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Solvent Effect in Photolysis of Chloro Substituted Benzyl Chlorides†

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Abstract:

The effect of solvent on photolyses of 3-chloro and 4-chloro substituted benzyl chlorides is described. Analysis of the products formed indicates that both radical and ionic intermediates are involved. In the first step, homolytic benzylic C-Cl bond cleavage occurs, resulting in a radical pair. Further reaction pathway, however, depends upon the solvent used. In cyclohexane and tetrahydrofuran, the products obtained are formed *via* an intermediate benzylic radical. Photolysis in acetonitrile, on the other hand, results in products, which can be interpreted through intermediate formation of both benzylic cation and benzylic radical. The presence of $LiAlH_4$ accelerates the reduction of the C-Cl bond in the aromatic ring, leading to toluene as the main product.

Introduction:

The photochemistry of heteroatomic benzylic bond has been the subject of investigation and mechanistic speculation for over 30 years. One of the intriguing discoveries is that partitioning between homolytic cleavage to give radicals and

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† Dedicated to Prof. Dr. Anton Šebenik

heterolytic cleavage to give ions is closely balanced. The balance can be tipped by changing the solvent and leaving group.

In order to determine the mechanism of degradation different benzylic systems ($PhCH_2X$) were investigated: benzyl acetates (X=OAc) [1], sulphonium salts ($X=(CH_3)_2S^+BF_4^-$) [2], ammonium salts ($X=(CH_3)_3N^+Cl^-$) [3], phosphonium salts ($X=Ph_3P^+Cl^-$), and a group of homobenzylic systems. However, the most thoroughly studied examples have been benzyl halides (X = Cl, Br), which set the pattern that is followed by other benzylic systems.

The first photochemical studies were performed in the gas phase [4]. Direct photolysis of benzyl chloride led to benzyl radical and a chlorine atom. Zimmerman and Sandel [1] investigated the photolysis of 3- and 4-methoxybenzyl acetates and related derivatives in ethanol-water solution and observed that direct irradiation of 3-methoxybenzyl acetate as well as 3-methoxybenzyl chloride gave the appropriate alcohol, the ether and lesser amounts of free-radical products. The solvolytic products were taken as an evidence for the formation of an intermediate 3-methoxybenzylic cation. The nature of the state and the sequence of reactions leading to the cation were left unspecified.

The earliest studies of photochemical reactions of benzyl chloride in solution gave contradicting results. Ratcliff reported that benzyl chloride is solvolytically stable when irradiated in ethanol [3]. This was contradicted by Kuz'min and co-workers [5], who observed that direct irradiation of a range of chloromethyl and bromomethyl derivatives of aromatic hydrocarbons including benzyl chloride in alcohol-water solution led to the corresponding carbinols in high yields. Since the results were the same even when the reaction was carried out in solution saturated with oxygen, these authors concluded that photosolvolysis proceeds by direct heterolytic bond cleavage from the excited singlet state.

Cristol and Greenwald reported [6] that direct irradiation of benzyl chloride in methanol gave no benzyl methyl ether, which is the expected heterolytic cleavage product, but only products derived from benzyl radicals and chlorine atom. However, they reported that sensitization of benzyl chloride with the triplet sensitizers (acetone or acetophenone) in methanol resulted in exclusive formation of the anticipated solvolytic product. These results imply that the excited singlet state of benzyl chloride cleaves homolytically and that in the presence of the triplet sensitizer some other state, responsible for heterolytic cleavage is formed.

Hyömäki and Koskiakllio [7] studied direct irradiation of benzyl chloride in methanol-water mixtures. They observed formation of both the alcohol and ether products characteristic of heterolytic cleavage and the radical coupling products characteristic of homolytic cleavage of the carbon-chlorine bond. On the basis of the changes in the relative amounts of these products with the solvent composition, these authors suggested that the excited singlet state is homolytically cleaved and that chlorine atom formed either abstracts hydrogen atom from the solvent or oxidizes the benzylic radical to cation.

McKenna and co-workers [8] also irradiated benzyl chloride in methanol. Direct photolysis gave products characteristic of both ionic and free-radical pathways. The results were in good agreement with those reported by Hyömäki and Koskiakllio [7]. Due to the similar findings in the photolysis of ammonium salts, McKenna and co-workers proposed the following mechanism. In the first step, both the singlet and the triplet excited state of benzyl chloride are homolytically cleaved. The triplet radical pair can undergo an intersystem crossing into the singlet radical pair, which is either in the equilibrium with the ions formed by electron transfer or is a contributor to a resonance hybrid that includes both the ions and the singlet radical pair. From the studies of CIDNP effect it is known that the interconversion between singlet and triplet states of a radical pair where the partners are already adequately separated can occur at a rate comparable to that of the final separation of the partners. This effect is the result of electron-nucleus interactions while spin-orbit relaxation may also contribute when one of the partners is a halogen atom.

Cristol and Bindel [9,10] have carried out an intensive investigation of the photochemical transformations of benzyl chloride and some of its derivatives in *tert*-butyl alcohol. They reported that the products obtained in both the direct and acetone-sensitized irradiations are the same (derived by radical and ionic pathway), but they are formed in different proportions. Cristol and Bindel concluded that the state responsible for the formation of ionic intermediates is an unspecified short-lived upper triplet state.

The influence of metal hydrides:

It is known that the presence of metal hydrides ($NaBH_4$, $LiAlH_4$, etc.) has a great impact on the photoreduction of organic halogenides. Recent investigations on photoreduction of aryl halides [11-16] in the presence of $NaBH_4$ revealed three pathways that are supported by experimental observations:

a) In the excited molecule of an aryl halide a homolytic cleavage of C-X bond occurs in the first step, generating an aryl radical and a halogen atom. These radicals abstract in the second step hydrogen atom from BH_4^- giving $BH_3^{-\bullet}$ which initiates an $S_{RN}1$-like chain reaction to form the products (ArH, BH_3, HCl, NaCl) [11].

$$ArCl^* \longrightarrow Ar^\bullet + Cl^\bullet \xrightarrow{2\,BH_4^-} ArH + HCl + 2\,BH_3^{\bullet-}$$

$$BH_3^{\bullet-} + ArCl \xrightarrow[S_{RN}1]{} Ar^\bullet + Cl^- + BH_3$$

b) Excited aryl halide reacts with BH_4^- and direct transfer of hydride ion occurs. The resulting products are the same as in the previous pathway [12,14].

$$ArCl^* + BH_4^- \xrightarrow{\text{hydride ion transfer}} ArH + Cl^- + BH_3$$

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 previously mentioned products [15,16].

$$ArCl^* + BH_4^- \xrightarrow[\text{transfer}]{\text{electron}} \left[ArCl^{\bullet-}BH_4^\bullet\right] \xrightarrow[\text{transfer}]{\text{hydrogen atom}} ArH + Cl^- + BH_3$$

Similar reaction mechanisms were proposed for photoreduction of organic halides by $LiAlH_4$ [17-21].

Krishnamurthy and Brown [22] have shown that clear solution of $LiAlH_4$ in tetrahydrofuran reduces organic halides rapidly and quantitatively even at room temperatures. Such reactions are usually far faster than those where a suspension is used. The lower reactivity of suspension was assigned to insoluble impurities that might have coated the undissolved $LiAlH_4$ and hindered its migration into solution and subsequent reaction.

Results:

The solvent effect on the phototransformation of 3- and 4-chlorobenzyl chlorides was studied by direct irradiation in cyclohexane, tetrahydrofuran and acetonitrile solution.

Irradiation of 0.1 M solution of **1a** for 22 hours in cyclohexane (Scheme 1) at 253.7 nm resulted in 92 % conversion. The resulting mixtures contained, besides starting substrate **1a,** 3-chlorotoluene (**2a**), toluene (**3**), 3-chlorophenylcyclohexylmethane (**4a**), cyclohexylphenylmethane (**5**), 1,2-bis(3-chlorophenyl)ethane (**6a**), 1-(3-chlorophenyl)-2-phenylethane (**7a**) and 1,2-diphenylethane (**8**). The product distribution is summarized in Table 1. Shortening of the reaction time from 22 to 4.5 hours led to both, decrease in conversion from 92 to 72 %, as well as to the change in product distribution (Table 1).

Irradiation of **1b** under the same reaction conditions as in the previous case (Scheme 1) resulted in 100 % conversion into a mixture of 4-chlorotoluene (**2b**), toluene (**3**), 4-chlorophenylcyclohexylmethane (**4b**), cyclohexylphenylmethane (**5**), 1,2-bis(4-chlorophenyl)ethane (**6b**), 1-(4-chlorophenyl)-2-phenylethane (**7b**) and 1,2-diphenylethane (**8**). The product distribution is summarized in Table 1. Again, shortening of the reaction time from 22 to 4.5 hours led to decreased conversion. The products formed were the same, however in changed relative ratio (Table 1).

Eight hours irradiation of 0.1 M solution of **1a** in tetrahydrofuran (Scheme 2) at 253.7 nm led to 100 % conversion. The products formed were toluene (**3**), 1,2-bis(3-chlorophenyl)ethane (**6a**), 1,2-diphenylethane (**8**), 3-chlorophenyl-(2-tetrahydrofuryl)-methane (**9a**) and phenyl-(2-tetrahydrofuryl)methane (**10**) and their relative ratio is shown in Table 2.

Irradiation of 0.1 M solution of 4-chlorobenzyl chloride (**1b**) in tetrahydrofuran (Scheme 2) under the same reaction conditions led to 100 % conversion into a mixture of 4-chlorotoluene (**2b**), toluene (**3**), 1,2-bis(4-chlorophenyl)ethane (**6b**), 1-(4-chlorophenyl)-2-phenylethane (**7b**), 1,2-diphenylethane (**8**), 4-chlorophenyl-(2-tetrahydrofuryl)-methane (**9b**) and phenyl-(2-tetrahydrofuryl)methane (**10**). Distribution of products is summarized in Table 2.

Irradiation of 0.1 M solution of 3-chorobenzyl chloride (**1a**) for 2.5 hours in tetrahydrofuran in the presence of a threefold excess of $LiAlH_4$ resulted in 100 % conversion. The reaction mixture obtained, consisted of only 3-chlorotoluene (**2a**) and toluene (**3**) in the ratio of 1:8 (Table 2).

Irradiation of the tetrahydrofuran solution of 4-chlorobenzyl chloride (**1b**) under the same reaction conditions resulted in 100 % conversion to 4-chlorotoluene (**2b**) and toluene (**3**) in the ratio of 1:6 (Table 2).

Irradiation of 0.1 M solution of 3-chlorobenzyl chloride (**1a**) for 22.5 hours in acetonitrile (Scheme 3) resulted in 84 % conversion. The resulting reaction mixture contained, besides starting substrate, 1,2-bis(3-chlorophenyl)ethane (**6a**), 3-chlorobenzaldehyde (**11a**), 1-cyano-2-(3-chlorophenyl)ethane (**12a**), *N*-acetylamino-(3-

SCHEME 1: Photolysis of chloro substituted benzyl chlorides (**1**) in cyclohexane (**a**: 3-chloro; **b**: 4-chloro)

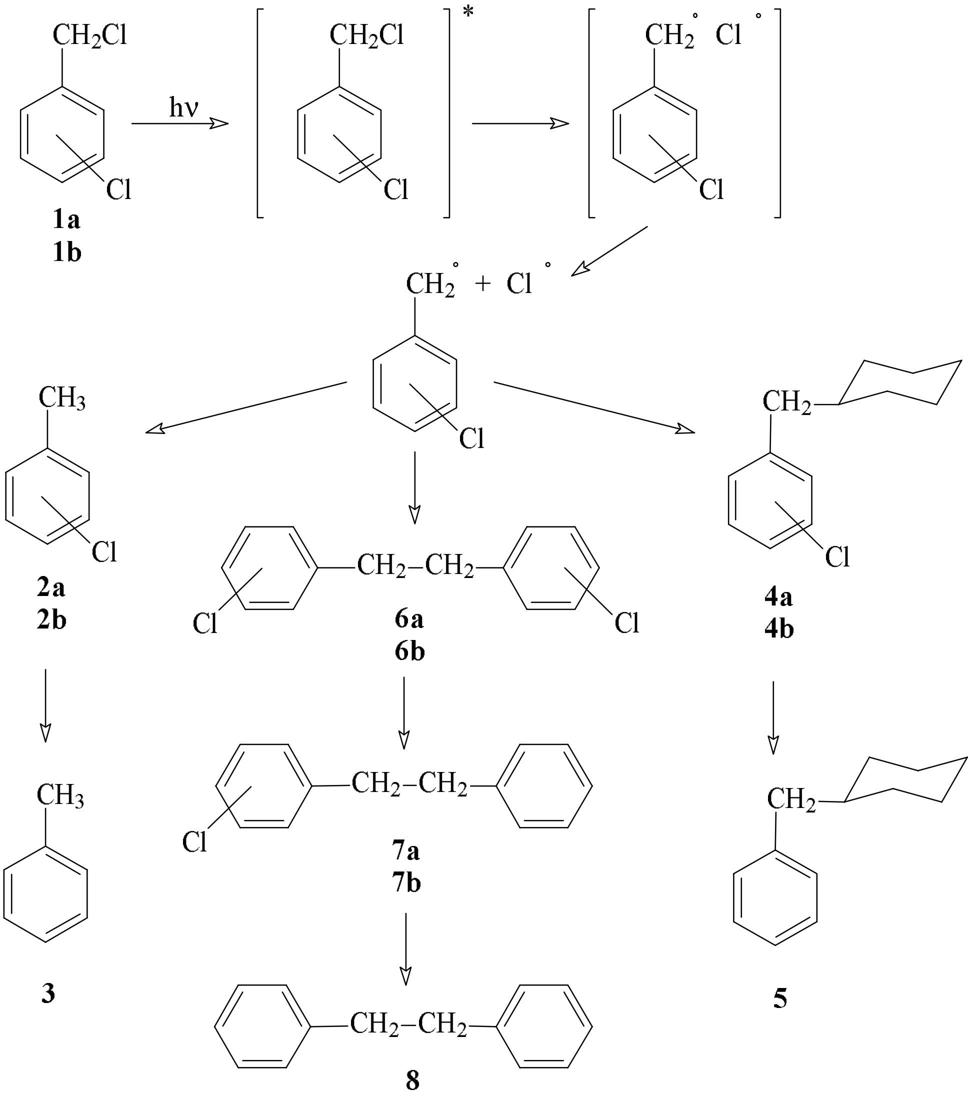


TABLE 1: Product distribution (relative yields (%))[a]

Starting compound[b]	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
3-chlorobenzyl chloride	8.0	1.7	0.3	33.4	30.5	9.1	9.5	7.5
3-chlorobenzyl chloride[c]	32.3	2.9	-	41.5	7.4	12.4	3.0	0.5
4-chlorobenzyl chloride	-	4.3	-	45.0	31.3	8.4	8.6	2.4
4-chlorobenzyl chloride[c]	18.2	1.1	-	40.0	16.3	13.8	7.3	3.3

a) Determined by GC/MS; b) Reaction conditions: substrate: 0.1 M; solvent: cyclohexane; irradiation time: 22 hours; λ = 253.7 nm. c) Irradiation time = 4.5 hours.

SCHEME 2: Photolysis of chloro substituted benzyl chlorides (**1**) in tetrahydrofuran (**a**: 3-chloro; **b**: 4-chloro)

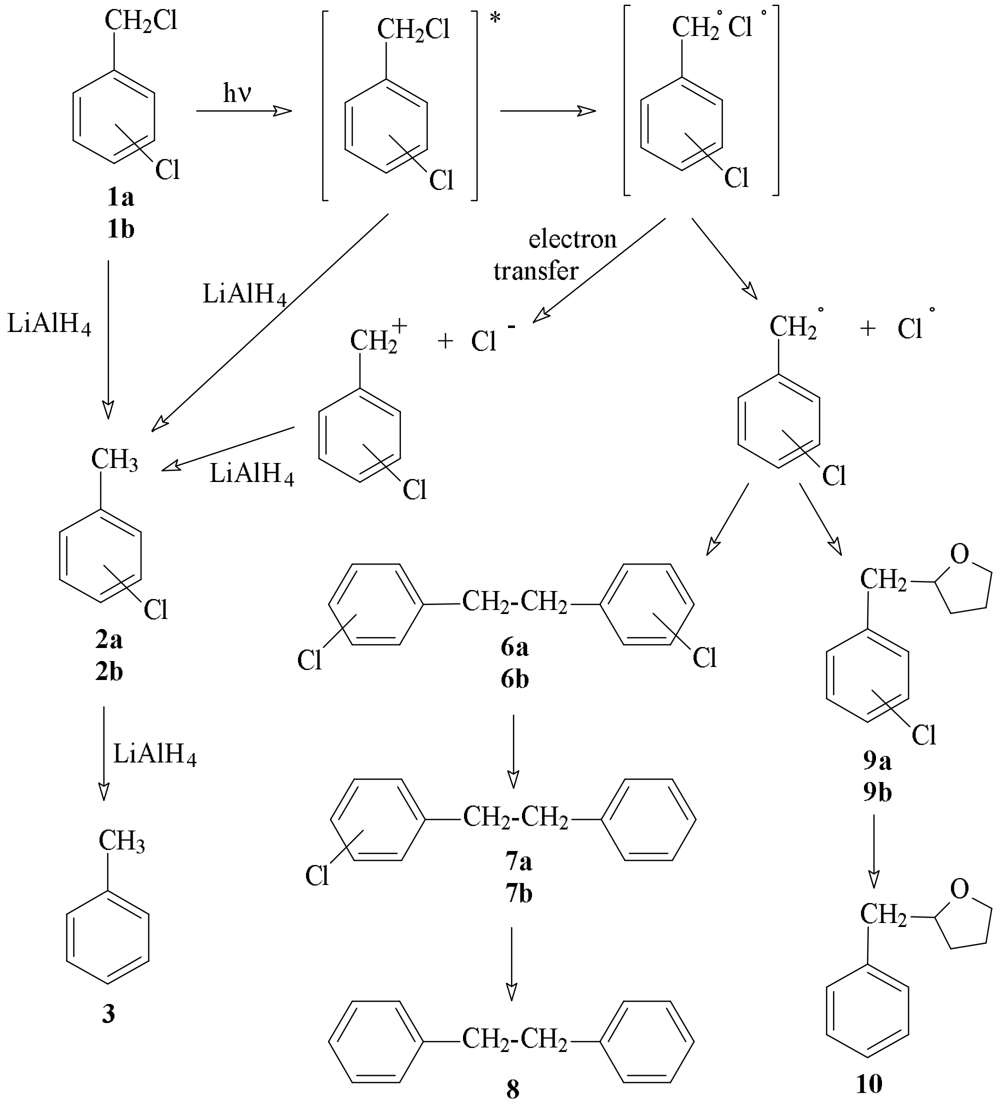


TABLE 2: Product distribution (relative yields (%))[a]

Starting compound[b]	2	3	6	7	8	9	10
3-chlorobenzyl chloride	-	0.2	5.8	-	23.6	4.6	65.8
3-chlorobenzyl chloride[c]	11.3	88.7	-	-	-	-	-
4-chlorobenzyl chloride	2.7	0.3	7.0	13.3	44.5	4.2	28.0
4-chlorobenzyl chloride[c]	14.5	85.5	-	-	-	-	-

a) Determined by GC/MS; b) Reaction conditions: substrate: 0.1 M; solvent: tetrahydrofuran; irradiation time: 8 hours; λ = 253.7 nm. c) Addition of $LiAlH_4$: 0.3 M; irradiation time = 2.5 hours

SCHEME 3: Photolysis of chloro substituted benzyl chlorides (**1**) in acetonitrile (**a**: 3-chloro; **b**: 4-chloro)

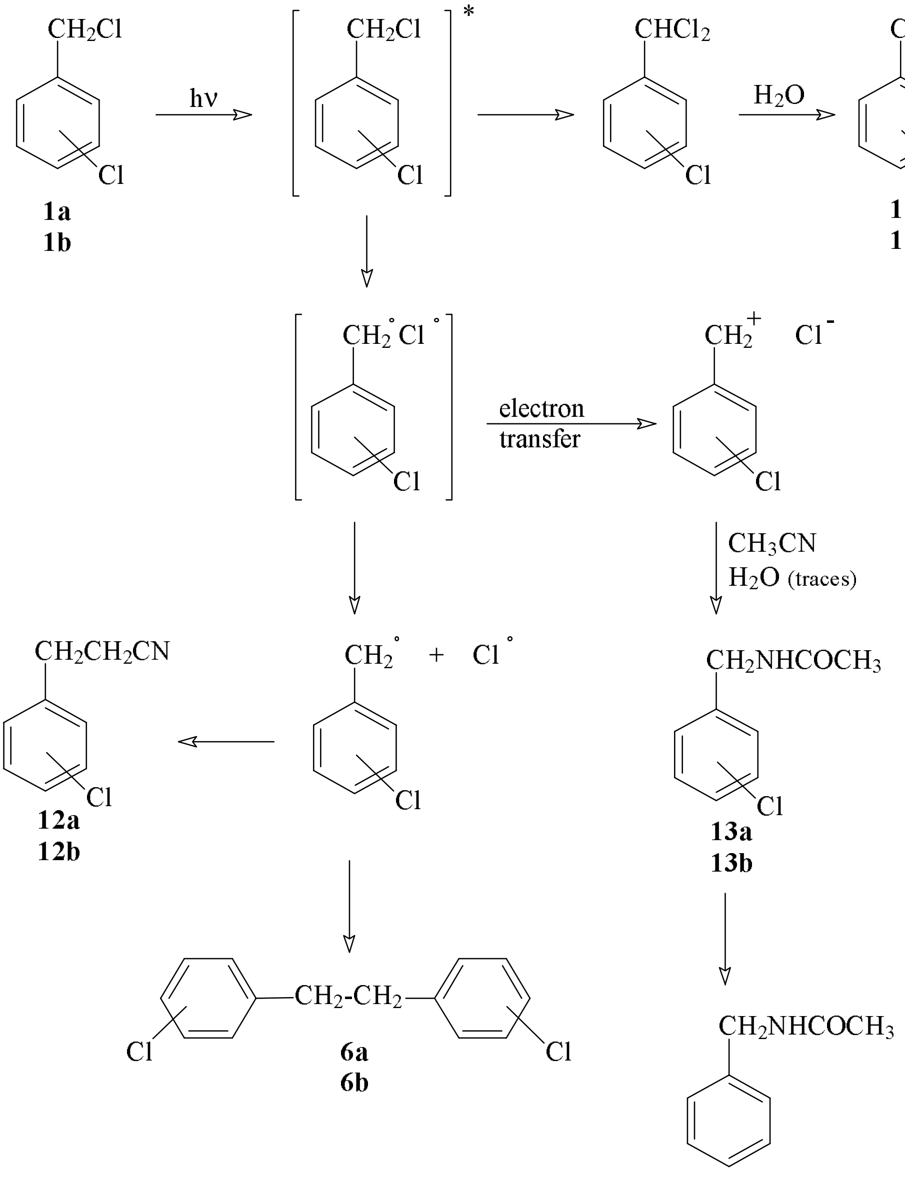


TABLE 3: Product distribution (relative yields (%))[a)]

Starting compound[b]	**1**	**6**	**11**	**12**	**13**	**14**
3-chlorobenzyl chloride	15.6	5.5	4.5	2.4	68.9	3.1
4-chlorobenzyl chloride	24.2	5.0	3.6	-	67.2	-

a) Determined by GC/MS; b) Reaction conditions: substrate: 0.1 M; solvent: acetonitrile; irradiation time: 23.5 hours; $\lambda = 253.7$ nm.

chlorophenyl)methane (**13a**) and *N*-acetylaminophenylmethane (**14**) in the relative ratio, shown in Table 3. Irradiation of 0.1 M solution of 4-chlorobenzyl chloride (**1b**) in acetonitrile (Scheme 3) under the same reaction conditions led to 76 % conversion and the following products were detected: 1,2-bis(4-chlorophenyl)ethane (**6b**), 4-chlorobenzaldehyde (**11b**), *N*-acetylamino-(4-chlorophenyl)methane (**13b**) and *N*-acetylaminophenylmethane (**14**). Their distribution is summarized in Table 3.

Discussion:

The results obtained by photolyses of 3- and 4-chlorobenzyl chlorides (**1**) in cyclohexane (Scheme 1) suggest that the first step is the homolytic cleavage of the benzylic C-Cl bond and the formation of a biradical pair. Separation of radicals is facilitated by abstraction of hydrogen atom from cyclohexane by chlorine atom, which results in benzylic and cyclohexyl radicals. Generated radicals can react further in either of the following manners: a) combination of two benzyl radicals to form 1,2-diphenylethane derivatives (**6**, **7** and **8**), b) combination of benzyl radical and cyclohexyl radical to form cyclohexylphenylmethane derivatives (**4** and **5**) or c) benzyl radical abstraction of hydrogen atom from cyclohexane to form chlorotoluene (**2**) (Scheme 1, Table 1).

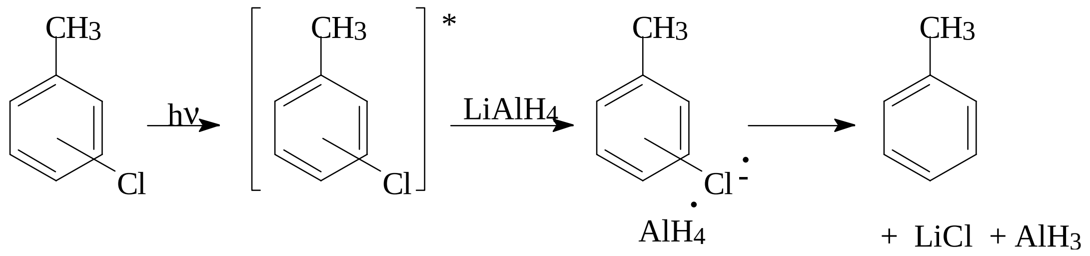
Photolyses of 3- and 4-chlorobenzyl chlorides (**1**) were further performed in tetrahydrofuran (Scheme 2), which is a good hydrogen donor and has also nucleophilic character. The results obtained revealed a similar reaction trend as observed in the case of cyclohexane as solvent. The main products obtained are 1,2-diphenylethane (**8**), formed by combination of two benzylic radicals, and phenyl-(2-tetrahydrofuryl)methane (**10**), generated by combination of 2-tetrahydrofuryl radical and benzyl radical (Scheme 2, Table 2). No products indicating intermediacy of benzylic cations were detected.

A substantial change in the reaction pathway was observed, when photolysis was performed in the presence of $LiAlH_4$. Chlorotoluene (**2**) and toluene (**3**) were the only products obtained (Table 2). Chlorotoluene (**2**) formation can be explained by either of the following processes:

- direct substitution of chloride ion by hydride ion
- reaction of the excited state of chlorobenzyl chloride with $LiAlH_4$
- benzylic cation formation from the radical pair followed by hydride ion transfer from $LiAlH_4$

The following reduction of C-Cl bond in the aromatic ring occurs *via* electron transfer from $LiAlH_4$ to the excited state of chlorotoluene (**2**) thus forming a complex, which after subsequent hydrogen atom transfer results in toluene (**3**) (Scheme 4).

SCHEME 4



Photolyses of 3- and 4-chlorobenzyl chlorides (**1**) in acetonitrile (Scheme 3) have shown, that the choice of solvent plays a crucial role in the rate of radical separation as well as in the single electron transfer. Acetonitrile is a poor hydrogen donor, while a polarized -C≡N bond offers a potential reaction site for bonding of ionic intermediates.

Indeed, the content of radical products (1,2-diphenylethane derivatives **6**, **7** and **8**), formed in the photolysis of either **1a** or **1b** in acetonitrile, is very low (Table 3). This indicates that the ease of separation of the biradical pair into separated radicals and thus formation of benzylic radical depends on the reaction of chlorine atom with solvent through hydrogen atom abstraction. In the case of acetonitrile with poor hydrogen donor abilities, an electron transfer process, wherein benzylic cation is generated, becomes predominant. The cation thus formed reacts further with -C≡N bond, and after hydrolysis *N*-acetylaminobenzyl derivative (**13**) is obtained as the main product (Scheme 3).

Experimental part:

The photochemical reactions were performed in the Photochemical Reactors Ltd. MLU 18 with 6RPR 253,7 nm lamps.

The chromatographic analyses were made on Hewlett Packard HP6890 equipped with FID detector and HP-5 column (temperature program: 100(3)/20/270(10)) and on Varian 3700 equipped with TIC detector and OV-17(5%) column (temperature program: 84(2)/10/210(10)).

The GC/MS analyses were made on Hewlett Packard 6890 and VG-Analytical Autospec EQ spectrometer.

The starting compounds are commercially available and were used without further purification. Cyclohexane ($LiAlH_4$), tetrahydrofuran ($LiAlH_4$) and acetonitrile (CaH_2) were refluxed over mentioned drying agents and distilled in an inert atmosphere before use.

Typical experimental procedure: 2.0 mmol of substrate was dissolved in 20 ml of solvent and the reaction mixture was irradiated at 253.7 nm for 2.5 to 24 hours. Analysis of the reaction mixture was performed by GC and GC/MS and by comparison to the authentic samples: 4-chlorophenylcyclohexylmethane (**4b**) [23], cyclohexylphenylmethane (**5**) [24], 1,2-bis(3-chlorophenyl)ethane (**6a**) [25], 1,2-bis(4-chlorophenyl)ethane (**6b**) [26], 1-(3-chlorophenyl)-2-phenylethane (**7a**) [27], 1-(4-chlorophenyl)-2-phenylethane (**7b**) [27], 4-chlorophenyl-(2-tetrahydrofuryl)methane (**9b**) [28], phenyl-(2-tetrahydrofuryl)methane (**10**) [29], *N*-acetylamino-(3-chlorophenyl)methane (**13a**) [30], *N*-acetylamino-(4-chlorophenyl)methane (**13b**) [30] and *N*-acetylaminophenylmethane (**14**) [31].

Irradiation in the presence of $LiAlH_4$: 1.0 mmol of substrate was dissolved in 9 ml of clear solution of $LiAlH_4$ in tetrahydrofuran (3.0 mmol, c = 0.3325 M) and irradiated for 2.5 hours. The solution was diluted with 10 ml of ether and poured into 10 ml of water to destroy the excess of $LiAlH_4$. Organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. Analysis of the reaction mixture was performed by GC and GC/MS and by comparison to the authentic samples.

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Povzetek:

Proučevali smo vpliv topil na potek fotolize 3-kloro in 4-kloro substituiranih benzil kloridov. Kot topila smo izbrali cikloheksan, tetrahidrofuran in acetonitril. V vseh izbranih topilih v prvi stopnji poteče homolitska cepitev benzilne C-Cl vezi in nastane biradikalski par. Le-ta se v cikloheksanu ali tetrahidrofuranu pretvori v prosti benzilni radikal, nasprotno pa je v acetonitrilu primarni proces prenos elektrona v biradikalskem paru na halogenski atom in nastanek ionskega para. Redukcija C-Cl vezi v aromatskem obroču poteče šele v naslednji stopnji. Dodatek $LiAlH_4$ pospeši redukcijo, tako da nastaneta le 3-kloro- ali 4-klorotoluen in toluen.