

## Photochemistry of Halogenated Benzene Derivatives. Part 2.1 Photoreactions of $\alpha$ -Substituted *p*-Chlorotoluenes

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Solution-phase photoreactions of  $\alpha$ -substituted *p*-chlorotoluenes of the general structure *p*-ClC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>X (X = H, Cl, CN, CO<sub>2</sub>H and OH) have been studied at wavelengths around 300 nm. The acetone-sensitized photolyses of the substrates with X = H, CN, CO<sub>2</sub>H and OH in deaerated CH<sub>3</sub>OH provided reductively dechlorinated photoproducts C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>X with yields of 10–52% based on photodecomposed starting material. The photoreactions of *p*-chlorobenzyl chloride (2) proceeded through homolytical and heterolytical cleavage of its side-chain C–Cl bond possibly *via* a triplet excited state. The main product of the photochemical reactions of (2) in deaerated CH<sub>3</sub>OH both with and without acetone present was *p*-chlorobenzyl methyl ether.

In order to achieve a better understanding of some photochemical aspects of the photolysis of substrate (2), the photoreactions of three halogenobenzaldehydes have been studied. The irradiation of *p*- and *m*-chloro- and *m*-bromo-benzaldehyde in deaerated CH<sub>3</sub>OH gave rise to the formation of the corresponding acetals as the sole principal products. The photoreactivity of *m*-BrC<sub>6</sub>H<sub>4</sub>CHO was 93 times greater than that of *m*-ClC<sub>6</sub>H<sub>4</sub>CHO.

In the past, numerous reports concerning the photoconversions of  $\alpha$ -substituted *p*-chlorotoluenes have appeared in the literature. Irradiation of chlorotoluenes in benzene solution,<sup>2</sup> *p*-chlorophenylacetic acid,<sup>3</sup> its sodium salt,<sup>3</sup> and anhydride,<sup>4</sup> as well as esters derived thereof,<sup>5</sup> have been described, using radiation of the wavelength ( $\lambda$ ) 254 nm. Photochemical transformations of substituted benzyl chlorides under sensitized and unsensitized conditions are also known,<sup>6</sup> including that of *p*-chlorobenzyl chloride in *t*-butyl alcohol.

In view of our interest in the photochemical fate of pollutants such as halogenated benzene derivatives in the environment,<sup>1</sup> we have now investigated the photochemistry of *p*-chlorotoluene and its  $\alpha$ -substituted derivatives of the general structure *p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>X at 280 <  $\lambda$  < 320 nm with methanol, methanol–acetone, and water–acetonitrile as solvents.

### Results

For the u.v. absorption spectra of the investigated substrates *p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>X (1)–(5), the values of  $\lambda_{\max}$  (the wavelengths at which maxima occur in the spectra) and log  $\epsilon_{\max}$  (logarithm of molar extinction coefficients,  $\epsilon$ , for the corresponding maxima) as well as those of  $\epsilon_{300}$  ( $\epsilon$  at  $\lambda = 300$  nm) are recorded in Table 1. The molar extinction coefficients at  $\lambda = 300$  nm of these compounds, with the exception of the substrates (3) and (4), are close to zero, but there is a positive overlap between the absorption spectrum and the emission profile of the radiation source (RPR–3 000 lamps) with all these substances.

On irradiating deaerated methanolic solutions of the substrates (1)–(5) for 48 h at  $\lambda > 280$  nm, only *p*-chlorobenzyl chloride (2) disappeared to a large extent (89%) (Table 2). Furthermore, in the case of the photolysis of compound (2) for 51 h in a water–acetonitrile (1 : 1, v/v) mixture, the percentage disappearance of the starting material was 46% (Table 2). The products arising from the direct photolysis of *p*-chlorobenzyl chloride (2) and *p*-chlorobenzyl alcohol (5), together with their yields (determined from the amounts of photodecomposed substrates), are also recorded in Table 2. This Table indicates that such photodegradation of the substrates (2) and (5) occurred through the scission of the side-chain, *i.e.* C–X bond. Moreover, major photoproducts of

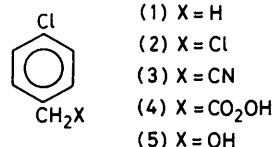
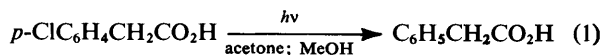


Table 1. Ultraviolet spectra of *p*-chlorotoluene and its  $\alpha$ -substituted derivatives of the type *p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>X in methanol

X	Substrate	$\lambda_{\max}$ /nm (log $\epsilon_{\max}$ )	$\epsilon_{300}$
H	(1)	276 (2.65), 268 (2.66), 263 (2.51), 255 (2.32), 224 (4.02), 220 (4.08)	<0.55
Cl	(2)	273 (2.29), 267 (2.47), 260 (2.41), 255 (2.35), 224 (4.15)	<0.44
CN	(3)	275 (2.56), 266 (2.67), 259 (2.58), 255 (2.45), 224 (4.33), 218 (4.40)	2.89
CO <sub>2</sub> H	(4)	276 (2.36), 267 (2.46), 260 (2.38), 255 (2.27), 219 (4.05)	9.56
OH	(5)	276 (2.35), 267 (2.45), 260 (2.37), 220 (4.11)	<0.67

compound (2) in deaerated CH<sub>3</sub>OH and H<sub>2</sub>O–CH<sub>3</sub>CN were *p*-chlorobenzyl methyl ether (8) and *p*-chlorobenzyl alcohol (5), respectively; these were solvolysis products.

The  $\alpha$ -substituted *p*-chlorotoluenes were also irradiated in deaerated methanol in the presence of acetone (0.533M) as sensitizer. The photoproducts, which were formed as a result of reductive dechlorination [*e.g.* reaction (1)], were quantified



using appropriate standard solutions (Table 3). 52% Of decomposed *p*-chlorotoluene (1) was converted into toluene. Similarly, the substrates (3)–(5) yielded 10% phenylacetonitrile, 40% phenylacetic acid, and 34% benzyl alcohol, respectively (see Table 3). *p*-Chlorobenzyl chloride (2) did not provide the photoproduct, benzyl chloride. Instead, the products of acetone-sensitized photoreaction of the substrate (2) included *p*-chlorobenzyl alcohol (5), *p*-chlorobenzyl methyl ether (8), *p*-chlorobenzaldehyde (9), *p*-chlorophenylethyl

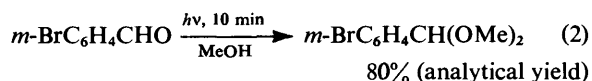
Table 2. Direct irradiation of  $\alpha$ -substituted *p*-chlorotoluenes ( $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{X}$ )

X	Substrate	Concn. ( $10^{-3}\text{M}$ )	Photoreaction time (h)	Substrate conversion (%)	Yields <sup>a</sup> of photoproducts
(I) In deaerated <sup>b</sup> methanol					
H	(1)	5.14	48	2.9	<i>c</i> <i>p</i> -Chlorotoluene (1) (1.0%), <i>p</i> -chlorobenzyl alcohol (5) (2.9%), methyl benzoate (7) (<1%), <i>p</i> -chlorobenzyl methyl ether (8) (37.0%), <i>p</i> -chlorobenzaldehyde (9) (1.7%), methyl <i>p</i> -chlorobenzoate (10) (6.7%), <i>p</i> -chlorophenylethyl alcohol (11) (15.5%), <i>p,p'</i> -dichlorobibenzyl (12) (3.1%)
Cl	(2)	5.62	48	89.0 <sup>d</sup>	
CN	(3)	5.74	48	<1	
CO <sub>2</sub> H	(4)	5.40	48	2.6	
OH	(5)	4.91	48	15.3 <sup>e</sup>	
(II) In water-acetonitrile <sup>f</sup> (1 : 1 v/v) mixture					
Cl	(2)	7.14	51	45.8	<i>p</i> -Chlorobenzyl alcohol (5) (58.6%), <i>p</i> -chlorobenzaldehyde (9) (33.0%), <i>p</i> -chlorobenzoic acid (14) (8.4%)

<sup>a</sup> Calculated from the amount of photoconverted starting material; the amount of undecomposed starting material present in a photolysate being used as an internal standard. <sup>b</sup> Nitrogen was flushed through the solvent for 2 h prior to irradiation. <sup>c</sup> No photoproduct observable on gas chromatograph. <sup>d</sup> 79.1% Photoconversion was observed when a methanol solution ( $5.65 \times 10^{-3}\text{M}$ ), aerated for 2 h, was used. <sup>e</sup> 8% Photoconversion was observed when a methanol solution ( $5.54 \times 10^{-3}\text{M}$ ), aerated for 2 h, was used. <sup>f</sup> Solvents were used without flushing with nitrogen or air prior to irradiation.

alcohol (11), and *p*-chlorobenzaldehyde dimethyl acetal (13). The methanolysis product, *i.e.* *p*-chlorobenzyl methyl ether (8), appeared again as the principal photoproduct (see Table 3). It is noteworthy that the quantum yields for the formation of the alcoholysis product during acetone-sensitized (300 nm) and non-sensitized (254 nm) irradiation of compound (2) in *t*-butyl alcohol are 0.26 and  $0.06 \pm 0.004$ , respectively.<sup>6</sup> Furthermore, during the acetone-sensitized photoreaction of *p*-chlorotoluene (1), in addition to toluene (reductively dechlorinated product), *p*-methoxytoluene (6) could be identified as the photoproduct. Finally, no *p*-chlorobenzyl alcohol (5) was formed, when *p*-chlorobenzyl chloride (2) ( $5.11 \times 10^{-3}\text{M}$ ) was irradiated in dry  $\text{CH}_3\text{CN}$  for 51 h.

We also studied the photoreactions of some halogenobenzaldehydes ( $5 \times 10^{-3}\text{M}$ ), namely *p*-chloro-, *m*-chloro-, and *m*-bromo-benzaldehyde, using deaerated methanol as solvent. Initially, the primary aim of the photochemical studies was to investigate the mode of formation of the acetal (13), which was identified amongst the photoproducts of (2) (see Table 3). U.v. spectra of these halogenobenzaldehydes in methanol are given in Table 4. It was noted that photolysis of each aldehyde gave rise to the corresponding acetal; this was the sole major photoproduct for the substrate. It is interesting to note that the photoreactivity of *m*-chlorobenzaldehyde in deaerated methanol to produce the acetal type compound was of the same order as that of the *para*-isomer (9). Photoreaction of *m*-bromobenzaldehyde [reaction (2)] however was *ca.* 93 times faster than that for *m*-chlorobenzaldehyde.



## Discussion

It is evident from Table 2 that *p*-chlorotoluene and its  $\alpha$ -substituted derivatives (containing CN, CO<sub>2</sub>H, and OH substituents) undergo no greater degradation than *p*-chlorobenzyl chloride (2) when subjected to direct photolysis in deaerated methanol and with radiation at 290–310 nm. Even the sub-

strate (2), which is photodegradable with relative ease under these conditions, fails to undergo reductive dechlorination of the benzene ring to give benzyl chloride (see Table 2). All these substrates, except compound (2), in the presence of acetone (0.553M) as sensitizer, however underwent reductive dechlorination to give photoproducts in 10–52% yield (based upon photodegraded material) (see Table 3). Table 3 clearly shows that the extent of replacement of *p*-chlorine substituent on  $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{X}$  by hydrogen depends upon the nature of the  $\alpha$ -substituent (X). The diminishing effect of X on the reductive dechlorination of these  $\alpha$ -substituted *p*-chlorotoluenes increases in the following order  $\text{H} < \text{CO}_2\text{H} < \text{OH} < \text{CN} \ll \text{Cl}$ . The failure of *p*-chlorobenzyl chloride (2) to give benzyl chloride is related to the fact that the C–Cl bond on the side-chain is more photolabile than that on the benzene ring.

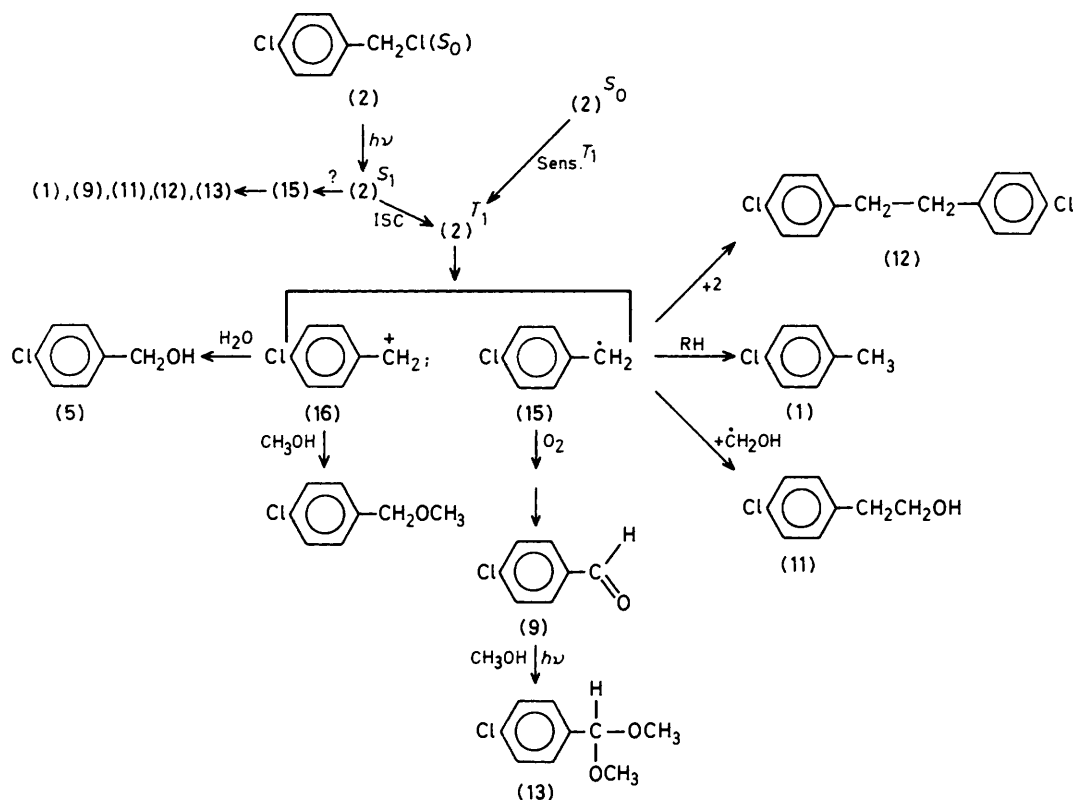
Reductive dechlorination of the substrates (1), (3), (4), and (5) *via* an acetone-sensitized photoreaction provides evidence that such a photochemical reaction may be an important route in the environment for the photodegradation of particular pollutants, which do not themselves absorb appreciably at wavelengths around 300 nm. It is noteworthy that acetone as well as acetaldehyde occurs in natural waters<sup>7</sup> and industrial waste waters.<sup>8</sup> Moreover, acetone is a well known triplet sensitizer<sup>9</sup> with  $E_T = 79\text{--}82 \text{ kcal/mol}$ <sup>10</sup> ( $E_T$  represents the energy of the first excited triplet state).

Although the photochemistry of benzyl halides has been the subject of extensive study,<sup>6,11–15</sup> the photochemical reactions of benzyl chloride have been the subject of conflicting reports. For example, Ivanov *et al.*<sup>12</sup> have stated that the photochemical solvolysis of halogenomethyl derivatives of aromatic compounds takes place *via* the formation of carbonium ion intermediates, generated from singlet excited state molecules. Later, Cristol and Greenwald<sup>13</sup> concluded that direct irradiation (at 254 nm) of benzyl chloride in hydroxylic solvents such as methanol, ethanol, propan-2-ol, acetic acid, or formic acid, gave products from benzyl radicals and chlorine atoms (which have been generated *via* the  $S_1$  state), while photosensitization with acetone or acetophenone leads to benzyl cations (which have been produced from the  $T_1$  state). Subsequently Cristol and Bindel<sup>6</sup> in a report on the photolysis of sub-

**Table 3.** Quantifying of the reductively dechlorinated <sup>a</sup> as well as other photoproducts formed during the photolysis of  $\alpha$ -substituted *p*-chloro-toluenes ( $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{X}$ ) in deaerated <sup>b</sup> methanol in the presence of 0.553M-acetone as sensitizer

X	Substrate	Concn. ( $10^{-3}\text{M}$ )	Irradiation time	% Disappearance	Yields <sup>c</sup> of photoproducts	
					Reductively dechlorinated <sup>d</sup>	Other <sup>e</sup>
H	(1)	5.14	9 h	54.5	51.8%	<i>p</i> -Methoxytoluene (6) (9.3%)
Cl	(2)	6.89	105 min	49.9	<i>f</i>	<i>p</i> -Chlorobenzyl alcohol (5) (4.1%), <i>p</i> -chlorobenzyl methyl ether (8) (40.2%), <i>p</i> -chlorobenzaldehyde (9) (1.1%), <i>p</i> -chlorophenylethyl alcohol (11) (2.8%), <i>p</i> -chlorobenzaldehyde dimethyl acetal (13) (5.5%)
CN	(3)	6.34	90 min	59.1	9.9%	1 Unidentified <sup>g</sup>
CO <sub>2</sub> H	(4)	5.04	4 h	47.7	40.2%	4 Unidentified <sup>g</sup>
OH	(5)	5.05	4 h	55.8	34.0%	Several unidentified <sup>g</sup>

<sup>a</sup> Reductive dechlorination takes place on the benzene nucleus. <sup>b</sup> Nitrogen was flushed through the solvent for 2 h prior to irradiation. <sup>c</sup> Calculated from the amount of photoconverted starting material. <sup>d</sup> The quantifications were conducted by utilizing standard solutions of the respective photoproducts. <sup>e</sup> For the quantifications, the amount of undecomposed starting material present in a photolysate was used as an internal standard. <sup>f</sup> The product, benzyl chloride, could not be observed. <sup>g</sup> Observable on gas chromatograph.

**Scheme**

stituted benzyl chlorides have stated that, in general, triplet states produced by (acetone) sensitization favour heterolysis, whereas the excited states produced as a result of direct light absorption disfavour heterolysis compared with homolysis. Appleton *et al.*<sup>14</sup> have reported that benzyl halides and benzyl acetates, give solvolysis products and products derived *via* non-ionic pathways on either direct (at 254 nm) or sensitized (at 300 nm) irradiation in alcoholic solvents. Similar conclusions were published by Appleton and his co-workers<sup>15</sup> in a recent article.

In our studies, the appearance of both radical-derived and cation-derived products during acetone-sensitized photoreaction of *p*-chlorobenzyl chloride (2) in deaerated methanol (see

Table 3) evidently shows that these photoproducts are generated *via* the excited triplet state of the substrate (2). The reason for such a conclusion is that, as mentioned above, acetone is a triplet sensitizer. The photochemical results for *p*-chlorobenzyl chloride (2) in different solvent systems may be explained in terms of the Scheme.

According to this reaction Scheme, on exposing ground-state molecules of *p*-chlorobenzyl chloride (2) to u.v. light, excited singlet ( $S_1$ ) molecules are produced. Subsequently, the molecules of the substrate (2) in the  $S_1$  state undergo an intersystem crossing (ISC) process to yield molecules in an excited triplet ( $T_1$ ) state. During triplet-sensitized photoreactions, the molecules of (2) in the  $T_1$  state can also be generated *via* energy

transfer from the sensitizer (Sens.) to the ground state singlet ( $S_0$ ) molecules of (2). These excited triplet species of compound (2) afford homolytic and heterolytic cleavage of the C-Cl bond on the side-chain of (2); thereby *p*-chlorobenzyl radicals (15) and *p*-chlorobenzyl carbonium ions (16) are created, respectively. The intermediate radicals (15) as well as the cations (16) are resonance stabilized. The radical species (15) abstract hydrogen atoms from solvents, *e.g.* methanol, to provide *p*-chlorotoluene (1). They also combine with hydroxymethyl radicals ( $\dot{C}H_2OH$ ), which may have been generated by hydrogen abstraction from the solvent by chlorine atoms and other intermediate free-radical species, to yield *p*-chlorophenethyl alcohol (11). *p,p'*-Dichlorobibenzyl (12) is formed *via* the dimerization of the intermediate radicals (15). Furthermore, the molecular oxygen present in the solvent systems reacts with *p*-chlorobenzyl radicals (15) and eventually *p*-chlorobenzaldehyde (9) is produced. The reaction of molecular oxygen with benzyl radicals is a well known process.<sup>16-20</sup> Approximate ceiling temperatures (the temperatures at which the ratio  $[C_6H_5CH_2\dot{O}_2]/[C_6H_5\dot{C}H_2] = 1$ ) for the gas-phase equilibrium [reaction (3)] at different partial



pressures of oxygen such as 1, 0.1, 0.01, and 0.001 atm are 160, 100, 60, and 25 °C, respectively.<sup>20</sup> The expected uncertainties in these ceiling temperatures are *ca.*  $\pm 50$  °C.<sup>20</sup> The significance of these ceiling temperatures is that for the given  $O_2$  pressure they tell us approximately the temperature at which the equilibrium concentration of  $C_6H_5CH_2\dot{O}_2$  and  $C_6H_5\dot{C}H_2$  would be expected to be equal. The acetal-type product (13) is, possibly, the photoproduct of the aldehyde (9). This view is confirmed by the observation that the acetal (13) appears as a main photoproduct of the independent photolysis of *p*-chlorobenzaldehyde (9). Furthermore, nucleophilic attacks by the solvents, *e.g.* methanol and water on the intermediate carbonium ions (16) take place; thus *p*-chlorobenzyl methyl ether (8) and *p*-chlorobenzyl alcohol (5), respectively are formed. Finally, the likelihood that the molecules of (2) in the excited triplet state are converted into radical pairs and ion pairs, *i.e.* [(15)  $\dot{C}l$ ] and [(16)  $Cl^-$ ], which may be responsible for the ultimate photoproducts, is not ruled out. Likewise, whether the  $S_1$  state of (2) also acts as a source of radical-derived products, such as compounds (1), (9), (11), (12), and (13) was not further investigated.

The appearance of methyl *p*-chlorobenzoate (10) amongst the photoproducts of the substrate (2) in deaerated methanol (see Table 2) may be attributed to the possibility that *p*-chlorobenzoic acid (14), another secondary photoproduct, is esterified *via* thermal reaction and/or photochemical reaction with methanol. Alternatively, it is likely that the benzylic hydrogen atom of the ether (8) is abstracted by the free radicals present in the reaction mixture. The benzylic radicals  $p-Cl-C_6H_4\dot{C}HOCH_3$ , formed in this manner, react with oxygen to give, finally, the ester (10). Similarly, the minor product, methyl benzoate (7) (see Table 2), is probably the reductively dechlorinated photoproduct of compound (10). Alternatively, the *p*-chlorine substituent on the photoproduct (8) is reduced to benzyl methyl ether, the methylene group of which is oxidized following the sequence of reactions discussed above to give a carbonyl group on the substrate. The appearance of (7) can also be related to the process of esterification of benzoic acid (a presumed product) with methanol.

It is remarkable that the acetal (13), the photoproduct of the substrate (2), is only produced by sensitized photolysis (Table 3), although the intermediate photoproduct, *p*-chlorobenzaldehyde (9) is formed in both direct and sensitized photo-reactions. However it is notable that halogenobenzaldehyde

**Table 4.** Ultraviolet spectra of halogenobenzaldehydes in methanol

Compound	$\lambda_{max}$ , nm (log $\epsilon_{max}$ )	$\epsilon_{300}$
<i>p</i> -Chlorobenzaldehyde <sup>a</sup>	254 (4.16), 210 (4.18), 206 (4.20)	$8.10 \times 10^4$
<i>m</i> -Chlorobenzaldehyde	288 (2.90), 243 (3.83), 206 (4.34)	$6.58 \times 10^2$
<i>m</i> -Bromobenzaldehyde	291 (2.88), 244 (3.80), 211 (4.30)	$6.83 \times 10^2$

<sup>a</sup> The expected maximum due to  $n \rightarrow \pi^*$  transitions at *ca.* 270–290 nm is overlapped by a maximum arising through  $\pi \rightarrow \pi^*$  transitions at 254 nm.

acetals are rather unstable. For instance, rate constants for the decomposition of *p*- and *m*-chlorobenzaldehyde diethyl acetals in water at 30 °C are 72.3 and 17.5 l mol<sup>-1</sup> s<sup>-1</sup>, respectively.<sup>21</sup>

The observation that *p*-chlorobenzyl alcohol (5), a photoproduct, does not appear on photolysing *p*-chlorobenzyl chloride (2) in dry acetonitrile, reflects that in the photolysis of (2) in aqueous acetonitrile (Table 2), the photoproduct (5) is not produced *via* the disproportionation of *p*-chlorobenzyl-oxy radicals but, instead, is mainly formed by nucleophilic attack of water on the carbonium ions (16) (see Scheme).

**Conclusions.**—Direct 48-h photolyses at wavelengths in the range 280–320 nm (mainly 300 nm) of deaerated methanolic solutions of *p*-chlorotoluene (1) and its derivatives bearing  $\alpha$ -substituents [*e.g.* CN (3) and CO<sub>2</sub>H (4)] do not result in their degradation. Thus, photoreaction of *p*-chlorobenzyl chloride (2) proceeds with 89% disappearance of the starting material, whilst for *p*-chlorobenzyl alcohol (5), 15% disappearance is observed. Acetone-sensitized irradiation of the substrates (1)–(5), with the exception of (2), provides corresponding reductively dechlorinated products namely toluene (52%), phenylacetonitrile (10%), phenylacetic acid (40%), and benzyl alcohol (34%); the % given represents that percentage of the 'disappeared' substrate which is converted into the corresponding product. *p*-Chlorobenzyl chloride (2) fails to supply such a photoproduct (*e.g.* benzyl chloride), the C-Cl bond being responsible for its photodegradation. *p*-Chlorobenzyl methyl ether (major), *p*-chlorobenzaldehyde, *p*-chlorobenzyl alcohol, and *p*-chlorophenethyl alcohol appear as photoproducts of the substrate (2) in deaerated MeOH both in the absence and the presence of acetone (0.553M). In addition, *p*-chlorotoluene, methyl benzoate, methyl *p*-chlorobenzoate, and *p,p'*-dichlorobibenzyl in the case of the former reaction and *p*-chlorobenzaldehyde dimethyl acetate during the latter reaction are identified amongst the photoproducts of (2). It is likely that both radical-derived and cation-derived products of (2) are formed *via* the triplet excited state. Furthermore, although the photoreactivity of *p*-chlorobenzaldehyde is of the same order as that of *m*-chlorobenzaldehyde to form acetal-type compounds exclusively, *m*-bromobenzaldehyde possesses 93 times the reactivity of *m*- and *p*-chlorobenzaldehydes.

The photosensitized replacement of the *p*-Cl substituent by hydrogen from  $\alpha$ -substituted *p*-chlorotoluenes is new.

**Environmental Significance.**—Acetone-sensitized photo-reactions of  $\alpha$ -substituted *p*-chlorotoluenes may play an important role in the photodegradation (especially for the reductive dechlorination) of pollutants of such types. The product *p*-chlorobenzyl alcohol, obtained from *p*-chlorobenzyl chloride, may persist in the environment as a result of its low photoreactivity. On the other hand, *p*-chlorobenzaldehyde (another significant photoproduct) is a very good

triplet sensitizer possessing an  $E_T$  value of 70.8 kcal/mol<sup>22</sup> and may accelerate the photodegradation of pollutants, e.g. chlorinated cyclodiene insecticides, polychlorinated biphenyls (PCBs) etc. It should be noted that cyclodienes, for instance heptachlor<sup>23</sup> and aldrin<sup>24</sup> and PCBs<sup>25,26</sup> with chlorine atoms  $\leq 4$  are less susceptible to degradation via direct photolysis.

## Experimental

**Substrates.**—Compounds (1)–(5) (Table 1) were obtained through the courtesy of Koninklijke/Shell-Laboratorium, Amsterdam.

**Solvents.**—Methanol was provided by J. T. Baker Chemical Co. Spectrograde acetone and acetonitrile were supplied by E. Merck. Demineralized tap-water from our laboratory was used.

**Standards.**—*p*-Chlorobenzaldehyde (9), *p*-chlorobenzoic acid, toluene, benzyl chloride, phenylacetonitrile, phenylacetic acid, *p*-cresol, and benzyl alcohol were available from the kit of standards supplied by Chem. Service, Inc., West Chester. *p*-Chlorophenylethyl alcohol (11) was provided by Aldrich-Europe (Beerse Belgium). The procedure of Rutherford *et al.*<sup>27</sup> was followed for the synthesis of *p*-chlorobenzyl methyl ether (8) from *p*-chlorobenzyl alcohol (5), compound (5) being refluxed for 2 h in a mixture of methanol and acetone in the presence of  $I_2$  (catalyst). *p,p'*-Dichlorobibenzyl (12) was synthesized by the reaction of *p*-chlorotoluene (1) with *t*-butyl peroxide according to the method described by Johnston and William.<sup>28</sup> *p*-Chloro-, *m*-chloro-, and *m*-bromobenzaldehyde dimethyl acetals were synthesized by refluxing the corresponding halogenobenzaldehydes in methanol for 5 h in the presence of a few drops of hydrochloric acid.

**Ultraviolet Spectra.**—These were recorded on a Cary-14 double beam spectrometer.

**Irradiations.**—The solution-phase photolyses were conducted in a Rayonet Photochemical Reactor (The Southern New England Ultra Violet Company) equipped with 16 RPR-3 000 Å lamps having an energy output of 90% between 290 and 310 nm. Photoreactions were performed in Pyrex tubes (containing 2 ml sample solution each) which transmit less than 1% of radiation below 280 nm. A merry-go-round apparatus was used for simultaneous photoreactions.

**Qualitative and Quantitative Analyses.**—These were carried out on a Hewlett-Packard 5830A instrument with a flame ionization detector and equipped with a 18850 GC terminal. Glass columns (2.5 m  $\times$  0.2 cm) containing 3% Carbowax 20 M on 100–120 Mesh Chromosorb W were used. A photoproduct formed through the reductive dechlorination on the benzene ring was quantified on this gas chromatograph (g.c.) by comparing its peak area with that of an authentic standard of known appropriate concentration, whilst for the quantifications of other products, undecomposed starting material of a photolysate was used as an internal standard. A similar procedure was followed for quantifying undecomposed starting material present in a photolysate.

**Combined Gas Chromatography–Mass Spectrometry.**—This was performed on a Hewlett-Packard 5984A system operating in the electron-impact mode at 70 eV. The glass column in this system was packed with 0.2% Carbowax 20 M on 100–120 mesh Chromosorb W. The g.c. conditions for analyses of irradiated samples on the g.c.–m.s. unit were as follows:

temperature 1 ( $T_1$ ) = 70 °C, time 1 ( $t_1$ ) = 2 min; rate = 8 °C/min;  $T_2$  = 240 °C; and  $t_2$  = 30 min.

**Identification of Photoproducts.**—The photoproducts were identified by comparison of their retention time and mass spectrum with those of standard compounds using g.c.–m.s. The acidic compounds and phenols were methylated by diazomethane prior to injection on g.c. and g.c.–m.s.

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