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Photolysis of Bromo- and Chloro-Substituted Benzyl Derivatives. Competition between Ionic and Radical Pathways

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Photolysis of 1-fluoro-2-halo-1,2-diphenylethanes was studied in solutions of tetrahydrofuran, acetonitrile, and cyclohexane. The effect of free radical inhibitor and metal hydrides on products formation as well as their ratio was analyzed to elucidate the reaction pathway. In the first step homolytic C−X bond cleavage occurs from a single excited state, resulting in a biradical pair. Further reaction path depends on the type of the halogen bonded and on the solvent polarity. Electron transfer within the radical pair cage is apparently more rapid for bromides than for chlorides and is opposite as expected on the basis of the relative electronegativities of chlorine and bromine. As radicals approach each other, they fall into ionic or radical product channels. This is influenced by solvent polarity, resulting in the larger yield of ionic products in the case of acetonitrile as in the case of less polar cyclohexane.

Introduction

The photochemistry of the heteroatomic benzylic bond has been extensively studied for over 30 years.[1] It results mainly in C−X cleavage due to the carbon−halogen bond absorption by n → σ^* transition. The discovery that partitioning between homolytic and heterolytic cleavage occurs was of great importance in further research.[2] The competition between the pathways for the formation of ionic and radical intermediates depends on many factors, including the leaving group and the solvent polarity.

To determine the reaction mechanism different benzylic systems ($PhCH_2X$) were investigated: benzyl acetates (X = OAc),[1,3] sulfonium salts ($X = (CH_3)_2S^+BF_4^-$),[4] ammonium salts ($X = (CH_3)_3N^+Cl^-$),[5] phosphites ($X = OP(OR)_3$),[6] and a group of homobenzylic systems.[7] The most thoroughly studied examples have been benzyl halides (X = Cl, Br).[8]

Previously, we studied the solvent effect on photolysis of 3-chloro- and 4-chloro-substituted benzyl chlorides.[9] Product analyses indicated that both radical and ionic intermediates were involved. We found that in the first step homolytic benzylic C−Cl bond cleavage occurred resulting in a radical pair. Further reaction pathway, however, depended upon the solvent used. In cyclohexane and tetrahydrofuran (THF), the products obtained were formed via benzylic radical intermediates. On the other hand, photolysis in acetonitrile resulted in products, which could be ascribed to both benzylic cation and benzylic radical intermediates. The presence of $LiAlH_4$ had a great impact on the photoreaction and accelerated the reduction of the C−Cl bond in the aromatic ring, leading to toluene as the main product. The crucial influence of $LiAlH_4$ on the reaction pathway was also shown in the photoreduction of various fluoro-substituted 1,2-diphenylethanes, which were practically stable in the presence of hydride alone, as well as when they were subjected to direct irradiation.[10]

Herein, the results of photolysis of bromo- and chloro-substituted benzyl derivatives, i.e., 1-chloro-2-fluoro-1,2-diphenylethane (**1a**) and 1-bromo-2-fluoro-1,2-diphenylethane (**1b**), are presented. The solvent effect was studied by direct irradiation of substrates in THF, cyclohexane, and acetonitrile. The influence of free radical inhibitor (2,6-di-*tert*-butyl-4-methylphenol (DBPC)) and metal hydride ($LiAlH_4$) on the reaction pathway and product distribution was investigated as well.

Results

THF as a Solvent. Eight hours irradiation of a 0.01 M solution of 1-chloro-2-fluoro-1,2-diphenylethane (**1a**)

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Scheme 1

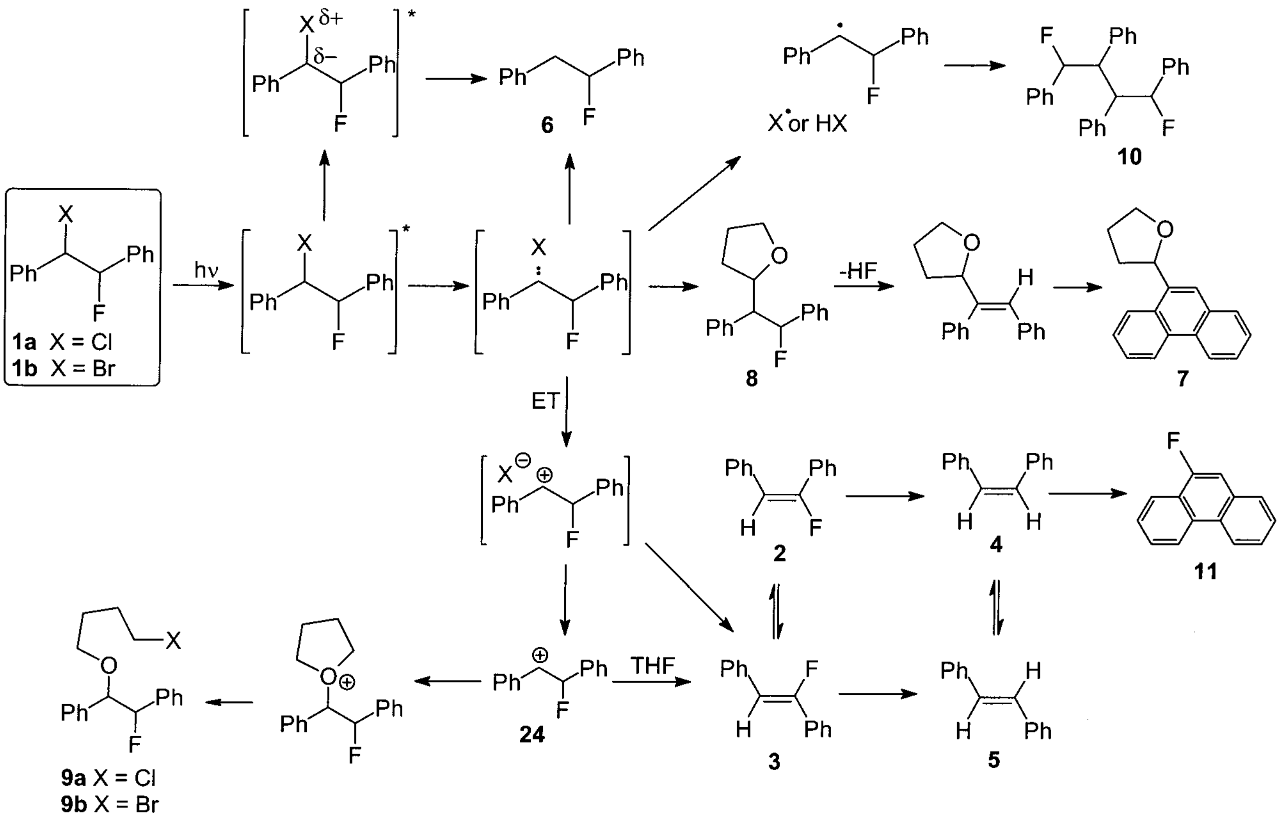

Table 1. Product Distribution[a] in Photolysis[b] of 1 in Tetrahydrofuran

	hν		hν + LiAlH$_4$		hν + DBPC	
product	**1a**	**1b**	**1a**	**1b**	**1a**	**1b**
2	8	17	1	9	11	25
3	5	28	1	8	6	16
4	2	5	9	22	2	6
5	3	14	10	23	6	9
6	8	15	19	5	10	12
7	3					
8	35		21		36	
9	21	16			22	27
10	15		11		7	
11		5				5
12			3	1		
13			5	10		
14			9	2		
15				6		
16			11	14		

[a] Relative yields in %, determined by GC/MS. [b] Irradiation time, 8 h; $\lambda = 253.7$ nm; concentration of substrate = 0.01 M, DBPC = 0.01 M, LiAlH$_4$ = 0.02 M.

in THF resulted in 100% conversion into a mixture of *cis*- (**2**) and *trans*-fluorostilbene (**3**), *cis*- (**4**) and *trans*-stilbene (**5**), 1-fluoro-1,2-diphenylethane (**6**), 9-(2-tetrahydrofuryl)phenanthrene (**7**), 1-fluoro-2-(2-tetrahydrofuryl)-1,2-diphenylethane (**8**), 1-(4-chlorobutoxy)-2-fluoro-1,2-diphenylethane (**9a**), and dimeric product 1,4-difluoro-1,2,3,4-tetraphenylbutane (**10**) in the relative ratio shown in Table 1. The products of direct photolysis of **1** in THF are presented in Scheme 1.

It is known that the presence of metal hydrides (NaBH$_4$, LiAlH$_4$, etc.) has a great impact on the photoreduction of organic halides. Investigations on photoreduction of aryl halides[11] in the presence of NaBH$_4$ revealed the following three pathways. (a) In the excited molecule of aryl halide a homolytic cleavage of the C−X bond occurs in the first step, generating an aryl radical and a halogen atom. In the second step these radicals abstract hydrogen atom from BH$_4^-$ giving BH$_3^{-\bullet}$, which initiates an S$_{RN}$1-like chain reaction.[11a] (b) Excited aryl halide reacts with BH$_4^-$ and direct transfer of hydride ions occurs.[11b,d] (c) Single electron transfer occurs in the first step from BH$_4^-$ resulting in a complex [ArX$^{-\bullet}$ BH$_4^\bullet$], which after intramolecular hydrogen atom transfer leads to reduced products.[11g] Similar reaction mechanisms were proposed for photoreduction of organic halides by LiAlH$_4$.[12] To establish the effect of metal hydride on the photobehavior of **1a** and **1b**, their photolyses in the presence of LiAlH$_4$ were studied. Resulting reaction mixtures were very complex, and their compositions differed from those obtained by direct photolysis (Table 1).

To distinguish the ionic versus the radical reaction path, photolyses were run in the presence of the free radical inhibitor as well. GC/MS analyses revealed the formation of the same products as in the case of direct photolysis, however, in different proportions (Table 1).

Photolysis of a 0.01 M solution of 1-bromo-2-fluoro-1,2-diphenylethane (**1b**) in THF under the same reaction conditions led to 100% conversion into *cis*- (**2**) and *trans*-

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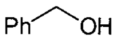
Table 2. Product Distribution[a] in Photolysis[b] of 1 in Cyclohexane and Acetonitrile

	$h\nu$				$h\nu$ + DBPC				$h\nu$ + O_2
	cyclohexane		acetonitrile		cyclohexane		acetonitrile		acetonitrile
product	**1a**	**1b**	**1a**	**1b**	**1a**	**1b**	**1a**	**1b**	**1b**
1	28	28	40	21	48	19	15	8	2
2	5	1	5	8	4	11	9	13	
3	6	27	4	18	3	37	17	13	
4			1	1	1	3	2	3	
5		7	1	4	2	9	6	3	
6	6			5	7	3	3	2	
10	7				3				
13	4	8	5	8	3	7	3	5	1
17	34				24				
18	4	8	5	2	4	9	7	14	23
19	1	13							13
20	5	8	3		1	2	2	2	9
21			36	33			36	37	44
22									5
23									3

[a] Relative yields in %, determined by GC/MS. [b] Irradiation time, 3 h; $\lambda = 253.7$ nm; concentration of substrate = 0.01 M, DBPC = 0.01 M.

fluorostilbene (**3**), *cis*- (**4**) and *trans*-stilbene (**5**), 1-fluoro-1,2-diphenylethane (**6**), 9-fluorophenanthrene (**11**), and 1-(4-bromobutoxy)-2-fluoro-1,2-diphenylethane (**9b**). In the presence of the hydride, besides the above-mentioned products, benzyl alcohol (**12**), phenanthrene (**13**), 1,2-diphenylethane (**14**), 1,2,3,4-tetraphenyl-1,3-butadiene (**15**), and 1-butoxy-2-fluoro-1,2-diphenylethane (**16**) were formed as well (Table 1).



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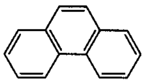

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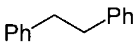

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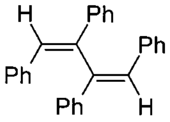

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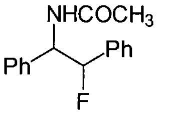

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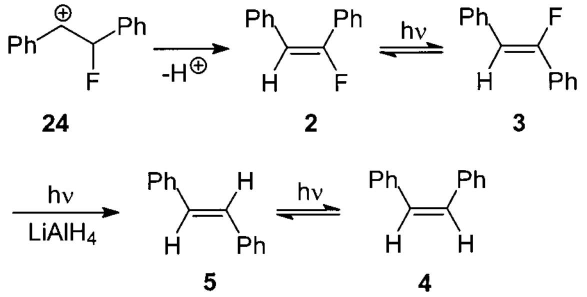
Cyclohexane as a Solvent. Three hours irradiation of a 0.1 M solution of **1a** in cyclohexane resulted in 72% conversion into a mixture of *cis*- (**2**) and *trans*-fluorostilbene (**3**), 1-fluoro-1,2-diphenylethane (**6**), phenanthrene (**13**), 1-cyclohexyl-2-fluoro-1,2-diphenylethane (**17**), dimer **10**, benzaldehyde (**18**), benzoic acid (**19**), and benzoyl fluoride (**20**). When the reaction was carried out in the presence of free radical inhibitor the yields of the last three products were lower, thus indicating their formation via out of cage radicals formed by the cleavage of the ethanic C−C bond (Table 2).

Photolysis of **1b** led under the same reaction conditions to 72% conversion (Table 2). Similarly as described above, the presence of the free radical inhibitor diminished the yields of **19** and **20** (Table 2).

Acetonitrile as a Solvent. Three hours irradiation of **1a** in acetonitrile at $\lambda = 253.7$ nm led to 60% conversion. A mixture of starting compound **1a**, *cis*- (**2**) and *trans*-fluorostilbene (**3**), *cis*- (**4**) and *trans*-stilbene (**5**), phenanthrene (**13**), benzaldehyde (**18**), benzoyl fluoride (**20**), and 1-(*N*-acetylamino)-2-fluoro-1,2-diphenylethane (**21**) was detected (Table 2).

Scheme 2



Photolysis of **1b** in acetonitrile under the same reaction conditions led to 79% conversion with the formation of almost the same products as described for **1a**, in relative yields shown in Table 2. Since the formation of benzaldehyde (**18**), benzoic acid (**19**), and benzoyl fluoride (**20**) could be ascribed to the presence of dissolved oxygen, we performed an additional experiment where the reaction mixture was purged by oxygen during irradiation. As expected, the relative yields of **18**−**20** increased, while the formation of 2-fluoro-1,2-diphenylethanol (**22**) and 2-fluoro-1,2-diphenylethanone (**23**) was observed as well (Table 2).

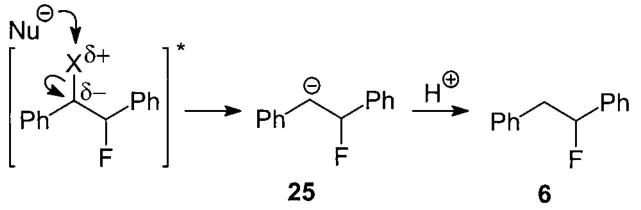
Discussion

Photolysis of **1a** and **1b** in THF, a good hydrogen donor of a nucleophilic character, led to the formation of a complex reaction mixture. Roughly, the formation of four main groups of products was observed: (a) stilbene products, (b) reduction products, (c) products resulting from reactions with solvent molecules, and (d) dimerization products.

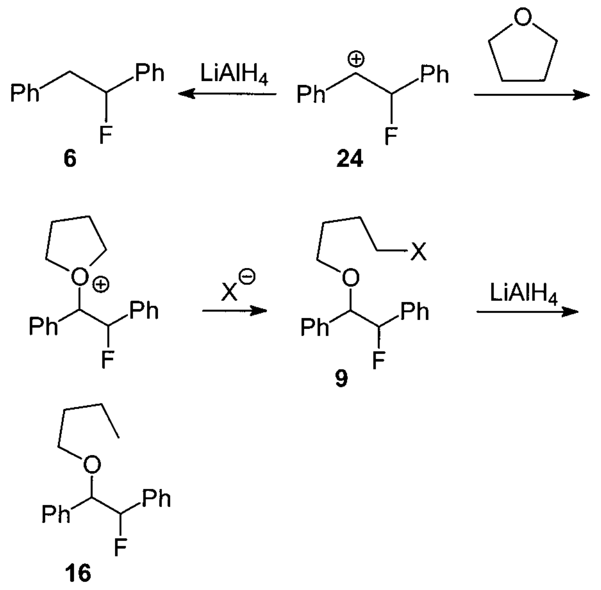
Fluorostilbene products **2** and **3** might arise from either the ion pair or free cation **24** by elimination of a proton (Scheme 2). Further photoreduction can lead to *cis*- and *trans*-stilbene (**4** and **5**, respectively). The *cis*- and *trans*-stilbene could be generated by photoelimination of HF from 1-fluoro-1,2-diphenylethane (**6**) as well; therefore the results obtained by direct photolysis were compared to those obtained by photolysis in the presence of $LiAlH_4$. The latter should act as a strong base and enhance the formation of **4** and **5**. The results indeed show the increase in the relative yields of **4** and **5**. However, the overall relative yields of stilbene products **2**−**5** were comparable in both cases, thus indicating that only a minor possibility of photoelimination of HF existed. Moreover, DBPC had an insignificant influence on the stilbene yields, suggesting that the free radical intermediate is not involved in formation of stilbene products and, additionally, confirming the intermediacy of carbocation **24** (Table 1).

The formation of reduction product **6** by direct photolysis of **1** can be explained via hydrogen atom abstraction of the out of cage radical. However, the presence of DBPC as free radical inhibitor (Table 1) was shown to have no effect on the yield of **6**, thus diminishing the possibility of this pathway. On the other hand, we cannot rule out the involvement of the caged radical pair. Alternatively, the formation of **6** can be explained by protonation of the carboanionic intermediate **25** (Scheme 3). The intermediate **25** can be generated by nucleophilic attack of tetrahydrofuran oxygen (or by chloride ion in the case of the cyclohexane solution) on the n,σ^* excited state of **1**. A similar mechanism was proposed by Kropp

Scheme 3



Scheme 4



Scheme 5

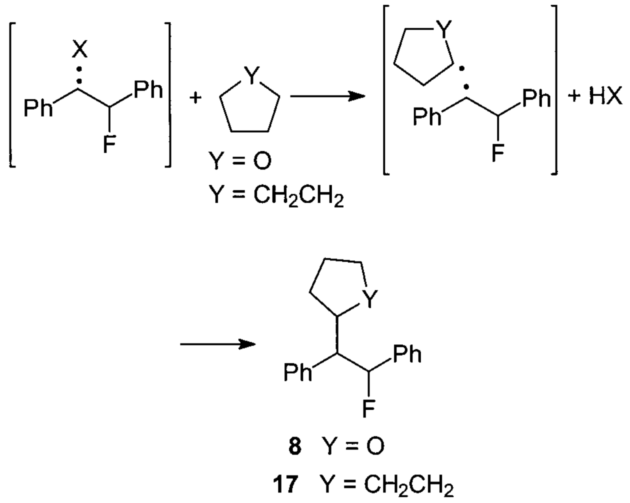


Table 3. Excess Energy after Bond Cleavage[a]

	1a	1b
$\lambda_{0,0}$[b]	462	450
D_0(R−X)[c]	290	231
D	172	219
E_a[d]	4.2	55.2

[a] In kilojoules per mole. [b] Estimated from the onset of absorption. [c] Values used are those for benzyl chloride and bromide: Freedman, A.; Yang, S. C.; Kawasaki, M.; Bersohn, R. *J. Chem. Phys.* **1980**, *72*, 1028−1033. [d] Values used are those for hydrogen abstraction from C_2H_6 by X•: March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992.

and co-workers in the photolysis of 1-bromo- and 1-iodonorbornane.[2c,13] However, when the irradiation of **1a** was carried out in the presence of $LiAlH_4$ (Table 1), a substantial increase of **6** was observed. This can be explained by attack of hydride on the intermediate carbocation **24**.

In the absence of the hydride, carbocationic intermediate **24** can be trapped by nucleophilic tetrahydrofuran oxygen. Subsequent ring opening by hydrogen halide results in the formation of 1-fluoro-2-(4-halobutoxy)-1,2-diphenylethane (**9**) (Scheme 4). It is not surprising that when experiments were run in the presence of $LiAlH_4$ product **9** is not detected; the photoreduction of the C−X bond mediated by $LiAlH_4$ occurs easily, resulting in 1-butoxy-2-fluoro-1,2-diphenylethane (**16**) (Table 1).

A significant amount of 1-fluoro-2-(2-tetrahydrofuryl)-1,2-diphenylethane (**8**) was formed in direct photolysis of **1a** (Table 1). Since the free radical inhibitor displayed no influence on the reaction pathway, and the possibility of the formation of **8** via carbocationic intermediate is scarce, its origin can be explained by the cage substitution process.[14] The initial formed radical pair is intercepted by a scavenging molecule, in our case by solvent molecule (THF or cyclohexane), thus forming a new pair of radicals which either combine or diffuse from solvent cage (Scheme 5). As expected, the product **8** is not formed by photolysis of bromo derivative **1b**. This could be ascribed to the lower tendency of bromine for hydrogen abstraction as a result of considerable activation energy for that process (Table 3). In this case, an electron transfer to bromine atom in a biradical pair, yielding an ionic pair, is a far more favorable process.

As shown in Table 1, irradiation of **1a** and **1b** in THF afforded a similar mixture of photoproducts. However, in the case of the chloro analogue the radical derived products were formed predominantly. To study the solvent effect, we further selected cyclohexane and acetonitrile.[15] Similarly to THF, cyclohexane possesses an ability to donate the hydrogen atom, but it lacks the nucleophilicity, while acetonitrile, as nucleophilic solvent, is able to trap the ion pair. Experiments in the presence of metal hydride were not performed for the solubility reasons.

Photolysis of **1a** and **1b** in cyclohexane (Table 2) gave similar results as in THF. On the other hand, mainly 1-(*N*-acetylamino)-2-fluoro-1,2-diphenylethane (**21**) was formed in acetonitrile (Table 2). The mechanism proposed for its formation involves addition of carbocationic intermediate **24** to the polarized CN bond of acetonitrile followed by hydrolysis. The formation of **18**−**20** was assumed to be an outcome of the competing reaction with oxygen dissolved in solvent; therefore an experiment where the reaction mixture was purged with O_2 was performed. Indeed, the yields of benzaldehyde (**18**), benzoic acid (**19**), and benzoyl fluoride (**20**) significantly increased. The mechanism for their formation as well as for the origin of **22** and **23** is proposed in Scheme 6.

The mechanism for direct photolysis of **1** in THF is outlined in Scheme 1. Initial homolytic cleavage from a single excited state produces a radical pair, which either

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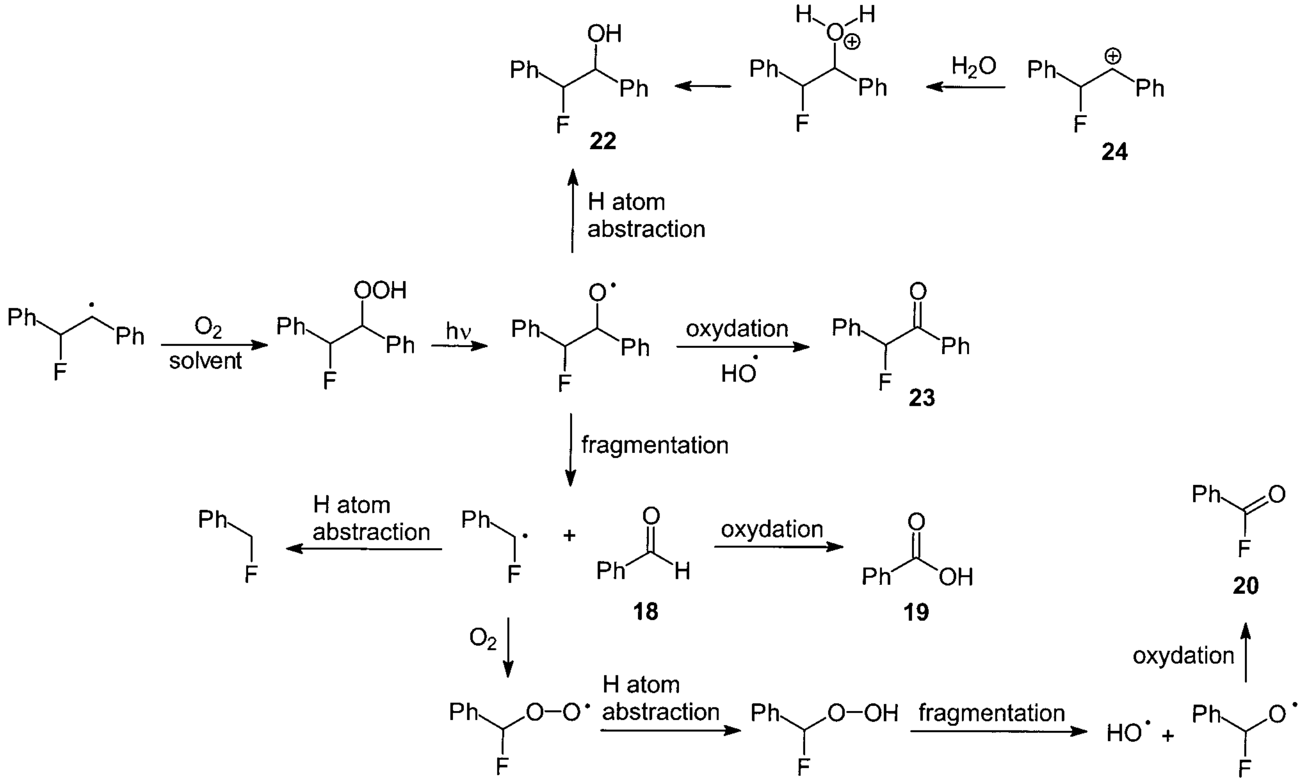
[13] Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135−8144.

[14] Leffler, J. E. *An Introduction to Free Radicals*; Wiley: New York, 1993.

[15] Electric dipole moment in debye units for acetonitrile, cyclohexane, and THF are 3.92, ~0, and 1.75, respectively. The values are taken from *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, 1995.

Scheme 6



diffuses from the cage resulting in the observed formation of radical products or is transformed into an ion pair by electron transfer. In accordance with this mechanism the overriding factors that determine the facility of electron transfer and diffusion of the radical out of cage are connected with the nature of the carbon−halogen bond and solvent polarity.

It is known that the balance of radical versus ionic photobehavior in alkyl halides is clearly related to the properties of radical pairs and depends on the type of halogen atom. Kropp and co-workers suggested that electron transfer to iodine might occur more readily than expected on the basis of electronegativity because of either its greater polarizability or the lesser charge point density compared with bromine.[13,16] On the basis of later results, Kropp and Adkins suggested that the difference in behavior is due to more rapid separation from the radical pair for bromides. This might arise from the difference between bond dissociation energy and energy of the n,σ^* electronic transition between the lowest vibrational levels of the ground and the excited states, being greater for bromides than for iodides.[17]

The presented results of the photobehavior of **1a** and **1b** show that chloride **1a** gives higher yields of products derived from the out of cage radical intermediates than the corresponding bromide **1b**. The results are in agreement neither with the difference in electronegativity nor with the difference between bond dissociation energy and energy of the n,σ^* electronic transition between the lowest vibrational levels of the ground and the excited states, which is greater for bromide than chloride (Table 3).

Apparently, there are prevailing factors that determine the facility of electron transfer, such as greater polarizability of bromine and the fact that formation of the bromide ion involves generation of a lesser point charge density comparing to chloride ion.[18] Another factor might be the difference in reactivity of the chlorine and bromine radicals toward hydrogen abstraction. The chlorine atom is more reactive for efficient hydrogen atom abstraction than bromine, thus inhibiting the competing electron transfer (Table 3).

The solvent effect on the ratio between ionic and radical products produced through the radical pair was investigated by several authors. Kropp established that the photobehavior of alkyl halides depends on the viscosity of the solvent.[13,16] The more viscous solvent 1,2-ethanediol resulted in a substantial increase in the ratio of ionic to radical products. The increased lifetime of the radical pair cage in a more viscous solvent apparently allows electron transfer to compete more efficiently with diffusion from the cage. Cristol and co-workers determined that polar solvent effects can be reflected in the following cases: polar solvents (acetonitrile) favor electron transfer, and the nonpolar solvents (THF and cyclohexane) are good hydrogen donors, so they could react with chlorine atoms of the radical pairs to divert the intermediate from an ion pair formation.[19] Walling and co-workers studied the thermolysis of acyl peroxides, which leads to products of both radical and ionic processes.[20] They proposed that first intermediate was a species that they termed as an "intimate ion-radical pair". This is an intermediate in which electronic interaction between the fragments is still extensive, and ionic and paired diradical formations represent contributing struc-

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[16] Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131−137.

[17] Kropp, P. J.; Adkins, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2709−2717 and references therein.

[18] Crystal ionic radii of bromide and chloride ions are 0.196 and 0.181 nm, respectively. The values are taken from *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, 1995.

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Table 4. Dependence of the Ratio of Ionic and Radical Products on Solvent in Direct Photolysis of 1

compound	ionic/radical ratio C_6H_{12}	THF	MeCN
1a	0.3	0.7	7.0
1b	2.0	5.5	12.0

tures of a resonance hybrid. The fragments become separated by solvent. Leffler and More reported the results of decomposition of bis(bicyclo[2.2.2]octane-1-formyl) peroxide and pivaloyl peroxide in a series of solvents of different dielectric constants.[21] The rate constant for the radical reaction is relatively insensitive to polar effect, while the rate constant for the ion pair reaction undergoes large changes. Less polar solvents favor a less polarized canonical structure, while a polar solvent favor a canonical structure, which provides conversion to the ion pair.

Our results show the possible existence of an intimate ion-radical pair, which in a polar solvent (acetonitrile) leads to substantially higher yields of ionic products. Namely, the ionic/radical ratio (I/R) increased with increasing solvent polarity from 0.3 in cyclohexane to 7.0 in acetonitrile for chloro derivative **1a**, while in the case of bromo derivative **1b** the I/R ratio increased from 2.0 in cyclohexane to 12.0 in acetonitrile (Table 4).[15] The considerable increase in ionic products in acetonitrile in comparison with THF reveals the importance of the solvent's ability to donate a hydrogen atom. The reaction between a halogen atom in a radical pair and a hydrogen atom from solvent is much faster with a chlorine than a bromine atom, which was already observed by Cristol and co-workers.[18]

Conclusions

The first step in photolysis of chloro- and bromo-substituted 1-fluoro-1,2-diphenylethanes (**1**) is the homolytic cleavage of the C−X bond from the single excited state and the formation of the biradical pair. This can be subsequently divided into either two separate radicals (out of cage radicals) or into an ionic pair via an electron-transfer process (within the caged radicals), which depends on both the halogen atom bonded and the solvent polarity. The larger I/R ratio for bromo than for chloro compounds are a consequence of the greater polarizability and the lesser charge point density of bromine, as well as the efficiency of the chlorine atom for hydrogen atom abstraction. Increasing solvent polarity increases the yields of ionic products, which might be an outcome of the intimate ion-radical pair where the polar solvent favors the ionic pathway, while in the less polar solvent (THF, cyclohexane) the ability of solvent to donate a hydrogen atom must be considered.

Experimental Section

The photochemical reactions were performed at $\lambda = 253.7$ nm. The NMR spectra were recorded in $CDCl_3$ at 302 K. Chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS for ^1H and ^{13}C spectra and to CCl_3F for ^{19}F spectra. The starting compounds **1a**[22] and **1b**[23] were prepared according to literature. Cyclohexane ($LiAlH_4$), THF ($LiAlH_4$), and acetonitrile (CaH_2) were refluxed over the mentioned drying agents and distilled in an inert atmosphere before use.

The reaction mixtures were analyzed by GC and GC/MS and by comparison of the spectral data of products to those of the authentic samples: *cis*- (**2**) and *trans*-fluorostilbene[24] (**3**), *cis*- (**4**) and *trans*-stilbene (**5**), 1-fluoro-1,2-diphenylethane[25] (**6**), 9-fluorophenanthrene (**11**), benzyl alcohol (**12**), phenanthrene (**13**), 1,2-diphenylethane (**14**), 1,2,3,4-tetraphenyl-1,3-butadiene (**15**), benzaldehyde (**18**), benzoic acid (**19**), benzoyl fluoride (**20**), 1-(*N*-acetylamino)-2-fluoro-1,2-diphenylethane[26] (**21**), 2-fluoro-1,2-diphenylethanol[27] (**22**), and 2-fluoro-1,2-diphenylethanon[28] (**23**). Compounds 1,2-diphenyl-1-fluoro-2-(2-tetrahydrofuryl)ethane (**8**), 1-(4-chlorobutoxy)-2-fluoro-1,2-diphenylethane (**9a**), 1-(4-bromobutoxy)-2-fluoro-1,2-diphenylethane (**9b**), 1,4-difluoro-1,2,3,4-tetraphenylbutan (**10**), 1-butoxy-2-fluoro-1,2-diphenylethane (**16**), and 1-cyclohexyl-2-fluoro-1,2-diphenylethane (**17**) were unknown and were isolated and characterized as reported.

Typical Experimental Procedure. First, 0.05 mmol of substrate was dissolved in 5 mL of solvent, and the reaction mixture was irradiated at 253.7 nm for the time listed in the Tables. Whenever stated (see Tables), 0.05 mmol of inhibitor was added prior to the reaction. The reaction mixtures were analyzed by GC and GC/MS. When the metal hydride was added, the substrate was dissolved in 5 mL of a clear solution of $LiAlH_4$[29] (0.10 mmol, $c = 0.02$ M) in THF, and after irradiation the excess of hydride was destroyed by pouring of the reaction mixture into water. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure prior to the analyses.

9-(2-Tetrahydrofuryl)phenanthrene (7) was formed in too small quantities for isolation (Table 1). It was characterized on the basis of its mass spectrum. GC/MS: 248(M^+, 100), 177(30), 71(12).

1-Fluoro-2-(2-tetrahydrofuryl)-1,2-diphenylethane (8). Four isomers of compound **8** were isolated by HPLC (semi-preparative silica gel column, 5 μm; mobile phase, hexane/diethyl ether (93:7); flow rate, 2 mL/min; UV detection at 254 nm) in the elution order as cited. **Isomer A.** ^1H NMR: δ 1.75−1.88 (m, 4H), 3.38 (ddd, $J = 5.4$, 9.1, 14.0 Hz, 1H), 3.79−3.88 (m, 1H), 3.91−3.99 (m, 1H), 4.07−4.16 (m, 1H), 6.05 (dd, $J = 5.4$, 45.5 Hz, 1H), 6.81−6.86 (m, 2H), 7.00−7.06 (m, 2H), 7.12−7.20 (m, 3H), 7.20−7.25 (m, 3H). ^{19}F NMR: δ −180.68 (dd, $J = 14.0$, 45.5 Hz). EIMS: 180 (100), 109 (16), 71 (35). HR EIMS calcd for fragment $C_{11}H_{13}FO$: 180.0950; found: 180.0952. **Isomer B.** ^1H NMR: δ 1.73−2.05 (m, 4H), 3.14 (dt, $J = 3.8$, 9.9 Hz, 1H), 3.72−3.79 (m, 2H), 4.59−4.67 (m, 1H), 5.84 (dd, $J = 10.0$, 46.7 Hz, 1H), 7.05−7.20 (m, 10H). ^{19}F NMR: δ −173.55 (dd, $J = 9.9$, 46.7 Hz). EIMS: 180 (96), 109 (14), 71 (100). HR EIMS calcd for fragment $C_{11}H_{13}FO$: 180.0950; found: 180.0955. **Isomer C.** ^1H NMR: δ 1.60−1.85 (m, 3H), 3.01 (ddd, $J = 4.4$, 7.9, 17.6 Hz, 1H), 3.68−3.78 (m, 3H), 3.85−3.92 (m, 1H), 5.91 (dd, $J = 7.8$, 47.0 Hz, 1H), 7.20−7.35 (m, 10H). ^{19}F NMR: δ −178.55 (dd, $J = 17.6$, 47.0 Hz). EIMS: 180 (94), 109 (11), 71 (100). HR EIMS calcd for fragment $C_{11}H_{13}FO$: 180.0950; found: 180.0950. **Isomer D.** ^1H NMR: δ 1.71−1.89 (m, 4H), 2.76 (ddd, $J = 2.4$, 10.1, 34.3 Hz, 1H), 3.90 (dt, $J = 6.8$, 8.4 Hz, 1H), 3.99 (dt, $J = 6.8$, 8.4 Hz, 1H), 4.53 (ddd, $J = 7.5$, 10.1, 14.0 Hz, 1H), 6.17 (dd, $J = 2.4$, 46.7 Hz, 1H), 6.90−7.02 (m, 4H), 7.13−7.18 (m, 6H). ^{19}F NMR: δ −195.6 (dd, $J = 34.3$, 46.7 Hz). EIMS: 180 (92), 109 (22), 71 (100). HR EIMS calcd for fragment $C_{11}H_{13}FO$: 180.0950; found: 180.0954.

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1-(4-Chlorobutoxy)-2-fluoro-1,2-diphenylethane (9a). Compound **9a** was isolated by HPLC as described for compound **8**. ^{1}H NMR: δ 1.67−1.91 (m, 4H), 3.43 (dt, J = 6.8, 8.4 Hz, 2H), 3.52 (t, J = 6.4 Hz, 2H), 4.52 (dd, J = 6.7, 14.0 Hz, 1H), 5.47 (dd, J = 6.7, 46.8 Hz, 1H), 6.03−7.07 (m, 4H), 7.19−7.24 (m, 6H). ^{19}F NMR: δ −182.47 (dd, J = 14.0, 46.8 Hz). EIMS: 199 (6), 109 (13), 107 (43), 91 (100). HR EIMS calcd for fragment $C_{11}H_{14}ClO$: 197.0733; found: 197.0734.

1-(4-Bromobutoxy)-2-fluoro-1,2-diphenylethane (9b). Compound **9b** was isolated by column chromatography (silica gel, Fluka, mesh 220−440) with hexane as eluent (R_f = 0.1). The ^{1}H NMR showed the presence of two isomers in the ratio of 5:2, which were not separated. ^{1}H NMR: δ 1.63−2.00 (m, 5.6H), 3.31−3.46 (m, 5.6H), 4.47 (dd, J = 5.9, 12.3 Hz, 0.4H), 4.52 (dd, J = 6.7, 14.1 Hz, 1H), 5.44 (dd, J = 5.9, 46.0 Hz, 0.4H), 5.47 (dd, J = 6.7, 46.7 Hz, 1H), 7.00−7.40 (m, 14H). ^{19}F NMR: δ −182.49 (dd, J = 14.0, 46.7 Hz, 5F), −183.61 (dd, J = 12.3, 46.0 Hz, 2F). EIMS: 332/330 (M$^+$ − HF, 0.5/0.5), 243/241 (20/20), 137/135 (97/100). HR EIMS calcd for fragment $C_{11}H_{14}BrO$: 241.0228; found: 241.0230.

1,4-Difluoro-1,2,3,4-tetraphenylbutan (10). Compound **10** was isolated by HPLC under conditions described for **8**. ^{1}H NMR: δ 3.48 (dddd, J = 1.2, 5.2, 9.5, 10.5 Hz, 1H), 4.3 (ddd, J = 5.2, 8.1, 17.2 Hz, 1H), 5.60 (dd, J = 9.5, 46.9 Hz, 1H), 5.83 (dd, J = 8.1, 46.8 Hz, 1H), 6.46−6.53 (m, 2H), 6.92−7.04 (m, 5H), 7.04−7.15 (m, 5H), 7.18−7.28 (m, 3H), 7.33−7.45 (m, 5H). ^{19}F NMR: δ −171.05 (dd, J = 10.5, 46.9 Hz), −173.33 (ddd, J = 1.2, 17.2, 46.8 Hz). EIMS: 398 (M$^+$, 6). HR EIMS calcd for $C_{28}H_{24}F_2$: 398.1846; found: 398.1856.

1-Butoxy-2-fluoro-1,2-diphenylethane (16). Two isomers of compound **16** were isolated by column chromatography (silica gel, Fluka, mesh 220−440) with hexane/ethyl acetate (20:1; R_f = 0.5) as eluent in the elution order as cited. **Isomer a.** ^{1}H NMR: δ 0.81 (t, J = 7.3 Hz, 3H), 1.15−1.31 (m, 2H), 1.41−1.51 (m, 2H), 3.17−3.27 (m, 1H), 3.31−3.41 (m, 1H), 4.47 (dd, J = 5.7, 13.0 Hz, 1H), 5.46 (dd, J = 5.7, 46.1 Hz, 1H), 7.15−7.38 (m, 10H). ^{19}F NMR: δ −184.25 (dd, J = 13.0, 46.0 Hz). ^{13}C NMR: δ 13.78, 19.18, 31.73, 69.25, 84.20 (d, J = 26.3 Hz), 95.39 (d, J = 177.6 Hz), 126.82 (d, J = 6.9 Hz), 127.82, 127.94, 127.95, 128.06, 128.27, 128.29, 137.27 (d, J = 20.4 Hz), 137.75 (d, J = 2.7 Hz). EIMS: 252(M$^+$ − HF, 0.2), 163(62), 107(100). HR EIMS calcd for fragment $C_{18}H_{20}O$: 252.1514; found: 252.1520. **Isomer b.** ^{1}H NMR: δ 0.87 (t, J = 7.3 Hz, 3H), 1.30−1.42 (m, 2H), 1.52−1.63 (m, 2H), 3.34−3.44 (m, 2H), 4.53 (dd, J = 6.8, 13.6 Hz, 1H), 5.47 (dd, J = 6.8, 46.8 Hz, 1H), 7.00−7.30 (m, 10H). ^{19}F NMR: δ −181.88 (dd, J = 13.5, 46.5 Hz). ^{13}C NMR: δ 13.88, 19.30, 31.88, 69.38, 84.83 (d, J = 23.2 Hz), 96.30 (d, J = 181.0 Hz), 126.73 (d, J = 6.9 Hz), 127.81, 127.97, 128.02, 128.24, 128.27, 136.71 (d, J = 20.3 Hz), 137.44 (d, J = 5.3 Hz). EIMS: 252 (M$^+$ − HF, 0.2), 163 (42), 107 (100). HR EIMS calcd for fragment $C_{18}H_{20}O$: 252.1514; found: 252.1521.

1-Cyclohexyl-2-fluoro-1,2-diphenylethane (17). Purification was done by thin-layer chromatography using hexane (R_f = 0.2). The mixture of two isomers was isolated in the ratio 1:1, as determined by ^{1}H NMR. ^{1}H NMR: δ 0.73−2.08 (m, 22H), 2.61 (ddd, J = 4.2, 8.8, 31.9 Hz, 1H), 3.07 (ddd, J = 5.7, 8.7, 13.3 Hz, 1H), 5.82 (dd, J = 8.7, 46.9 Hz, 1H), 6.00 (dd, J = 4.2, 46.9 Hz, 1H), 6.92−7.04 (m, 6H), 7.08−7.21 (m, 14H). ^{19}F NMR: δ −174.05 (dd, J = 13.4, 47 Hz), −190.48 (dd, J = 32, 47 Hz). EIMS: 282 (M$^+$,1), 173 (83). HR EIMS calcd for $C_{20}H_{23}F$: 282.1784; found: 282.1790.

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