_2) formation of **6** was suppressed, and **8** was virtually absent in the reaction product.

[10] Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635.

[11] De Costa, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8948.

[12] The rearrangement should yield a tertiary aromatic phosphine; no signals in the expected range of δ_P −4–40 ppm were observed in the ^{31}P NMR spectra of the photolysis product. Tebby, J. C. *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; CRC Press: Boca Raton, 1991; Chapter 6.



$$ArCH_2{-}PPh_3^+\ BF_4^- \xrightarrow{h\nu,\ CH_3OH} \underset{}{PhH} + \underset{\mathbf{6}}{ArCH_3} + \underset{\mathbf{8}}{(ArCH_2)_2} + \underset{\mathbf{10}}{ArCH_2{-}OCH_3} + Ph_3PO{\cdot}BF_3 + Ph_2P(O)OCH_3 + \text{unidentified P product} \qquad (2)$$

shown in eq 2 were formed in negligible quantities, and the proportions of the products were well reproducible. The proportions of products derived from arylmethyl species are given in Table II.

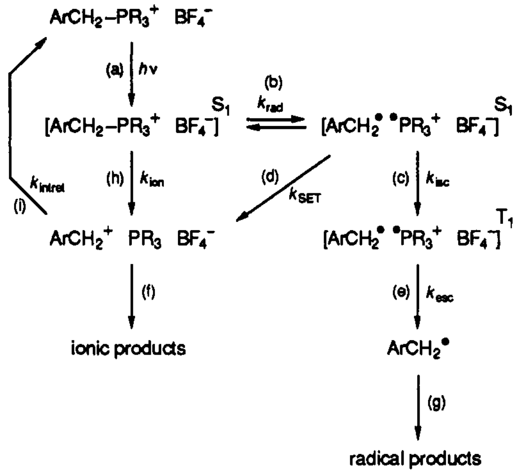
(Arylmethyl)phosphonium Salts 4 and 5. In general, irradiation of substrates 4 and 5 in acetonitrile led to the formation of almost identical non-phosphorus compounds as for 1–3, but the proportions of individual products changed dramatically. Using the same analytical methodology as before, we determined quantitatively those photoproducts and their relative yields are incorporated into Table I.

Table II. Non-Phosphorus Products of the P–CH$_2$ Bond Cleavage in the Photolysis of Substrates 1 and 3 (unless otherwise stated, Y$^-$ = BF$_4^-$) in Methanol at 30 °C

substrate	products[a] 6	8	10
1a	4.9	21.5	73.6
Y$^-$ = Cl$^-$	10.2	18.1	71.7
Y$^-$ = Br$^-$	9.3	15.1	75.6
Y$^-$ = I$^-$	5.4	44.8	49.8
1b	3.4	6.6	90.0
1c	5.9	9.2	84.9
1d	13.6	20.0	66.4
1e	1.4	6.7	91.9
1f	6.2	13.3	80.5
1g	35.5	64.4	≤0.5
3	10.7	14.1	75.2

[a] See Table I, footnote.

Scheme II



Discussion

The photolysis of the ring-substituted benzyltriphenylphosphonium salts with a nonoxidizable counterion (BF$_4^-$) will be discussed first. According to Saeva,[4] photolysis of the onium salts involves homolytic bond cleavage yielding a singlet radical/cation-radical pair in a solvent cage. That first intermediate can undergo intersystem crossing to the triplet state, a precursor for the out-of-cage radical products. In the S$_1$ radical/cation-radical pair a single electron transfer (SET) can, however, also occur,[13] yielding a carbocation which is then trapped by solvent (or any other nucleophilic species) to form the ionic products. The above mechanism is incorporated in Scheme II (steps a–g). Alonso *et al.*[5], on the basis of flash photolysis experiments, preferred a SET mechanism but left open the possibility of direct P–C heterolysis. Costa and Pincock assumed in their study on the photolysis of naphthylmethyl esters[11] that SET, and not a direct heterolysis, is responsible for ionic products. By applying those models to the photolysis of ions 1–5 (with tetrafluoroborate as a nonoxidizable counterion), one arrives at a general mechanism accounting for the formation of the observed products (Scheme II). If the internal return pathway ($k_{\rm intret}$) is ignored, it follows from the mechanism that the composition of the product results from the competition between the electron transfer ($k_{\rm SET}$) and the escape from the solvent cage ($k_{\rm esc}$) of a radical/cation-radical pair formed in the homolytic cleavage of the P–CH$_2$ bond. Sensitization (acetone, 300 nm, solvent acetonitrile) resulted in a virtual elimination of product 9, with the retention of the formation of products 6–8, thus indicating that 9 is derived from S$_1$ and that the T$_1$ state of the pair is reactive to form the radical pair (precursor for 6–8). De Costa and Pincock[11] estimated the $k_{\rm SET}$ values for different ester substrates and correlated them with the oxidation potentials of the corresponding radicals. The correlation revealed that the easily oxidized radicals gave rise to the so-called Marcus inverted region[14] in which the electron transfer becomes prohibitively exothermic. We observed exactly the same behavior of ions 1 upon photolysis in acetonitrile (and, to a lesser extent, in methanol) where the remarkable feature of the results is a very low contribution of the ionic product 9 observed not only for **1g**, but also for a substrate containing a strongly electron-donating substituent (**1d**).[15] Assuming that the recent results[16] showing that so-called "meta effect" introduced by Zimmerman[17] which is unnecessary to explain photolysis of 4-methoxybenzyl esters can be applied to phosphonium derivatives, this result is inconsistent with a mechanism involving initial competitive fragmentation of the exctited substrate to the ionic and radical arylmethyl species ($k_{\rm ion}/k_{\rm rad}$), as the former should be most prominent for **1d**. We have determined the ionic/radical selectivity (expressed as log (I/R), where I = yield of 9 or 10, and R = combined yields of 6–8) for the photolysis of the tetrafluoroborates of **1a–g** and 3 in acetonitrile, and in methanol, and plotted those values against the oxidation potentials of the corresponding arylmethyl radicals (Figure 1). Bell-shape plots, similar to that reported[11] for the photolysis of arylmethyl carboxylates, was obtained, with the curvature occurring at the value of $E_{1/2}{}^{\rm ox} < 0.8$ V, and the 4-OMe substituent clearly located in the inverted region of the plot. Figure 1 could be therefore taken as a support of the phenomena of the suppression of the

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[13] Saeva, F. D. Personal communication.

[14] Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

[15] Since the low yield of 9 was not expected for the photolysis of **1d**, the analysis of the product was carried out several times, always giving yields of 9 distinctly lower than those obtained for **1a–c,e,f**, and comparable with that obtained for **1g**.

[16] Hilborn, J. W.; MacKnight, E.; Pincock, J. A.; Wedge, P. J. Unpublished. We thank Professor Pincock, Halifax, for providing us with unpublished results.

[17] Zimmerman, H. E.; Sandel, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 49.

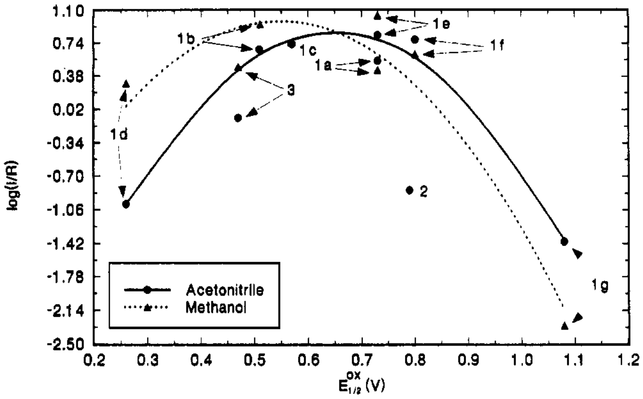

Figure 1. Log (I/R) vs $E_{1/2}{}^{ox}$ for the photolysis of phosphonium salts.

electron transfer process that leads to the formation of a resonance-stabilized carbocation.[18]

There is, however, another explanation that may be offered to account for the remarkably low yield of the ionic product **9** in the photolysis of the *p*-methoxy derivative **1d**. According to the mechanism presented in Scheme II, the arylmethyl carbocation, formed either *via* the direct heterolytic cleavage or *via* the electron transfer, can react with the solvent ("ionic products" **9** or **10**) or can react with the corresponding tertiary phosphine to regenerate the phosphonium substrate (k_{intret}). The latter pathway would allow for the "recycling" of the phosphonium ion, thus would lead to the decrease in the [ionic]/[radical] products ratio. The feasibility of the "internal return" pathway (arylmethylation of a tertiary phosphine) was confirmed in the photolysis experiments carried out in the presence of diphenylferrocenylphosphine (Table I, footnote c). Under those conditions we observed a dramatic decrease in the formation of the acetamide derivative **9**, together with the formation of considerable quantities of a new phosphonium species, (arylmethyl-)diphenylferrocenylphosphonium ion.[19] This result demonstrates that a tertiary phosphine can successfully compete with the solvent in trapping an intermediate carbocation, so under the usual conditions some of the cation will be converted back to the starting phosphonium ion. Since the nucleophilicity of Ph_2PFc is greater than that of triphenylphosphine,[20] the former, when introduced to the reaction mixture, will intercept a large proportion of the carbocation. The data in Table I also reveal that the effect of the added diphenylferrocenylphosphine is much greater in the photolysis of **1d** than of **1a** (63 *vs* 9% of the new phosphonium ion formed, as well as much greater drop in the formation of the solvent-trapped product **9**). This is what should be expected for a mechanism involving partitioning of an intermediate carbocation between the nucleophilic species present, including the parent phosphine or any other phosphine introduced to the system. 4-Methoxybenzyl carbocation, the most stable in the series, would be the most selective with respect to the available nucleophiles, hence should react preferably with the parent triphenylphosphine ("internal return") or with PPh_2Fc when it was present in the medium.[21] Changing the solvent from acetonitrile to methanol had, on the other hand, different effect: the proportion of the product of the reaction of the arylmethyl carbocation with the solvent (ethers **10**) has increased significantly in almost all cases (Table II). The more nucleophilic solvent competes in that case more effectively with triphenylphosphine with respect to the intermediate carbocation. Contrary to the results obtained in acetonitrile, photolysis carried out in methanol in the presence of diphenylferrocenylphosphine did not result in the decrease of **9** and in the formation of a new phosphonium ion. It is clear that in methanol the carbocation's lifetime is not long enough to allow its recombination with any phosphine species present in the system. We propose, therefore, that the proportion of the ionic *vs* radical products in the photolysis of the phosphonium tetrafluoroborates is determined, according to Scheme II, by *both* the electron tranfer (k_{SET}) and the recombination with the phosphine (k_{intret}) processes.

Table III. Effect of the Counterion on the Ionic/Radical Selectivity $I/R^{a,b}$ in the Photolysis of Salts 1

	counterion			
substrate	BF_4^-	Cl^-	Br^-	I^-
1a	3.72	1.16	0.59	0.11
1a in MeOH	2.79	2.53	3.09	0.99
1d	0.087	0.036		
1e	6.75	2.10		
1f	6.14	2.68		
1g	0.0052	0.316	0.103	

[a] $I/R = \sum(\mathbf{6, 7, 8})\ (\%)/\mathbf{9}(\%)$. [b] Unless otherwise stated, photolysis in acetonitrile.

When the PPh_3^+ group in the substrate salts has been changed to the $PFcPh_2^+$ (**4**) or the PBu_3^+ (**5**) groups, the proportion of the ionic to the radical products again changed dramatically (Table I, last two entries *vs* first entry). The proportion of the ionic product **9** was greatly suppressed, as expected for the substrates that yield upon P–CH_2 bond cleavage a more nucleophilic phosphine ($PFcPh_2$ or PBu_3), thus increasing the contribution of the "internal return" pathway.

The product distribution in the photolysis of **1**–**5** can be significantly modified not only by the variation in the structure of a phosphonium ion or a solvent, but also by the choice of a counterion. Table III shows the variation in the ratio of the ionic to the radical products as a function of a counterion. The observed trend is that the change from a nonoxidizable anion (BF_4^-) to the progressively more oxidizable halide ions is followed by a significant (and approximately constant) decrease in the I/R ratio. The exceptions are the photolysis of **1a** in methanol (where the ratio remains approximately constant and drops only for the iodide counterion) and the photolysis of **1g** (where the trend is reversed). Since we have established that

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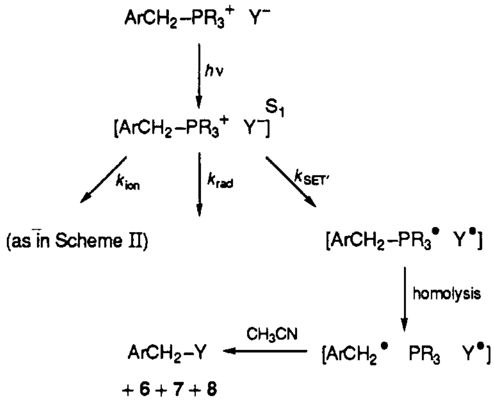
(18) The phenomenon may be more common than initially believed. For example, analysis of the quantum yields of the photosolvolysis and photohomolysis in the photolysis of benzyl chlorides reveals a similar lack of correlation between the former products and polar substituent constants. Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951.

(19) The product composition could, of course, reflect in this case also a subsequent photolysis of the new phosphonium ion. Fortunately, as it was shown in the independent experiments, the newly formed phosphonium ions, $ArCH_2PPh_2Fc^+$, undergo photolysis much slower than ions **1**, and at least 24 h of irradiation (*vs* 3 h for **1**) was necessary for significant conversion into photolysis products. Another independent experiment in which a solution of **1d** and diphenylferrocenylphosphine (1:1) in MeCN was incubated *in the dark* for 3.5 h at 40 °C showed no exchange of the phosphine groups, thus confirming the validity of the photolysis experiments carried out in the presence of Ph_2PFc.

(20) McEwen, W. E.; Sullivan, C. E.; Day, R. O. *Organometallics* **1983**, *2*, 420.

(21) Selectivities of carbocations toward azide ion and water measured as the ratio [RN_3/ROH] show strong dependence on the stability of a carbocation. Raber, D. J.; Harris, J. M.; Hall, R. E.; von Rague Schleyer, P. *J. Am. Chem. Soc.* **1971**, 93, 4821.

Scheme III



during the photolysis of the phosphonium halides the corresponding arylmethyl halides are formed as intermediates, the most obvious conclusion would be that the change in the product composition results from the subsequent photolysis of those intermediates. We have found, however, that the independent photolysis of benzyl chloride or bromide in acetonitrile gives predominantly the ionic product, acetamide **9** (63 and 78%, respectively).

The first report about the strong anion dependence on product formation during the photolysis of onium salts was that of Sakurai and co-workers concerning [(ethoxycarbonyl)methyl]triphenylphosphonium salts,[22] followed by the recent contribution of Hacker and co-workers on the photolysis of diphenyliodonium halides.[23] The results of the latter report were interpreted in terms of the salts $Ph_2I^+Y^-$ ($Y^- = Cl^-, Br^-, I^-$) existing in acetonitrile as tight ion pairs, which give charge-transfer excited states that decompose to the radical species, precursors of the radical products. The ionic products observed in aqueous acetonitrile were taken as a consequence of the solvent separated pairs, in which charge transfer involving a halide ion is less favored. The proposed mechanism is in full agreement with our results on the effect of a counterion on the product distribution. In acetonitrile, the electron transfer from the halide ion (as originally proposed by Griffin and Kaufman[3]) to phosphorus can take place in the tight ion pair, offering and additional pathway for the radical products, and competing with the direct photolysis of the phosphonium cation, thus decreasing the contribution of the ionic products. The more readily oxidizable the counterion, the more of the final product results from that process. It has been demonstrated that the reaction between benzyltriphenylphosphonium ion and a hydrated electron involves the cleavage of the $P–CH_2$ bond with the formation of the benzyl radical.[24] The mechanism proposed here incorporates both, the mechanism proposed by Breslin and Saeva[4] for the tetrafluoroborate salts and the interpretation of the photolysis of phosphonium chlorides given by Griffin and Kaufman.[3] As compared with the mechanism presented in Scheme II, for a salt with an oxidizable anion an additional pathway is available in a less polar solvent, as shown in Scheme III. Assuming that substrates **1–5** exist in methanol as solvent-separated ion pairs, it is clear that the halide–phosphorus electron transfer should be suppressed, hence the product composition would be expected to show little dependence on the counterion. This may not be fully true for an iodide salt, both because of the high oxidizability of I^- ion, and because of a higher degree of ion pairing.[25]

Contrary to other substrates **1**, irradiation of **1g** in acetonitrile yields more of the ionic product for the halide counterion than for the tetrafluoroborate salt. Again, the intermediate formation of the arylmethyl halide has been demonstrated, and the independent irradiation of 4-cyanobenzyl bromide yielded the corresponding amide **9** as a major product (80%). It is possible therefore that in the case of **1g** recombination of the arylmethyl radical and halogen atom occurs to a high degree yielding a large proportion of the corresponding benzyl halide, $ArCH_2–Y$ (Scheme III, Ar = $4\text{-}NCC_6H_4$, Y = Cl or Br). The intermediate benzyl halide would then solvolyze to the final acetamide product according to the mechanism proposed by Schuster and co-workers[26] for the photosolvolysis of (iodomethyl)naphthalenes, in which the product-generating step involves the nucleophilic solvolysis of a complex between a halogen atom and the arylmethyl halide. The solvolysis would be expected to be most efficient for a substrate carrying a strongly electron-withdrawing substituent in the Ar group (**1g**).

In conclusion, preparative photolysis of phosphonium salts results in the formation of a variety of products derived from both radical and ionic intermediates formed *via* different pathways, depending on the structure of the ion, the solvent, and the nature of the counterion. We are exploring the photosolvolysis of other phosphonium ions, including those that involve the photolytic cleavage of the $P–CH_2Fc$, $P–NR_2$, and $P–OR$ bonds.

Experimental Section

All solvents and commercially available reagents were purified by standard methods immediately before use. Photolysis experiments were carried out in a Rayonet Model RPR-208 photochemical reactor fitted with a "merry-go-round" attachment and either 253.7- or 300.0-nm lamps. NMR specra were recorded on a Bruker AC 300 spectrometer with TMS (^1H) as an internal or 85% H_3PO_4 (^{31}P) as an external standard. Unless otherwise indicated, $CDCl_3$ was used as a solvent. UV spectra were recorded in methanol or acetonitrile using a Bausch and Lomb Spectronic 2000 spectrophotometer. Elemental analyses were performed by the Materials Science and Technology Division, C.S.I.R., Pretoria. Melting points are uncorrected. Acetonitrile was dried over calcium hydride and fractionally distilled. Methanol was dried by treating it with metallic magnesium followed by fractional distillation. The following arylmethyl halides required for the synthesis of the substrates were prepared. **Benzyl iodide** was prepared from benzyl alcohol by treatment with Me_3SiCl, followed by Me_3SiCl/NaI.[27] **4-Chloro-, 4-methyl-, and 4-*tert*-butylbenzyl chlorides** were prepared by reduction of the corresponding benzoic acids (LAH), followed by treatment with $SOCl_2$. The following standards required for the GC identification of the photolysis products were prepared by standard methods.

1,2-Diarylmethanes ($(ArCH_2)_2$) 8 were prepared from arylmethyl halides and the Grignard reagents prepared from the

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Table IV. Quaternary (Arylmethyl)phosphonium Salts 1–5[a]

	mp (°C)[b]	δ_P	δ_H (J, Hz)[c]	anal. calcd (found) (or MS)
1a	215–216	24.2	4.70 (2H, d, J_{HP} = 14.3), 6.92 (2H, dd, J = 7.6, 2.1), 7.11 (2H, t, J = 7.6), 7.22 (1H, dt, J = 7.6, 2.1)	C 68.2 (68.1), H 4.8 (5.1)
1b	206–207	22.9	2.24 (3H, s), 4.63 (2H, d, J_{HP} = 14.0), 6.78 (2H, dd, J = 2.5, 8.2), 6.92 (2H, d, 8.2)	C 68.8 (68.5), H 5.3 (5.0)
1c	200–201	23.1	1.20 (9H, s), 4.61 (2H, d, J_{HP} = 13.9), 6.83 (2H, dd, J = 2.5, 8.2), 7.13 (2H, d, J = 8.2)	C70.2 (70.3), H 6.1 (6.2)
1d	197–198	23.5	3.69 (3H, s), 4.57 (2H, d, J_{HP} = 13.6), 6.62 (2H, d, J = 8.6), 6.81 (2H, dd, J = 2.3, 8.6)	C 66.4 (66.2), H 5.1 (5.2)
1e	191–192	23.5 (J_{PF} 6.7)	4.69 (2H, d, J_{HP} = 14.1), 6.78 (2H, t, J = 8.6), 6.89 (2H, m) δ_F[d] −155.8, −116.9	C 65.5 (65.5), H 4.6 (4.8), F 20.7 (20.8)
1f	203–204	23.4	4.70 (2H, d, J_{HP} = 14.4), 6.88 (2H, dd, J = 2.5, 8.3), 7.06 (2H, d, J = 8.3)	C 63.3 (63.3), H 4.5 (4.2), Cl 7.5 (8.2)
1g	204–205[e]	24.3	4.80 (2H, d, J_{HP} = 15.3), 7.10 (2H, dd, J = 2.5, 8.3), 7.25 (2H, d, J = 8.3)	C 67.1 (67.1), H 4.5 (4.7), N 3.0 (3.1)
1h	186–188	24.3	4.77 (2H, d, J_{HP} = 15.4), 7.16 (2H, dd, J = 2.5, 8.9), 8.03 (2H, d, 8.9)	C 62.1 (61.9), H 4.7 (4.4), N 2.6 (2.9)
2	184–186	23.2	3.50 (3H, s), 4.66 (2H, d, J_{HP} = 14.2), 6.48 (1H, m), 6.75 (2H, m), 7.00 (1H, t, J = 8.1)	C 66.2 (66.4), H 4.9 (5.1)
3	223–224	22.5	4.99 (2H, d, J_{HP} = 13.9), 6.96–7.69 (7H, m)	C 71.0 (71.0), H 4.9 (4.9)
4	221–222 (dec)	27.6	4.24 (2H, d, J_{HP} = 14.7), 6.66–7.58 (5H, m)	*m/z*: 461 ($PhCH_2PPh_2Fc^+$, 0.2%), 371 (9), 370 (27), 341 (27), 340 (100), 339 (63), 250 (9), 249 (52)
5	130–131	32.4	3.68 (2H, d, J_{HP} = 14.7), 7.27–7.35 (5H, m)	C 60.0 (59.6), H 9.0 (8.3)

[a] Spectroscopic data were practically independent on the counterion. The only difference was the downfield shift observed for the signals of the methylene group of the chloride salts (0.1–0.8 ppm) indicating sensitivity of the shielding of those protons to the nature of a counterion in the ion pair. For all salts, only one signal was observed in the ^{31}P NMR spectra, and ^1H NMR spectra contained only the signals expected for a given phosphonium ion. [b] For tetrafluoroborates. [c] For clarity's sake, only signals of the $ArCH_2$ group are included. [d] Relative to $CFCl_3$. [e] Literature[4] mp 203–204 °C.

same halides.[28] Ar = Ph (75% yield) mp 52–53 °C; δ_H 2.92 (4H, s), 7.16–7.31 (10 H, m). Ar = 4-MeC_6H_4 (72% yield): oil; δ_H 2.30 (3 H, s), 2.84 (4 H, s), 7.00 (8H, s). Ar = 4-$Bu^tC_6H_4$ (70% yield): oil; δ_H 0.52 (18 H, s), 2.82 (4 H, s), 7.05 (8 H, s). Ar = 4-$MeOC_6H_4$ (80% yield): mp 128–129 °C; δ_H 2.81 (4 H, s), 3.77 (6 H, s), 6.78–6.82 (4H, m), 7.04–7.07 (4 H, m). Ar = 4-FC_6H_4 (40% yield): mp 95–96 °C; δ_H 2.85 (4 H, s), 6.85–7.12 (8 H, m). Ar = 4-ClC_6H_4 (55% yield): oil; δ_H 2.84 (4 H, s), 7.01–7.12 (8 H, m). Ar = 1-$C_{10}H_7$ (32% yield): oil; δ_H 3.50 (4 H, s), 7.25–8.20 (14 H, m).

***N*-(Arylmethyl)acetamides ($ArCH_2NHC(O)CH_3$) 9** were prepared by N-acetylation of the corresponding amines with acetyl chloride. Ar = Ph (86% yield): mp 65–66 °C; δ_H 1.95 (3 H, s), 4.34 (1 H, s), 4.36 (1H, s), 6.27 (1 H, br s), 7.18–7.30 (5 H, m). Ar = 1-$C_{10}H_7$ (80% yield): mp 125–126 °C; δ_H 1.98 (3 H, s), 4.85 (1 H, s), 4.87 (1 H, s), 7.39–8.05 (7 H, m).

Arylmethyl methyl ethers ($ArCH_2OCH_3$) 10 were prepared from sodium methoxide and the corresponding arylmethyl halides. Ar = Ph (30% yield), distilled bulb-to-bulb: δ_H 3.39 (3 H, s), 4.46 (2 H, s), 7.25–7.35 (5 H, m). Ar = 4-MeC_6H_4 (45% yield), distilled bulb-to-bulb: δ_H 2.33 (3 H, s), 3.35 (3 H, s), 4.40 (2 H, s), 7.15–7.24 (4 H, m). Ar = 4-$MeOC_6H_4$ (72% yield), distilled bulb-to-bulb: δ_H 3.34 (3 H, s), 3.79 (3 H, s), 4,38 (2 H, s), 6.86–6.88 (2 H, m), 7.23–7.26 (2 H, m). Ar = 4-FC_6H_4 (60% yield), distilled bulb-to-bulb: δ_H 3.35 (3 H, s), 4.40 (2 H, s), 6.99–7.04 (2 H, m), 7.24–7.31 (2 H, m). Ar = 4-ClC_6H_4 (65% yield), distilled bulb-to-bulb: δ_H 3.38 (3 H, s), 4.40 (2 H, s), 7.23–7.31 (4 H, m).

Preparation of the Phosphonium Salts 1–3. General Procedure. Typically, triphenylphosphine (5 g, 0.02 mol) was dissolved in dry benzene, and an equimolar quantity of arylmethyl halide was added dropwise with stirring. The solution was then heated under reflux for 3–4 h, cooled, and filtered, and the product was washed with ether (3 × 5 mL) and recrystallized from acetonitrile/ether.

An alternative procedure involved mixing the arylmethanol with an equimolar amount of triphenylphosphine; after the addition of concd HCl solution (1 mL/mmol of substrate), the mixture was heated under reflux for 12 h. The solution was then evaporated to dryness and the residue was washed with ether and purified by crystallization. The yield of the halide salts was in the range of 50–80%; for the photolysis experiments the salts were crystallized several times from acetonitrile/ether until sharp melting points were obtained and NMR (^1H, ^{31}P) spectra showed absence of any impurities.

Benzyldiphenylferrocenylphosphonium chloride 4 and **benzyltributylphosphonium chloride 5** were prepared from diphenylferrocenylphosphine[29] or tributylphosphine and benzyl chloride by heating under reflux in benzene for 12 h and purified by crystallization from ether/acetonitrile.

Tetrafluoroborate salts were prepared[4] from the halides by dissolving the latter (2 g) in water (30 mL) and adding $NaBF_4$ (4 g) dissolved in water (20 mL). The precipitated salt was filtered off, washed several times with ether, and recrystallized from acetonitrile/ether. The yields of the tetrafluoroborate salts were in the range of 80–100% (based on a halide). Some data for the phosphonium salts 1–5 used in the photolysis experiments are given in Table IV.

Photolysis. Typically, 30 mg of substrate was placed in a quartz tube and the solvent (5 mL) was added. The tube was sealed with a septum, immersed in a cooling bath (0 °C), and purged with argon by means of a syringe needle. Solvent losses were negligible. The solution was then irradiated for the required period of time, samples (0.5 mL each) were transferred to separate containers for direct GC analysis, and the remaining solution was examined (after evaporation) by NMR spectroscopy. All salts were perfectly stable under the same conditions in the dark.

GC and GC/MS Analysis. GC analysis was carried out using a Varian 3700 gas chromatograph linked to a Varian 4270 recorder/integrator. A 25-m long glass capillary column of 0.3-mm i.d. with a 0.3-μm thick stationary phase film of polymethylsiloxane (SE30) was used throughout. Hydrogen was used as a carrier gas at a linear flow rate of 50 cm s^{-1}. A flame ionization detector was employed with nitrogen (30 cm min^{-1}) as a makeup gas. The temperature program was set at 36 °C isothermal for 2 min, followed by a ramp of 10 °C min^{-1} up to 260 °C, followed by another isothermal period of 10 min at 260 °C. GS/MS analyses were performed on either a Hewlett-Packard 5988A or a VG Micromass 7070H instrument with the same column and temperature program as above, using helium as carrier gas.

A volume of 500 μL of the irradiated solution was transferred to a vial and 100 μL of each of the two standard solutions was added. The standards used for quantitative determinations were anisole (retention time 5.7 min) and either triphenyl phosphate (t_R 24.3 min) or 2,6-di-*tert*-butyl-*p*-cresol (t_R 15.2 min). The

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latter standard was used when the quantitative determination of phosphorus-containing products was not required. The solution was then injected in a splitless mode, opening the split valve at 0.7 min after injection in order to reduce splitter discrimination between the more- and the less-volatile components of the sample. Reproducibility of the detector response factors were further enhanced by a "sandwich" injection of a 0.4 μL sample plug placed between air (0.1 μL) and solvent (0.2 μL) plugs in a 1 μL syringe before injection. Splitless injection did not allow a reliable quantitation of benzene (the peak appeared on the tail of the solvent peak), so benzene was determined by an independent injection in the normal split mode.

The analysis of the photolysis products was carried out as follows. Tentative identification was obtained from the ^{1}H and ^{31}P NMR spectra of the mixture. When the expected products were commercially available or independently prepared, their solutions were injected into the gas chromatograph and the photolysis products were identified by comparing the respective retention times or by coinjection of a sample and the standard solution. Products **7** were identified by GC/MS, and the tetraphenylphosphonium salts by ^{31}P NMR spectroscopy. A typical quantitative determination of the products was achieved as follows. A solution containing known concentrations of benzene and products **6**, **8**, and **9** was injected in the gas chromatograph. Relative detector response factors were then determined experimentally with internal standard (anisole) as reference. Repeated injections gave results reproducible to within 10%. The determination of the above photolysis products was then based on the relative response factors and the corresponding peak areas. Poor peak area reproducibility obtained for the phosphorus-containing compounds prevented reliable quantitative determination of those products. For the product for which no experimentally determined response factors were available (ring-substituted benzyl derivatives, ethers **10**), relative response factors were calculated using the approach of "Effective Carbon Numbers" (ECN).[30] The validity of the approach was confirmed by comparing the experimentally determined response factors described above with the corresponding factors calculated according to the ECN approach. Good internal agreement (±6%) was obtained in each case.

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