

Photochemical Reactions of Benzaldehyde and Chloro-substituted Benzaldehydes with 3-Chloro-2-methyl-1-propene

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The structure of the main oxetane products in the photolyses of benzaldehyde and mono-chloro-substituted benzaldehydes with 3-chloro-2-methyl-1-propene was established by ^1H and ^{13}C nuclear magnetic resonance, infrared, and mass spectrometry. The main oxetane products were in all cases 2-aryl-*cis*-3-chloro-methyl-3-methyloxetane and 2-aryl-*trans*-3-chloromethyl-3-methyloxetane in a ratio of 1:1.1.

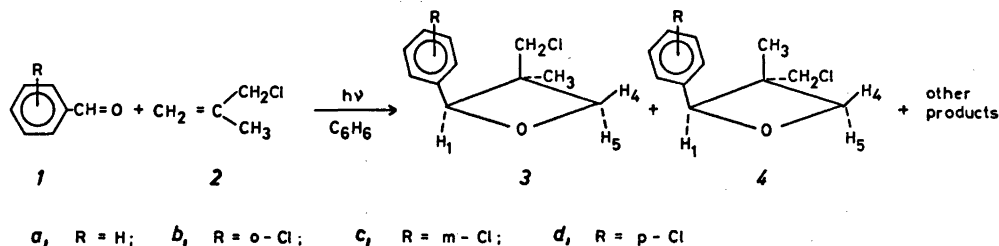
Aromatic aldehydes have been found to react photochemically with olefins to give oxetanes and alcohols.¹⁻⁵ The formation of the major products, oxetanes, is in general non-stereospecific and non-regiospecific. For example, the reaction of benzaldehyde with ethyl vinyl ether produces 4- and 3-ethoxy-substituted 2-phenyloxetanes in a ratio of 30:70,³ and in the reaction of benzaldehyde with 2-methyl-2-butene the ratio between the isomeric oxetanes 2-phenyl-3,4,4-trimethyloxetane to 2-phenyl-3,3,4-trimethyloxetane is 39:61.¹

In the study of side-chain reactions of 2-aryloxetanes we have been interested in preparing 2-aryloxetanes with suitable 3-substituents in the oxetane ring. For nucleo-

philic side-chain reactions of oxetanes the chloromethyl group is a proper substituent. Photochemical cycloaddition of aromatic aldehydes and substituted alkenes provides a facile synthetic route for preparing 3-substituted 2-aryloxetanes. In this work the photochemical preparation of 2-aryl-3-chloromethyl-3-methyloxetanes as starting materials of side-chain reactions has been investigated. The structure of these oxetanes is confirmed with the help of NMR, IR and mass spectrometry.

RESULTS

Irradiation of the benzene solution of aromatic aldehyde (1) and 3-chloro-2-methyl-1-propene (2) with a 700 W high-pressure mercury lamp used through a Pyrex filter produced 3,3-disubstituted 2-aryloxetanes 3 and 4 in moderate yields (Scheme 1). The overall yields and the isomer distributions are presented in Table 1. The yields and isomer ratios were measured by gas chromatography and ^1H NMR spectrometry, using integration over the signals of methyl groups or methine protons H-1 of



Scheme 1.

Table 1. The oxetane yields and isomer ratios from the photochemical cycloaddition of aromatic aldehydes (1) to 3-chloro-2-methyl-1-propene (2) in benzene.

Products	Yield of oxetane / %	Isomer ratio ^a 3:4
3a, 4a	18	1:1.1
3b, 4b	39	1:1.1
3c, 4c	30	1:1.1
3d, 4d	18	1:1.1

^a The average of NMR and GLC measurements.

diastereomers 3 and 4. Toluene was used as an internal standard in the NMR measurements and biphenyl in the gas chromatographic analyses.

The main oxetane products were isolated by preparative gas chromatography and the structures were established by ¹H and ¹³C NMR, IR

and mass spectrometry. The NMR data of the diastereomers 3 and 4 are summarized in Tables 2 and 3, and the IR and mass spectral data are presented in the experimental part. The by-products were separated by gas chromatography and identified by spectroscopy.

DISCUSSION

The major products in the photolyses of aromatic aldehydes (1) and 3-chloro-2-methyl-1-propene (2) were the diastereomers 2-aryl-*cis*-3-chloromethyl-3-methyloxetane (3) and 2-aryl-*trans*-3-chloromethyl-3-methyloxetane (4). The product ratio varied only slightly being of the order of 1:1.1 in all cases. The practical reaction time in a Pyrex reactor (see experimental) was 24–30 h in all cases. By that time the reaction was 80–90 % complete. If the reaction time was 40–50 h or if a quartz reactor was used, the overall oxetane yields were reduced because of polymerization and other

Table 2. The ¹H NMR chemical shifts of diastereomeric oxetanes 3 and 4 in CCl₄ and C₆D₆.

Proton	Solvent	Chemical shift (δ) ^a							
		3a	3b	3c	3d	4a	4b	4c	4d
CH ₃	CCl ₄	1.54 s	1.68 s	1.56 s	1.55 s	0.87 s	0.95 s	0.91 s	0.88 s
	C ₆ D ₆	1.18 s	1.43 s	1.10 s	1.11 s	0.67 s	0.75 s	0.56 s	0.55 s
CH ₂ Cl	CCl ₄	2.95 d	3.17 d	3.02 d	2.97 d	3.77 d	3.82 dd	3.74 d	3.74 d
		3.52 d	3.45 d	3.49 d	3.46 d	3.91 d	4.16 d	3.91 d	3.93 d
	C ₆ D ₆	2.75 dd	3.04 dd	2.68 d	2.66 d	3.20 d	3.47 dd	3.10 d	3.10 d
H ₄	CCl ₄	3.36 d	3.33 d	3.19 d	3.19 d	3.36 d	3.74 d	3.26 d	3.27 d
	C ₆ D ₆	4.41 s	4.45 s	4.41 s	4.40 s	4.26 d	4.19 dd	4.26 d	4.25 d
H ₅	CCl ₄	4.21 dd	4.24 dd	4.12 s	4.14 s	3.96 d	3.97 dd	3.82 d	3.84 d
	C ₆ D ₆	4.41 s	4.45 s	4.41 s	4.40 s	4.50 d	4.73 d	4.50 d	4.51 d
H ₁	CCl ₄	4.25 d	4.29 d	4.12 s	4.14 s	4.20 d	4.61 d	4.10 d	4.10 d
	C ₆ D ₆	5.55 s	5.80 s	5.52 s	5.50 s	5.54 s	5.57 s	5.53 s	5.53 s
H ₁	CCl ₄	5.37 s	5.77 s	5.18 s	5.17 s	5.48 s	5.75 s	5.31 s	5.33 s
	C ₆ D ₆								

^a s=singlet, d=doublet, dd=doublet of doublets.

Table 3. The ¹³C NMR chemical shifts of diastomeric oxetanes 3 and 4 in CDCl₃.

Carbon ^a	Chemical shift (δ)							
	3a	3b	3c	3d	4a	4b	4c	4d
CH ₃ q	22.1	22.3	22.0	22.1	18.2	18.1	18.2	18.2
CH ₂ Cl t	50.0	49.7	49.7	49.8	52.2	51.8	52.0	52.1
C-2 d	89.5	87.0	88.4	88.7	88.2	85.0	87.2	87.4
C-3 s	44.5	44.7	44.5	44.5	44.6	45.0	44.6	44.6
C-4 t	77.4	77.7	77.3	77.3	77.5	77.3	77.3	77.3

^a In off-resonance spectra: q=quartet, t=triplet, d=doublet, s=singlet.

side-reactions. Regioselectivity is very high in the oxetane formation and 3,3-disubstituted oxetanes are the major products (over 90%). Stereoselectivity is very low in the formation of the diastereomeric oxetanes 3 and 4.

The structures of the diastomers 3 and 4 were established mainly by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectra the signal of the methyl group in compounds 4a, 4b, 4c, and 4d, compared with the signal of the methyl group of compounds 3, is shifted to higher field by 0.67, 0.73, 0.65, and 0.67 ppm in CCl_4 and by 0.51, 0.68, 0.54, and 0.56 ppm in C_6D_6 . These shifts are due to the long-range shielding of the aromatic ring in position 2. The shift of the 3-methyl signal in the oxetanes 3 and 4 is similar to that of 3-methyl-2-phenyl-oxetane diastereomers (0.56 ppm),⁶ 2-methyl-3-phenyloxetane (0.52 ppm)⁷ and 3,3-dimethyl-2-phenyloxetane (0.6 ppm).⁸ The ^1H signals of chloromethyl groups appear at higher fields in isomers 3 than in isomers 4, which is also due to the long-range shielding by the *cis*-aryl group. The methylene protons at the oxetane ring position 4 (H_4 and H_5) resonate at 4.2–4.7 ppm. The identification of these protons was established by using an $\text{Eu}(\text{fod})_3$ shift reagent. The protons nearby the oxygen atom of the oxetane ring (H_1 , H_2 , and H_3) are shifted more than the other protons.

The geminal coupling constants between the protons of the chloromethyl group are 10.8–11.0 Hz. The coupling between the oxetane ring protons H_4 and H_5 is 6.6–6.0 Hz, which is an increase relative to that of 3,3-dimethyl-2-phenyloxetane (5 Hz).⁸ The larger coupling constants may be due to the different oxetane ring conformation.

The ^1H NMR spectra were measured in CCl_4 and C_6D_6 solutions. The chemical shifts of the methyl and chloromethyl groups induced by the C_6D_6 are largest when these groups are in the *trans*-position relative to the aryl group of the oxetane ring.

In the ^{13}C NMR spectra the carbon atoms of the methyl group of 4a, 4b, 4c, and 4d show signals at 3.9, 4.2, 3.8, and 3.9 ppm respectively, at higher fields than the corresponding methyl carbon atoms of compounds 3. Similarly, the signals of the carbon atoms of the chloromethyl groups of 3a, 3b, 3c, and 3d are shifted to higher fields by 2.2, 2.1, 2.3, and 2.3 ppm, respectively,

compared with the absorptions of the carbons of the chloromethyl groups of the isomers 4. These shifts are due to the ring current effect of the aromatic substituent.⁹

In compounds 4 the chemical shifts of the C-2 are shifted upfield by 1.3, 2.0, 1.2, and 1.3 ppm (a, b, c, and d, respectively) compared with compounds 3. These shifts may be derived from the difference of the *γ-gauche* effects of the isomers 3 and 4.^{9,10} This effect is greater in isomers 4, because the chloromethyl group has free rotation. In isomers 3 this rotation is somewhat hindered and in 3b the hindrance is greatest and the difference in chemical shifts of C-2 of the isomers 3b and 4b is thus greatest.

The mass spectra of isomers 3 and 4 are very similar and cannot be used for differential analysis. The molecular ion peak is very small (about 1%) in all cases. The characteristic oxetane ring fragments consist of an ion at *m/e* value $\text{M}^+ - 30$ (the loss of formaldehyde) and an acylium ion $\text{Ar}-\text{C}\equiv\text{O}^+$. The base peak in each case corresponds to the ion $\text{Ar}-\text{CH}=\text{OH}^+$, which is generated by the hydrogen rearrangement from the 3-methyl or 3-chloromethyl group to the oxygen atom of the oxetane ring.¹¹

The IR of 3 and 4 are also very similar. Only in the "fingerprint" regions is the shape of the spectra slightly different. In the characteristic absorption region of the oxetane ring (approx. $10\ \mu$)^{3,6,12} the isomers 3 absorb at slightly higher wavelength than the corresponding isomers 4. The difference is about $10\ \text{cm}^{-1}$.

The photolysis also produced about 5% 2-aryl-4-chloromethyl-4-methyloxetanes, which were separated by gas chromatography and whose structure was confirmed by mass spectrometry. The base peak was the same ion $\text{Ar}-\text{CH}=\text{OH}^+$ formed by hydrogen rearrangement as in the case of isomers 3 and 4. The ion which separates these 2,4,4-trisubstituted oxetanes from the diastereomers 3 and 4 is the characteristic $\text{Ar}-\text{CH}-\text{CH}_2^+$ (*m/e* 104, if $\text{Ar}=\text{phenyl}$, and 138/140, when $\text{Ar}=\text{chlorophenyl}$). No attempts were made to separate or identify the diastereomers of 2-aryl-4-chloromethyl-4-methyloxetanes.

Furthermore, the following products were found after irradiation of a mixture of benzaldehyde and 3-chloro-2-methyl-1-propene: acetophenone, benzylalcohol, 3-methyl-1-

phenyl-3-buten-1-one, 3-chloromethyl-1-phenyl-3-buten-1-ol and its dehydration product 2-chloromethyl-4-phenyl-1,3-butadiene. The other photolyses produced corresponding side-products. The by-products were identified by mass, NMR, and IR spectroscopy. These by-products are formed during the photolysis by radical reactions between the starting materials and/or products.

EXPERIMENTAL

Apparatus and methods. The ^1H NMR spectra were determined on 10 % solutions of CCl_4 and C_6D_6 with a Varian Model T-60 spectrometer, using TMS as an internal standard. The ^{13}C NMR spectra were run on CDCl_3 solutions with TMS as an internal standard, using a Jeol JNM-FX100 FT-spectrometer operating at 25.06 MHz. The ^{13}C NMR spectra were recorded with proton noise-decoupling to assess chemical shifts, and with coherent proton decoupling off-resonance to identify the carbon atoms of the oxetane ring. The IR spectra were recorded with a Perkin-Elmer IR Spectrophotometer Model 457 in CCl_4 solutions. Mass spectra were determined at 70 eV on the Hitachi Perkin-Elmer RMU 6E mass spectrometer. In the direct inlet the probe temperature was 40 °C and the chamber temperature 80 °C, while in the indirect inlet the temperatures were 120 and 100 °C, respectively. The qualitative gas chromatographic analyses were performed on a Perkin-Elmer F30 gas chromatograph with a flame ionization detector, using steel columns packed with 10 % Carbowax 20 M on 80–100 mesh Chromosorb W (3.2 mm o.d. \times 1 m) or with 20 % Silicone Gum Rubber SE-30 on Chromosorb W (3.2 o.d. \times 2 m) and nitrogen as a carrier gas (15 ml/min). Preparative GLC analyses were performed on a Varian Aerograph Model 700 with a hot wire detector, using helium as a carrier gas. The column temperatures varied between 170 and 200 °C. The photolyses were performed in a 1 l forced circulation reactor (produced by Otto Fritz GmbH, Germany) equipped with a high-pressure Hanau 700-W mercury lamp (TQ 718).

Starting materials. Benzaldehyde, *o*-, *m*-, and *p*-chlorobenzaldehyde (Fluka AG, purum) were distilled before use. 3-Chloro-2-methyl-1-propene (Fluka AG) was dried with calcium chloride and fractionally distilled. Benzene (E. Merck AG, "reinst") was distilled before use.

Photolyses. An example of the photolyses is presented below. 2-Chlorobenzaldehyde, 22 g (0.16 mol), and 32 g (0.35 mol) of 3-chloro-2-methyl-1-propene is dissolved in 450 ml benzene and the solution is irradiated through a Pyrex filter for 30 h at ambient temperature. After evaporation of the solvent, the residue

weighed 35 g. The distillation (b.p. 120–150 °C/7 Pa) gave 24 g of product mixture, which was separated by preparative gas chromatography.

The mass and IR spectral data of compound 3a is presented in the following list. The mass and IR spectra of other oxetanes are analogous to the discussed case.

cis-3-Chloromethyl-3-methyl-2-phenyloxetane (3a). Mass spectrum: m/e 196 (1 %, M), 166 (1.8, [M-HCHO]), 161 (0.7, [M-Cl]), 131 (10, [M-HCHO-Cl]), 116 (2), 115 (5), 107 (100, Ph-CH=OH⁺), 106 (10, Ph-CH=O⁺), 105 (58, Ph-C≡O⁺), 91 (8, C₆H₇⁺), 90 (9, [M-PhCHO]), 79 (20, [107-CO]), 77 (19, [105-CO]), 55 (18, C₆H₇⁺), 51 (10, C₆H₅⁺); m^* 131→91, obs. 63.2, calc. 63.2; 107→79, obs. 58.4, calc. 58.3; 105→77, obs. 56.5, calc. 56.6; 77→51, obs. 33.8 calc. 33.8.

IR (CCl_4): 1496 (m), 1456 (s), 1440 (m), 1384 (s), 1355 (m), 1292 (s), 1272 (m), 1253 (m), 1215 (w), 1178 (w), 1112 (m), 1079 (w), 1032 (m), 1002 (s), 986 (s), 960 (s), 915 (m), 860 (w), 728 (m), 702 (s), 677 (m), and 626 (w) cm^{-1} .

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