Tetrahedron Vol. 47, No. 43, pp. 9071-9082, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00
Pergamon Press plc

Photoreduction of 1,1-Diphenyl-2-haloethenes by Metal Hydrides

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(*Received in UK* 30 *August* 1991)

Abstract – *The nature of the photochemical carbon – halogen bond cleavage in the presence of sodium borohydride or lithium aluminium hydride as reducing agents was studied when a halogen atom is bonded to the* sp^2 *hybridized carbon atom, which is a part of a vinyl system. Irradiation of 1,1-diphenyl-2-bromoethene, or 1,1-diphenyl-2-chloroethene, in the presence of the metal hydrides resulted in an increased formation of the photoreduced product 1,1-diphenylethene in comparison to reactions run in their absence. Conversion of the starting compound and the products distribution depended on the halogen atom bonded, the reducing agent, and the solvent used.*

Introduction

Photochemical reduction of organic compounds with inorganic metal hydrides has been extensively studied. Photoenhanced reduction of aliphatic and aromatic ketones by sodium borohydride to corresponding alcohols was observed.[1] Special attention has been paid to photochemical reductive dehalogenation of halosubstituted compounds due to their role in environmental pollution.[2] Irradiation of aromatic hydrocarbons,[3] nitriles, nitro compounds,[4] or halides[2a,5] in the presence of sodium borohydride gives products from formal substitution of hydride onto the aromatic nucleus.

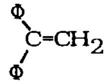
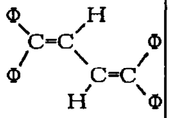
Much attention has been given to define the mechanism of photoreduction of aryl halides with sodium borohydride and some complex metal hydrides.[2a,6–8] Photoreduction of halobenzenes (hal.= Cl, Br, I) with sodium borohydride proceeds via a free radical chain reaction,[6] while in the case of some aryl iodides and bromides in the presence of radical initiator electron transfer from $BH_3^{-\cdot}$ to ArX was proposed.[7] On the other hand, the suggested photoreduction of chlorobiphenyls involves direct attack of a hydride ion on the photoexcited biphenyl.[2a,2b] M. Kropp and G.B. Schuster[9] proposed several mechanisms in the photoreduction of halosubstituted arenes with borates and borohydride, among others an electron transfer – hydrogen transfer mechanism.

Irradiation of several organic halides in the presence of lithium aluminium hydride,[10] also in the presence of radical initiators,[11] resulted in the enhanced formation of photoreduction products.

Results and Discussion

It is known that UV irradiation of 1,1-diphenyl-2-haloethenes in ether solution results in the formation of three products: 1,2-diphenylacetylene, 1,1-diphenylethene, and 1,1,4,4-tetraphenylbutadiene.[12] The ratio depends on the type of halogen atom bonded and the percent of 1,1-diphenylethene increased from chloro to iodo derivative. The explanation for these phototransformations includes the excited molecule undergoing C-X bond fission thus forming a radical pair. In subsequent electron transfer, this creates an ion pair intermediate which, by migration of a phenyl group and loss of the proton, forms diphenylacetylene. On the other hand, the radical pair formed can be transformed to a free radical which can abstract the hydrogen atom from the solvent leading to 1,1-diphenylethene, or dimerize to 1,1,4,4-tetraphenylbutadiene. The lower dissociation energy of the carbon - halogen bond increases the percent of 1,1-diphenylethene formed,[12] showing that the rate of a free radical formation and the rate of the electron transfer reaction in a diradical species depends on the type of the halogen atom bonded. The nature of the solvent, as a hydrogen atom donor, also has an influence on the 1,1-diphenylethene formation (Table 1).

Table 1: The Effect of Solvent on Products Distribution in Photochemical Reactions of 1,1-Diphenyl-2-haloethenes[a)]

halogen atom	solvent	conversion of (%)	relative yields of products (%)		
			$\Phi{-}C{\equiv}C{-}\Phi$ 4	 3	
Cl	ether[b)]	37	40	44	16
Cl	acetonitrile[c)]	18	98	2	-
Cl	tetrahydrofuran[c)]	16	92	8	-
Br	ether[b)]	33	34	51	15
Br	acetonitrile[d)]	39	84	16	-
Br	tetrahydrofuran[d)]	50	32	68	-
I	ether[b)]	33	28	76	9

[a)] λ= 253.7 nm, T= 32°C, relative yields determined by analytical glc,
[b)] see ref. 12
[c)] irradiation time 4 hours
[d)] irradiation time 1 hour

From the literature it is known, that the photoreduction of aliphatic and aromatic organic compounds can be enhanced by using inorganic metal hydrides, but only a few reports could be found concerning the photoreduction of vinyl halides.[1-9] For this reason, it was decided to study phototransformations of 1,1-diphenyl-2-haloethenes in the presence of sodium borohydride or lithium aluminium hydride. From the results obtained, it will be possible to give some new information about the reaction mechanism proposed.[9]

Acetonitrile, as a poor hydrogen donor, was chosen as solvent and 1-hour UV irradiation of 1,1-diphenyl-2-bromoethene (1) resulted in 39% conversion, with 1,1-diphenylethene (3) and diphenylacetylene (4) formation in the relative ratio of 16 : 84, which is quite different from the results obtained in ether solution (Table 1, Scheme 1). In order to establish the effect of a bonded halogen atom, 1,1-diphenyl-2-chloroethene (2) was chosen as a substrate. After a 4-hour irradiation of the compound 2 in acetonitrile solution, only 18% of the starting compound was transformed to 1,1-diphenylethene (3) and diphenylacetylene (4) in a ratio of 2 : 98 (Table 1).

In the presence of an equimolar amount of sodium borohydride in acetonitrile solution, the conversion of 1,1-diphenyl-2-bromoethene (1) was 36% with an increased percent of the reduced product (3), the relative ratio of 3 : 4 being 75 : 25. A higher concentration of sodium borohydride in the reaction mixture decreased conversion of the starting compound and enhanced photochemical reduction. When the molar ratio of 1,1-diphenyl-2-bromoethene (1) and sodium borohydride being 1 : 3, the conversion was 22%, with the formation of only 1,1-diphenylethene (3) (Table 2).

Table 2: Irradiation of 1,1-Diphenyl-2-bromoethene (1) in the Presence of Sodium Borohydride[a)]

		conversion of	relative yields (%)	
c_{NaBH_4}/c_1	H_2O (%)	1 (%)	3	4
0	0	39	16	84
0	10	48	19	81
0	50	25	8	92
1	0	36	75	25
1	10	48	42	58
1	50	30	23	77
3	0	22	99	1
3	10	73	58	42
3	50	33	28	72
3[b)]	0	0	0	0
3[b)]	10	0	0	0

[a)] Irradiation time: 1 hour; solvent: acetonitrile; $\lambda = 253.7$ nm; T= 32°C; relative yields determined by analytical glc

[b)] Dark reaction: reaction time 24 hours; T= 22°C

The comparison of the results obtained by irradiation of 1,1-diphenyl-2-bromoethene (1) in an acetonitrile solution in the presence of sodium borohydride showed that the metal hydride did not increase the conversion of haloethene 1 but had great influence on product distribution. The formation of 1,1-diphenylethene (3), as nearly the sole product, and only a trace of diphenylacetylene (4) observed in the product mixture when the reaction was carried out with an excess of sodium borohydride indicated that the BH_4^- ion must be included in the reaction pathway. There are three possible pathways in which a metal hydride can be operative which are presented in Scheme 1.

To establish the most probable pathway in our case, several experiments were run. An 1-hour irradiation of 1,1-diphenyl-2-bromoethene (1) and sodium borohydride (molar ratio 1 : 3) was carried out in the presence of a radical quencher acrylonitrile to prove the reaction pathway D as operative. Photochemical reaction resulted in the same conversion of the starting compound, with 1,1-diphenylethene (3) and diphenylacetylene (4) formation in the relative ratio of 76 : 24 (Table 3). From the results obtained, it can be concluded that the reaction pathway D (Scheme 1) can not be the main reaction course in which sodium borohydride is operative.

Table 3: Irradiation of 1,1-Diphenyl-2-bromoethene (1) in the Presence of a Radical Quencher[a)]

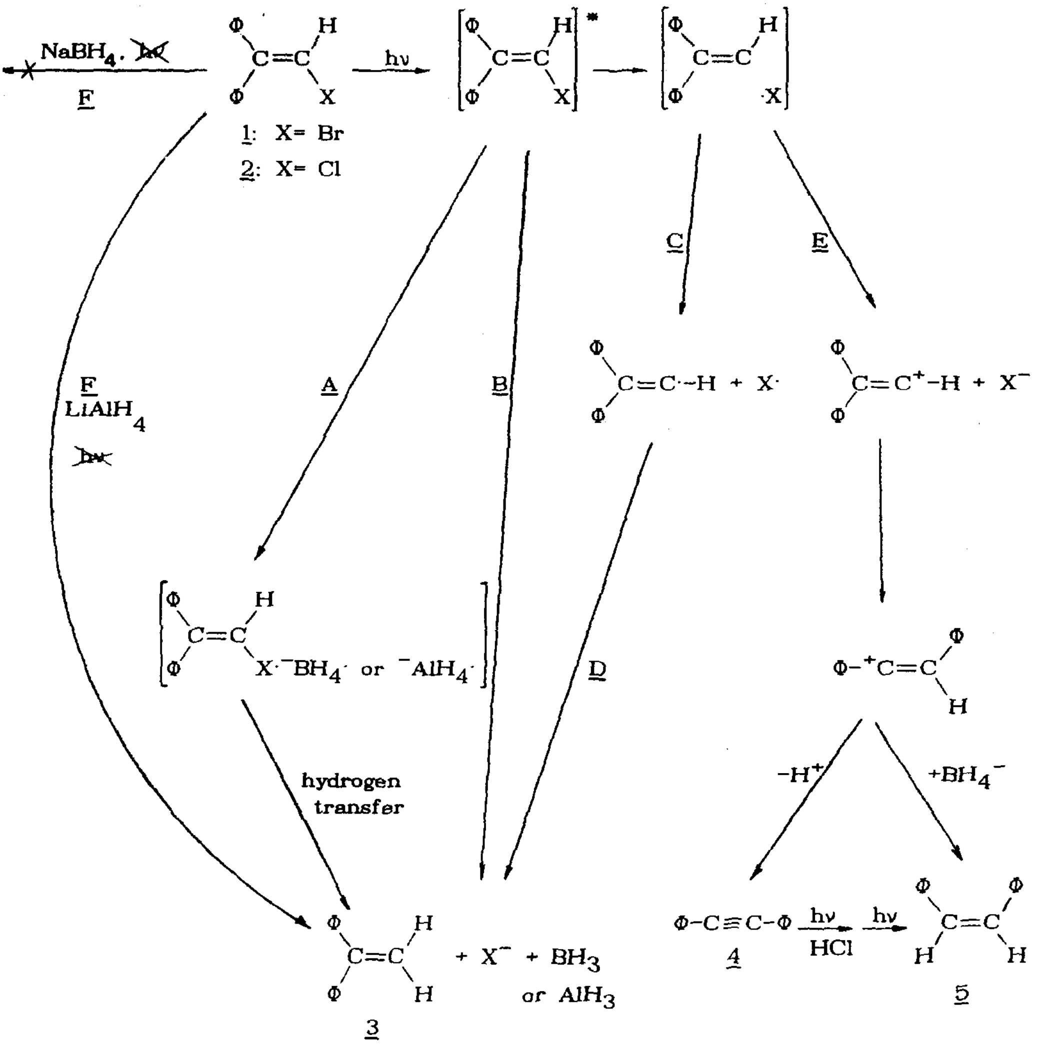
quencher	conversion of 1 (%)	relative yields (%) 3	4
-	22	99	1
acrylonitrile	33	76	24
hydroquinone	30	89	11

[a)] Irradiation time: 1 hour; λ= 253.7 nm; T= 32°C; solvent: acetonitrile; concentration of 1,1-diphenyl-2-bromoethene (1): 0.016 $mol.l^{-1}$; concentration of sodium borohydride 0.048 $mol.l^{-1}$; of quencher: 0.064 $mol.l^{-1}$; relative yields determined by analytical glc

An experiment using sodium borodeuteride, instead of sodium borohydride, was carried out to establish if the hydrogen incorporated in the product 1,1-diphenylethene (3) comes from the reducing agent used. After an 1-hour irradiation of 1,1-diphenyl-2-bromoethene (1) in acetonitrile solution in the presence of sodium borodeuteride in the molar ratio of 1 : 3, it was determined by analytical glc that the reaction resulted in 32% conversion of the starting alkene (1) with the formation of 1,1-diphenylethene (3) and diphenylacetylene (4) in the ratio of 99 : 1. To establish the contents of the deuterium incorporated in 1,1-diphenylethene (3), mass spectrum and ^1H NMR spectrum of the crude reaction mixture were recorded. In the mass spectrum a molecular peak of monodeuterated 1,1-diphenylethene at m/z= 181 was detected, while in the ^1H NMR spectrum, besides the signal at δ= 5,50 ppm (s, 2H), corresponding to 1,1-diphenylethene (3), a singlet signal at δ= 5,30 ppm corresponding to one hydrogen atom in monodeuterated 1,1-diphenylethene, was observed. From the spectrum it was possible to calculate the ratio of 1,1-diphenylethene (3) and monodeuterated 1,1-diphenylethene which was 36 : 64.

From the results obtained, it can be concluded that metal hydride as well as the solvent used are the source of the hydrogen atom incorporated in 1,1-diphenylethene (3). This means that the reaction can proceed predominantly via two possible

Scheme 1:



A: electron transfer from BH_4^- or AlH_4^-; B: hydride transfer from BH_4^- or AlH_4^-; D: hydrogen atom abstraction from BH_4^- or from the solvent; E: electron transfer; F: dark reaction pathways represented in Scheme 1: via the pathway A where electron transfer from BH_4^- to the excited molecule of 1,1-diphenyl-2-bromoethene (1) is followed by a hydrogen transfer and the halogenide anion elimination, or via the pathway B where a direct hydride transfer from BH_4^- to the excited molecule of 1,1-diphenyl-2-bromoethene (1) and elimination of the halogenide anion from the molecule takes place.

To establish the effect of the nature of the bonded halogen atom in the 1,1-diphenyl-2-haloethenes on the photoreduction by sodium borohydride, 1,1-diphenyl-2-chloroethene (2) was chosen as a substrate. From the results presented in Table 4 it can be seen that the nature of the bonded halogen atom has a substantial influence on the photoreduction with sodium borohydride and that electron transfer in the primarily formed diradical species is the main reaction pathway observed in this case (reaction pathway E, Scheme 1). The degree of conversion of the compound 2 and the amount of 1,1-diphenylethene (3) formed was very little effected by the concentration of the sodium borohydride added (Table 4). The formation of cis-stilbene (5), which was also observed in some cases, can be explained by a photochemical addition of hydrogen chloride on the triple bond of diphenylacetylene (4), followed by a photochemical reduction of intermediary formed Z-1,2-diphenyl-1-chloroethene under conditions mentioned, or by an attack of hydride ion on the rearranged carbonium ion (Scheme 1).

The reaction of 1,1-diphenyl-2-haloethenes with sodium borohydride in acetonitrile solution proceeds only by UV irradiation and no dark reaction was observed (Table 2, Table 4).

Table 4: Irradiation of 1,1-Diphenyl-2-chloroethene (2) in the Presence of Sodium Borohydride[a)]

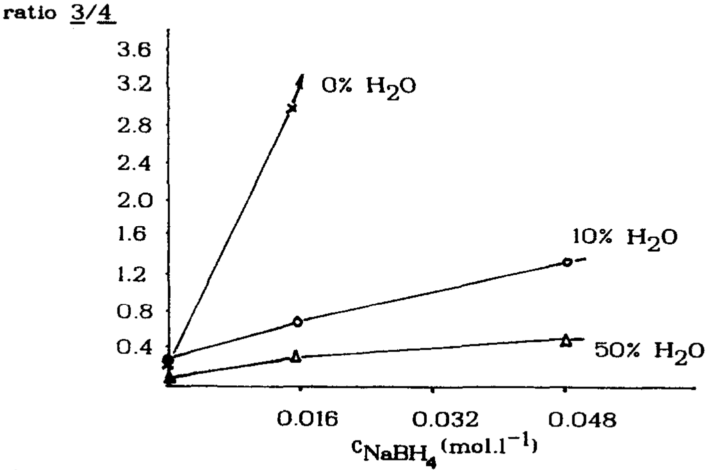
c_{NaBH_4}/c_2	H_2O (%)	conversion of 2 (%)	relative yields (%) 3	4	5
0	0	18	2	98	0
0	10	17	2	98	0
1	0	14	2	91	7
1	10	15	6	94	0
3	0	13	4	92	4
3	10	13	10	90	0
3[b)]	10	0	0	0	0

[a)] Irradiation time: 4 hours; λ= 253.7 nm; solvent: acetonitrile; T= 32°C; relative yields determined by analytical glc

[b)] Dark reaction: reaction time 24 hours; T= 22°C

We were also interested how the amount of water added to acetonitrile as a solvent affects the nature of the carbon - halogen bond cleavage in 1,1-diphenyl-2-bromoethene (1), since it is known that water can act as a hydrogen donor in photoreduction reactions with borohydrides.[3b,9] After 1-hour irradiation of 1 in acetonitrile/water in the ratio 9 : 1, the percent of ionic product diphenylacetylene (4) formed was 81%, which is very similar to the results obtained in pure acetonitrile solution (Table 2). When the experiment was run in a solution of acetonitrile and water in the ratio of 1 : 1, diphenylacetylene (4) as an ionic product and 1,1-diphenylethene (3) as a radical one were formed in the ratio of 92 : 8 (Scheme 1). The conversion of starting material diminished to 25%. In order to determine the effect of water concentration in acetonitrile on the photoreduction of 1,1-diphenyl-2-bromoethene (1) with sodium borohydride, 10% water was added to acetonitrile as a solvent of equimolar concentrations of 1,1-diphenyl-2-bromoethene (1) and sodium borohydride. The conversion observed was 48% and the relative ratio of the products formed: diphenylacetylene (4) as an ionic product vs. 1,1-diphenylethene (3), was 58 : 42. This means that a decrease in the formation of a photoreduction product in comparison with the reaction where no water was added, took place (Table 2). When 50% water was added to the acetonitrile solution, the conversion of 1,1-diphenyl-2-bromoethene (1) was only 30%, while the ratio of the products 3 : 4 was 23 : 77 (Table 2). Similar effects when adding water to acetonitrile as solvent on the photochemical reduction of 1,1-diphenyl-2-bromoethene (1) were observed when higher concentrations of sodium borohydride were used. When the molar ratio of 1,1-diphenyl-2-bromoethene (1) to sodium borohydride was 1:3 the percent of the reduction product 1,1-diphenylethene (3) decreased from 99% in pure acetonitrile to 42% when 10% water was added, or 28% when 50% water was added to acetonitrile. The effect of adding water to acetonitrile as solvent on the products ratio 1,1-diphenylethene (3) vs. diphenylacetylene (4) is presented in the Scheme 2. It can be seen from the plots that the addition of water changed the effect of concentration of the reducing agent sodium borohydride on the products ratio.

Scheme 2: The Effect of Water on the Products Ratio in Photochemical Reaction of 1,1-Diphenyl-2-bromoethene by NaBH$_4$[a]



[a] Irradiation time: 1 h; λ= 253.7 nm; T= 32°C; conc. of 1: 0.016 mol.l^{-1}; relative yields determined by analytical glc

The results obtained after 4-hour irradiation of acetonitrile solution of 1,1-diphenyl-2-chloroethene (2) containing different amounts of water and sodium borohydride are presented in Table 4. It can be seen that adding water did not change this reaction substantially.

From the results obtained, it can be concluded that water was probably not acting as a hydrogen donor. The amount of 1,1-diphenylethene (3) formed was diminished and the amount of ionic product diphenylacetylene (4) was increased in comparison to the reaction without water added which shows that water has an influence on the stabilization of ionic intermediate (Tables 2 and 4).

Photochemical reactions of 1,1-diphenyl-2-haloethenes in the presence of lithium aluminium hydride as a reducing agent also were studied. It has been reported that alkyl[10] and aryl halides in the presence of radical initiators[11] undergo photoreductive dehalogenation with lithium aluminium hydride. It is also well known that lithium aluminium hydride can be used for thermal reductive dehalogenations not only of alkyl halides,[13] but also bridgeheaded halides.[14] Allyl and benzyl bromides are reduced instantaneously by $LiAlH_4$.[15] Heating of 2-bromo-2-methylstyrene for 24 hours in dimethoxyethane in the presence of lithium aluminium hydride resulted in 81% conversion to 2-methylstyrene.[14] 2-Bromostyrene and aryl halides also exhibit considerable reactivity toward $LiAlH_4$.[15] After 1 hour, from 2-bromostyrene in tetrahydrofuran 2%, and after 24 hours 22% styrene was formed[15] at room temperature. Reduction of 2-bromostyrene by $LiAlH_4$ under photochemical condition in ether solution is enhanced substantially, while in 0.5 hour 55% of styrene is formed.[10] An 1.6 h irradiation of 2-bromopropene in tetrahydrofuran resulted in the formation of propene with a 66% yield.[11] These reports do not mention the amount of the reduced product formed by photochemical reaction of vinyl halides without the addition of $LiAlH_4$.[10,11]

From Table 1 it can be seen that tetrahydrofuran, as well as ether as a solvent, can act as good hydrogen donors in the photochemical reaction of 1,1-diphenyl-2-haloethenes. In order to establish the effect of $LiAlH_4$ on photochemical reduction of 1,1-diphenyl-2-haloethenes, 1,1-diphenyl-2-bromoetehene (1) was irradiated for 1 hour in a tetrahydrofuran solution. Results of the experiments, in which different molar ratios of $LiAlH_4$ to substrate 1 were used, are presented in Table 5. The presence of different amounts of $LiAlH_4$ has a diverse effect on the degree of conversion, but increases the formation of the reduction product 1,1-diphenylethene (3).

From the results obtained in the dark reaction it can be seen that the reduction by $LiAlH_4$ proceeds also without UV irradiation, but conversion of 1,1-diphenyl-2-bromoethene (1), after 1 hour, was very low (only 6%), with 1,1-diphenylethene (3) as the sole product formed (Table 5). On the other hand, the photoreduction in the tetrahydrofuran solution, without the addition of a reducing agent, is certainly not negligible (Table 5).

To study the effect of the nature of the bonded halogen atom in 1,1-diphenyl-2-haloethene on photoreduction by $LiAlH_4$, 1,1-diphenyl-2-chloroethene (2) was irradiated in a tetrahydrofuran solution in the presence of $LiAlH_4$ at different molar ratios for the vinyl halide 2. The results presented in Table 6 show that the addition of $LiAlH_4$ enhanced the formation of 1,1-diphenylethene (3), but the conversion of the starting alkene remained small and almost unchanged even at higher molar ratios of $LiAlH_4$ to 1,1-diphenyl-2-chloroethene (2). The dark reaction was also observed and, in 4 hours at room temperature, 1.5% of starting alkene (2) was reduced to 1,1-diphenylethene (3).

Table 5: Irradiation of 1,1-Diphenyl-2-bromoethene (1) in the Presence of $LiAlH_4$[a)]

c_{LiAlH_4}/c_{1}	conversion of 1 (%)	relative yields (%) 3	4
0	50	68	32
1	48	74	26
2	44	77	23
3	64	88	12
4.5	78	90	10
9[b)]	6	100	0

[a)] Irradiation time: 1 hour; solvent: tetrahydrofuran; λ= 253.7 nm; T= 32°C; relative yields determined by analytical glc

[b)] Dark reaction: reaction time: 1 hour; T= 22°C

Table 6: Irradiation of 1,1-Diphenyl-2-chloroethene (2) in the Presence of $LiAlH_4$[a)]

c_{LiAlH_4}/c_{2}	conversion of 2 (%)	relative yields (%) 3	4
0	16	8	92
1	20	35	65
2	19	44	56
3	24	54	46
3[b)]	1.5	100	0

[a)] Irradiation time: 4 hours; solvent: tetrahydrofuran; λ= 253.7 nm; T= 32°C; relative yields determined by analytical glc

[b)] Dark reaction: reaction time: 4 hours; T= 22°C

Conclusions:

- Better hydrogen donating properties of the solvent used increase the formation of a radical product in the photochemical reaction of 1,1-diphenyl-2-bromoethene (1) but have a much smaller effect on the products distribution (radical vs. ionic) in the reaction of a chloro derivative (2)
- The use of the reducing agent $NaBH_4$ enhances the formation of the photoreductive product 1,1-diphenylethene (3) in 1,1-diphenyl-2-bromoethene (1) but has no influence on the reaction pathway in 1,1-diphenyl-2-chloroethene (2)
- The experiments with radical quenchers and sodium borodeuteride show that the photochemical reaction of 1,1-diphenyl-2-bromoethene (1) proceeds in two possible

reaction pathways, as follows:

- an electron transfer from BH_4^- to the excited 1,1-diphenyl-2-bromoethene (1) followed by hydrogen atom transfer from $BH_4^{-\cdot}$ with the elimination of the halogenide anion, or
- a direct hydride ion transfer from BH_4^- species to photoexcited 1,1-diphenyl-2-bromoethene molecule with the elimination of the bromide anion.

- In the presence of $LiAlH_4$ in the reaction mixture, the percent of the reduction product is increased in the photochemical reaction of both 2-chloro- (2) and 2-bromoderivative (1) of 1,1-diphenylethene, which indicates a different effect as observed in the case of $NaBH_4$.

Experimental

IR spectra were recorded by using a Perkin Elmer 1310 spectrometer. ^1H NMR spectra were determined with a Varian EM 360 L spectrometer from CCl_4 or $CDCl_3$ solutions with Me_4Si as an internal reference. Analytical gas liquid chromatography was carried out with a Varian Aeroghraph, Model 3700 with LDC-Milton Roy CI-10B integrator, and preparative separations with a Varian Aerograph, Model 2700.

Irradiation was carried out in a Rayonet Photochemical Chamber Reactor, Model RPR-100, with RPR 253.7 nm lamps.

Materials

1,1-Diphenyl-2-bromoethene (1),[16] and 1,1-diphenyl-2-chloroethene (2)[17] were synthesized. Sodium borohydride, sodium borodeuteride, and lithium aluminium hydride were obtained from commercial sources and were used without further purification. Acrylonitrile was distilled and hydroquinone was crystallized before use. Solvents were purified by established procedures.

General Procedure

a) *Irradiation of Solutions of 1,1-Diphenyl-2-haloethenes*

0.25 mmol of 1,1-diphenyl-2-haloethene was dissolved in 16 ml of acetonitrile or tetrahydrofuran, or acetonitrile with the appropriate amount of water added. The solution was irradiated at room temperature for 1 hour in the case of 1,1-diphenyl-2-bromoethene (1) or for 4 hours in the case of 1,1-diphenyl-2-chloroethene (2) as substrate with RPR 253.7 nm lamps. The solution was poured into 20 ml of water and extracted with dichloromethane. The organic phase, washed with water and dried over anhydrous Na_2SO_4, was evaporated under reduced pressure. The crude reaction mixture was analysed by analytical glc (OV 17 (10%) and FFAP (30%) on CHROM G A/W, 80/100 at 220°C), and separated by preparative glc (OV 101 (15%) on CHROM W A/W 60/80 at 195°C). The results are presented in Table 1.

b) *Irradiation in the Presence of Sodium Borohydride*

0.25 mmol of 1,1-diphenyl-2-haloethene with an appropriate amount of sodium borohydride were dissolved in 16 ml of acetonitrile, or in the acetonitrile with the appropriate amount of water added. The solution was irradiated at room temperature for 1 hour in the case of 1,1-diphenyl-2-bromoethene (1) or for 4 hours in the case of 1,1-diphenyl-2-chloroethene (2) as substrate with RPR 253.7 nm lamps. The solution was poured into 20 ml of water and extracted with dichloromethane. The organic phase, washed with water and dried over anhydrous Na_2SO_4, was evaporated under reduced pressure. The crude reaction mixture was analysed by analytical glc (OV 17 (10%) and FFAP (30%) on CHROM G A/W, 80/100 at 220°C), and separated by preparative glc (OV 101 (15%) on CHROM W A/W 60/80 at 195°C). The results are presented in Tables 2 and 4.

c) *Irradiation in the Presence of Sodium Borodeuteride*

65 mg (0.25 mmol) of 1,1-diphenyl-2-bromoethene (1) and 32 mg (0.75 mmol) of sodium borodeuteride were dissolved in 16 ml of acetonitrile and the solution was irradiated (λ= 253.7 nm) at room temperature for 1 hour. The reaction mixture poured into 20 ml of water was extracted with dichloromethane. The organic phase, washed with water and dried over anhydrous Na_2SO_4, was evaporated under reduced pressure. The crude reaction mixture was analysed by analytical glc (OV 17 (10%) and FFAP (30%) on CHROM G A/W, 80/100 at 220°C), and by ^1H NMR and mass spectroscopy. The results are presented in the text.

d) *Irradiation in the Presence of Quenchers*

65 mg (0.25 mmol) of 1,1-diphenyl-2-bromoethene (1), 28.5 mg (0.75 mmol) of sodium borohydride, and 1 mmol of the appropriate quencher (acrylonitrile, hydroquinone) were dissolved in 16 ml of acetonitrile and the solution was irradiated with RPR 253.7 nm lamps for 1 h. The reaction mixture was poured into 20 ml of water and extracted with dichloromethane. The organic phase, washed with water and dried over anhydrous Na_2SO_4, was evaporated under reduced pressure. The crude reaction mixture was analysed by analytical glc (OV 17 (10%) and FFAP (30%) on CHROM G A/W, 80/100 at 220°C). The results are presented in Table 3.

e) *Irradiation in the Presence of Lithium Aluminium Hydride*

Experiments were the same to those using sodium borohydride as a reducing agent except that the solvent used was tetrahydrofuran. The results are presented in Tables 5 and 6.

f) *Dark Reactions*

0.25 mmol of 1,1-diphenyl-2-haloethene and 0.75 mmol of sodium borohydride were dissolved in 16 ml of acetonitrile or in acetonitrile/water (9:1). The solution was allowed to stand at room temperature in darkness for 24 hours. The isolation procedure and analysis of the crude reaction mixture obtained was the same as in the photochemical reactions above.
0.25 mmol of 1,1-diphenyl-2-haloethene and 0.75 mmol of lithium aluminium hydride in the case of the compound 2 or 2.25 mmol in the case of the compound 1 were dissolved in 16 ml of tetrahydrofuran. The solution was allowed to stand at room temperature in darkness, protected from moisture, for 1 hour for 1,1-diphenyl-2-bromoethene (1) or 4 hours for 1,1-diphenyl-

2-chloroethene (2). The isolation procedure and analysis of the crude reaction mixture was the same as above. The results are presented in Tables 2, 4, 5, and 6.

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