

## Short Communications

## Preparation of 2-Aryl-3-oxetanols

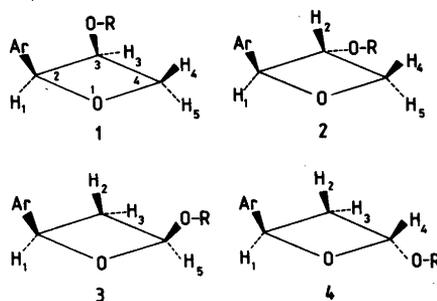
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The literature reports describe only a few reactions in which formation of 3-oxetanols is observed. These compounds are formed in the Norrish type II photoreactions of ketones,<sup>1-11</sup> in the reduction of oxetanones<sup>12</sup> or oxetanyl acetates,<sup>13</sup> in the cleavage of ether linkage of some substituted oxetanes,<sup>14,15</sup> in the photoaddition of acetone to its enol at low temperature,<sup>16</sup> in the chlorination of some  $\beta,\gamma$ -unsaturated  $\alpha$ -hydroxy ketones<sup>17</sup> and in the ring closure of derivatives of substituted 1,2,3-triols.<sup>18</sup>

In this work we have synthesized 3-acetoxy-2-aryloxetanes and 2-acetoxy-4-aryloxetanes from vinyl acetate and aromatic aldehydes through a photochemical reaction. The basic hydrolysis of the oxetanyl acetate mixture gave a mixture of *cis*- and *trans*-2-aryl-3-oxetanols. The major product in each case was *cis*-2-aryl-3-oxetanol, which was purified by crystallization and identified by spectroscopic methods.

The photolyses of benzaldehyde or *o*-chlorobenzaldehyde with vinyl acetate were carried out in benzene solution in a photochemical reactor equipped with a high pressure mercury lamp. In both of the reactions a mixture of four oxetanyl acetates 1-4 (R=COCH<sub>3</sub>, Scheme 1) was formed. The mixtures were analyzed by gas chromatography and <sup>1</sup>H NMR spectrometry. The product ratio was 61:16:5:18 for 1*a*, 2*a*, 3*a* and 4*a* and 60:18:5:17 for 1*b*, 2*b*, 3*b* and 4*b*. The overall oxetanyl acetate yields were 23 % for the compounds *a* and 37 % for the compounds *b*. The isomers 1, 2, 3 and 4 were isolated by preparative gas chromatography. The structures of the isolated compounds were established by means of <sup>1</sup>H and <sup>13</sup>C NMR, infrared and mass spectra. The NMR data of oxetanes are presented in the Tables 1-3.



Scheme 1. *a*, Ar=phenyl, R=COCH<sub>3</sub>; *b*, Ar=*o*-chlorophenyl, R=COCH<sub>3</sub>; *c*, Ar=phenyl, R=H; *d*, Ar=*o*-chlorophenyl, R=H.

The NMR signal of the methyl protons of the acetyl group was diagnostic in the identification of the pairs of *cis*- and *trans*-3-acetoxy-2-aryloxetanes (compounds 1*a*, 2*a* and 1*b*, 2*b*). The signal of the methyl protons is at a higher field by 0.44 ppm in compound 1*a* than in compound 2*a* and at a higher field by 0.35 ppm in 1*b* than in 2*b* in CDCl<sub>3</sub> solution. The chemical shifts of the protons of the carbon atom three of the oxetane ring are characteristic for the 2-acetoxy-4-aryloxetanes (compounds 3*a*, 3*b*, 4*a* and 4*b*), because these signals are at high field compared with the other possible methylene protons (chemical shifts about 3 ppm).

Hydrolysis of the mixture of oxetanyl acetates in aqueous sodium hydroxide solution gave a mixture of *cis*- and *trans*-2-aryl-3-oxetanols. Only the major product, *cis*-2-aryl-3-oxetanol (1*c* and 1*d*), was separated in a pure form from the mixture. The acetates prepared from the purified oxetanols 1*c* and 1*d* were identical with the compounds 1*a* and 1*b*, respectively.

**Experimental.** The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> solutions at 100 MHz and 25.06 MHz, respectively, on a Jeol JNM-FX100 instrument. The IR spectra were recorded on a Perkin-Elmer 457 spectrometer and the mass spectra on a Hitachi Perkin-Elmer RMU 6E mass spectrometer. The photolyses were performed in a one-litre photoreactor (manufac-

Table 1. The  $^1\text{H}$  NMR chemical shifts ( $\delta$ , ppm)<sup>a</sup> and coupling constants ( $J_{\text{HH}}$ , Hz) of oxetanes 1–4 in  $\text{CDCl}_3$ .

Compound	H-1	H-2	H-3	H-4	H-5	$\text{CH}_3$
1a	5.96 d $J_{1,3}=6.5$	–	5.74 m	4.71 dd $J_{4,5}=7.4$ $J_{3,4}=5.1$	5.01 dd $J_{4,5}=7.4$ $J_{3,5}=6.1$	1.69 s
2a	5.65 d $J_{1,2}=5.1$	5.23 m	–	4.88 dd $J_{4,5}=7.3$ $J_{2,4}=6.6$	4.62 dd $J_{4,5}=7.3$ $J_{2,5}=5.7$	2.13 s
1b	6.22 d $J_{1,3}=6.3$	–	5.88 m	4.56 dd $J_{4,5}=7.7$ $J_{3,4}=4.6$	5.07 dd $J_{4,5}=7.7$ $J_{3,5}=6.0$	1.80 s
2b	6.02 d $J_{1,2}=5.1$	5.30 m	–	4.87 dd $J_{4,5}=7.4$ $J_{2,4}=6.5$	4.61 dd $J_{4,5}=7.4$ $J_{2,5}=5.6$	2.15 s
3a	5.50 t	2.72 m	3.33 m	–	6.57 dd	2.16 s
4a	5.88 t $J_{1,2}=7.3$ $J_{1,3}=7.3$	2.92 m	3.00 m	6.57 dd $J_{2,4}=5.3$ $J_{3,4}=3.8$	–	2.17 s
3b	5.79 t $J_{1,2}=6.8$ $J_{1,3}=6.8$	2.43 m	3.49 m	–	6.56 dd $J_{2,5}=4.3$ $J_{3,5}=5.6$	2.12 s
4b	6.07 t $J_{1,2}=7.2$ $J_{1,3}=7.2$	2.79 m	3.15 m	6.51 dd $J_{2,4}=3.4$ $J_{3,4}=5.7$	–	2.19 s
1c	5.77 d $J_{1,3}=5.6$	–	4.8 m	4.40 m	4.8 m	–
1d	5.96 d $J_{1,3}=5.6$	–	4.8 m	4.35 m	4.8 m	–

<sup>a</sup>s=singlet, d=doublet, dd=doublet of doublets, m=multiplet, t=triplet.

Table 2. The  $^{13}\text{C}$  NMR chemical shifts (ppm) of some oxetanes in  $\text{CDCl}_3$ .

Compound	C-2	C-3	C-4	$\text{CH}_3$
1a	87.0	69.5	74.5	20.2
1b	83.7	68.8	75.7	20.4
1c	88.6	67.5	79.3	–
1d	86.6	67.5	78.5	–

Table 3.  $^1J_{\text{C-H}}$  coupling constants (Hz) of oxetanols in  $\text{CDCl}_3$ .

Compound	$J_{\text{H}_1\text{C}_2}$	$J_{\text{H}_3\text{C}_3}$	$J_{\text{H}_4\text{C}_4}$	$J_{\text{H}_5\text{C}_4}$
1c	152.7	156.3	150.4	150.4
1d	153.8	156.9	150.7	150.7

tured by Otto Fritz GmbH, Germany) equipped with a high-pressure Hanau 700-W mercury lamp (TQ 718).

**Photolysis of *o*-chlorobenzaldehyde and vinyl acetate.** 57.4 g (0.41 mol) of *o*-chlorobenzaldehyde and 54.0 g (0.63 mol) of vinyl acetate in 700 cm<sup>3</sup> of benzene were irradiated through a pyrex filter at ambient temperature in a photoreactor for 24 h. After evaporation of the solvent, the residue was distilled in vacuum (b.p. about 170 °C/10Pa). The yield of the mixture of oxetanes *1b*, *2b*, *3b* and *4b* was 34 g (37 % based on *o*-chlorobenzaldehyde). The compounds of the mixture were separated by preparative gas chromatography (1.2 m long glass column Silicone Gum Rubber SE-30 as a stationary phase, temperature programme from 120 to 140 °C) for structural elucidation.

The <sup>1</sup>H NMR spectra of the isomeric oxetanes are presented in Table 1. The mass and IR spectral data of the compounds *1b* and *4b* are presented in the following list. The mass and IR spectra of the compounds *2b* and *3b* are highly similar to the spectra of the compounds *1b* and *4b*, respectively.

**cis-3-Acetoxy-2-(2-chlorophenyl)oxetane (1b).** Mass spectrum: *m/z* 228 (0.1 %, M), 226 (0.3, M), 185 (3), 183 (9), 156 (1), 154 (4), 143 (4), 141 (12), 139 (2), 131 (1), 127 (3), 125 (9), 91 (1), 89 (4), 86 (15), 77 (4), 75 (3), 73 (2), 44 (4), 43 (100); *m\** 183 → 141, obs 108.5, calc. 108.6.

IR spectrum (cm<sup>-1</sup> in CCl<sub>4</sub>): 3060 (w), 2950 (m), 2880 (m), 1745 (s), 1470 (m), 1440 (s), 1370 (s), 1360 (m), 1230 (s), 1145 (m), 1105 (s), 1055 (s), 1035 (m), 980 (s), 940 (m), 915 (s), 690 (m), 630 (w).

**trans-2-Acetoxy-4-(2-chlorophenyl)oxetane (4b).** Mass spectrum: *m/z* 228 (0.1 %, M), 226 (0.3, M), 185 (2), 183 (5), 169 (1), 168 (6), 167 (4), 166 (18), 143 (8), 142 (2), 141 (28), 140 (6), 139 (18), 138 (14), 137 (2), 131 (20), 127 (1), 125 (3), 113 (3), 111 (3), 104 (2), 103 (22), 102 (4), 91 (3), 89 (3), 86 (3), 77 (16), 76 (3), 75 (6), 74 (2), 63 (2), 51 (8), 50 (4), 44 (6), 43 (100).

IR spectrum (cm<sup>-1</sup> in CCl<sub>4</sub>): 3050 (w), 3010 (w), 2960 (w), 2910 (w), 1755 (s), 1470 (m), 1435 (m), 1375 (m), 1360 (m), 1340 (w), 1220 (s), 1145 (m), 1120 (m), 1070 (m), 1055 (m), 1030 (m), 995 (s), 960 (s), 680 (w).

**Photolysis of benzaldehyde and vinyl acetate.** Photolysis was performed as described above in the case of *o*-chlorobenzaldehyde. The time of irradiation was 48 h and the yield of isomeric oxetanes was 23 % of the theory. The <sup>1</sup>H NMR data of the separated oxetanes are presented in Table 1. The IR and mass spectral data of the isomeric oxetanes *1a*, *2a*, *3a* and *4a* are similar to

the data of the compounds *1b*, *2b*, *3b* and *4b*, respectively.

**cis-2-(2-Chlorophenyl)-3-oxetanol (1d).** 34 g of the mixture of the oxetanes *1b*, *2b*, *3b* and *4b* were dissolved into 200 cm<sup>3</sup> of methanol. Into this solution potassium hydroxide solution (25 g KOH, 100 cm<sup>3</sup> H<sub>2</sub>O and 200 cm<sup>3</sup> methanol) was added in drops for 1 h. Methanol was evaporated in a rotary evaporator and 500 cm<sup>3</sup> of water was added. The organic compounds were extracted by methylene chloride. The combined extracts were washed with water and the solvent was evaporated. The residue was distilled in vacuum (b.p. ca. 120 °C/5 Pa). The solid distillate, which was a mixture of oxetanols, *o*-chlorocinnamaldehyde and other compounds, was crystallized several times from diethyl ether. The recrystallized product (m.p. 88–89 °C) weighed 8.2 g. On the basis of the spectroscopic properties, the product was oxetanol *1d*. Acetylation of the pure product yielded an oxetanyl acetate which was identical to the compound *1b*. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound *1d* are presented in the Tables 1–3.

Mass spectrum: *m/z* 186 (<0.1 %, M), 184 (0.1, M), 156 (3), 154 (9), 143 (27), 142 (7), 141 (100), 140 (5), 139 (32), 127 (5), 125 (15), 119 (10), 115 (6), 114 (3), 113 (20), 112 (5), 111 (13), 105 (5), 91 (23), 90 (6), 89 (19), 77 (62), 76 (9), 75 (14), 74 (4), 65 (5), 63 (15), 51 (18), 50 (16), 44 (47), 43 (24); *m\** 143 → 115, obs. 92.4, calc. 92.5; 141 → 113, obs. 90.5, calc. 90.6; 139 → 111, obs. 88.6, calc. 88.6; 113 → 77, obs. 52.5, calc. 52.5; 115 → 77, obs. 51.4, calc. 51.6.

IR spectrum (cm<sup>-1</sup> in CCl<sub>4</sub>): 3595 (s), 3440 (m), 3060 (w), 2950 (s), 2870 (s), 1465 (s), 1400 (m), 1330 (m), 1260 (m), 1200 (s), 1170 (s), 1050 (s), 1030 (s), 990 (s), 880 (m), 685 (m).

**cis-2-Phenyl-3-oxetanol (1c).** 5 g of the mixture of the oxetanyl acetates *1a*, *2a*, *3a* and *4a* were hydrolyzed as described above. Recrystallization of the crude product from diethyl ether gave 1.4 g of oxetanol *1c*, which has a melting point at 69–70 °C. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compound *1c* are described in the Tables 1–3.

Mass spectrum: *m/z* 150 (1 %, M), 120 (16), 119 (2), 108 (7), 107 (100), 106 (4), 105 (32), 92 (10), 91 (62), 90 (4), 89 (8), 79 (55), 78 (9), 77 (40), 65 (14), 63 (9), 51 (21), 50 (10), 44 (26), 43 (14).

IR spectrum (cm<sup>-1</sup> in CCl<sub>4</sub>): 3560 (s), 3420 (m), 3025 (m), 3010 (m), 2950 (s), 2870 (s), 1490 (m), 1450 (m), 1400 (m), 1330 (w), 1300 (w), 1200 (m), 1135 (s), 1070 (w), 1025 (m), 980 (s), 875 (s), 700 (s).

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