# SYNTHESIS OF ACYL 1-ACETOXY-2-PHENOXYETHANES AND THE CORRESPONDING HYDROXY DERIVATIVES

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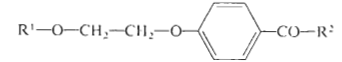
Acyl 1-acetoxy-2-phenoxyethanes *Ia—Id* were prepared by aluminium chloride or polyphosphoric acid-catalyzed Friedel–Crafts acylation. Subsequent hydrolysis gave the corresponding alcohols *IIa—IId*. The formation of *ortho*-isomers during acylation was not observed.

The product obtained on introduction of a keto group into a polymer can be used for further polymer-analogous transformations or an advantage can be taken of its interaction with light. For this purpose a need arose for keto alcohols amenable to further conversion into methacrylates. Since aryl ketones show more pronounced absorption in the UV region they are more efficacious in photochemical applications. It appeared to us of advantage to attach the alcoholic portion through the aromatic ring and, since acylated benzyl alcohols could not be easily prepared, we have decided to use acylated phenoxyethanols. In this class of substances 2-(4-benzoylphenoxy)-1--hydroxyethane[1,2] and 2-(4-acetylphenoxy)-1-hydroxyethane[3–5] have been previously prepared. These, as well as ethyl 4-acetylphenoxy acetates[6], were obtained by etherification of the corresponding keto phenols.

The main reason for our deciding to prepare the title compounds in a way different from that described was the difficulty involved in the etherification of deactivated phenols, *e.g.* we were unable to etherify successfully 1-(4-hydroxyphenyl)-1,2-propanedione, and the fact that compared with phenols, acylation of phenyl ethers is easier to perform and it occurs almost exclusively at the *para*-position. Since 2-phenoxyethanol as such can not be acylated we have acylated its acetate. Owing to their pronounced reactivity, acylation of phenyl ethers can be performed under mild conditions and it can reasonably be assumed that the ester linkage would not be affected during this reaction[7–11]. In fact, Friedel–Crafts acylation of 1-acetoxy--2-phenoxyethane afforded good yields of *para*-derivatives *Ia—Id* and these were converted to the corresponding alcohols *IIa—IId*. The acylation was carried out in polyphosphoric acid or in the presence of aluminium chloride. When the reaction with liquid acids, *e.g.* propanoic acid, was performed in polyphosphoric acid the

desired products were obtained in virtually quantitative yields. On the other hand, 1-acetoxy-2-(4-benzoylphenoxy)ethane could only be obtained by aluminium chloride-catalyzed reaction and in low yield.



*Ia*: $R^1 = CH_3CO$, $R^2 = CH_3$
*Ib*: $R^1 = CH_3CO$, $R^2 = C_2H_5$
*Ic*: $R^1 = CH_3CO$, $R^2 = C_6H_5$
*Id*: $R^1 = CH_3CO$, $R^2 = C_6H_5CH_2$

*IIa*: $R^1 = H$, $R^2 = CH_3$
*IIb*: $R^1 = H$, $R^2 = C_2H_5$
*IIc*: $R^1 = H$, $R^2 = C_6H_5$
*IId*: $R^1 = H$, $R^2 = C_6H_5CH_2$

## EXPERIMENTAL

The IR spectra were measured with IR-71 and IR-75 (C. Zeiss, Jena, GDR) spectrometers. The UV spectra were recorded with a Specord UV-VIS (C. Zeiss, Jena, GDR) instrument. The $^1$H-NMR spectra (60 MHz) were measured at 30°C with a Tesla BS 467 spectrometer (Tesla, Brno, ČSSR) using hexamethyldisiloxane as the internal standard. The mass spectra were obtained with a JMFD 100 (Jeol, Japan) spectrometer. The purity of products was monitored by thin-layer chromatography on Silufol UV 254 using chloroform as the mobile phase. Melting points were determined with a Boetius apparatus and the given values are uncorrected.

1-Acetoxy-2-(4-acetylphenoxy)ethane (*Ia*)

Polyphosphoric acid[12] (80 ml) was added to a mixture of 1-acetoxy-2-phenoxyethane (18 g, 0·1 mol) and acetic acid (99%, $d = 1{\cdot}06$, 12 g, 0·2 mol). The reaction flask was closed, the mixture was homogenized and kept at room temperature for four days after which time 1-acetoxy-2-phenoxyethane could not be detected. The mixture was poured into water (500 ml), the precipitated material was filtered, dissolved in diethyl ether, the ethereal solution was washed with water, dried with $MgSO_4$ and concentrated. Acetic anhydride (10 ml, 0·1 mol) and concentrated $H_2SO_4$ (2 drops) were added to the residue, the mixture was heated on a water bath for 2 h, poured into water (200 ml), the precipitated material was filtered, dissolved in ether and the ethereal solution was washed with 5% $Na_2CO_3$ and water (twice). The solution was dried with $MgSO_4$, decolorized by percolation through a 3 cm layer of silica gel and concentrated. The residue was extracted with n-heptane from which the title compound crystallized (15 g, 68%), m.p. 56–57°C. Recrystallization from ethanol gave material melting at 60–60·5°. For $C_{12}H_{14}O_4$ (222·2) calculated: 64·85% C, 6·35% H; found: 64·90% C, 6·36% H. IR Data ($CCl_4$): $\nu_{max}$ = 950, 1060, 1170, 1230, 1260, 1460, 1500, 1600 (C—C arom.), 1680 (C=O, ketone), 1740 (C=O, ester), 2330, 2940 cm$^{-1}$. UV Data ($CHCl_3$): $\lambda_{max}$ = 268 nm ($\log \varepsilon = 4{\cdot}38$), 323 nm ($\log \varepsilon = 2{\cdot}48$). $^1$H-NMR Data ($CDCl_3$): $\delta = 2{\cdot}05$ (s, 3 H, $CH_3COO$), 2·50 (s, 3 H, $CH_3CO$), 4·26 (m, 4 H, $-CH_2CH_2-$), 6·90 (m, 2 H, aromatic), 7·88 (m, 2 H, aromatic). Mass spectral data: $m/e$ = 222 [$M^+$], 179, 163, 121, 87, 43.

1-Acetoxy-2-(4-propanoylphenoxy)ethane (*Ib*)

Propanoyl chloride (50·8 g, 0·55 mol) followed by a solution of 1-acetoxy-2-phenoxyethane (99 g, 0·55 mol) in carbon disulphide (120 ml) was added dropwise at 0°C to a mixture of anhydrous aluminium chloride (83 g, 0·62 mol) in carbon disulphide (90 ml). The mixture was stirred at ambient temperature until it thickened and then kept at room temperature for 30 min. The reaction was terminated by very slow addition of ice, the product extracted with chloroform, the chloroform solution was washed with water, dried, concentrated, and the residue was distilled at 13 Pa. The fraction that distilled at 140–148°C solidified on cooling. It was crystallized from n-heptane and ethanol, yield 62 g (47%), m.p. 50–51°C. For $C_{13}H_{16}O_4$ (263·3) calculated: 66·08% C, 6·82% H; found: 66·51% C, 6·98% H. IR Data ($CCl_4$): $\nu_{max}$ = 915, 950, 1005, 1060, 1110, 1170, 1225, 1305, 1360, 1375, 1415, 1505, 1605 (C—C arom.), 1685 (C=O, ketone), 1750 (C=O, ester), 2970 $cm^{-1}$. UV Data ($CHCl_3$): $\lambda_{max}$ = 268 nm (log $\varepsilon$ = 4·70) and 313 nm (log $\varepsilon$ = 2·38). $^1$H-NMR Data ($CDCl_3$): $\delta$ = 1·08 (t, 3 H, $CH_3$), 2·0 (s, 3 H, $CH_3COO$), 2·88 (m, 2 H, $CH_2CO$), 4·25 (m, 4 H, O—$CH_2CH_2$—O), 6·9 (m, 2 H, aromatic), 7·96 (m, 2 H, aromatic). Mass spectral data: *m/e* [$M^+$], 207, 120, 87, 43. The same product (76%) was obtained following the procedure described for the preparation of *Ia*, except for the reaction time, which was prolonged to 19 days, and the excess of propanoic acid used, which was 50%.

1-Acetoxy-2-(4-benzoylphenoxy)ethane (*Ic*)

The title compound (m.p. 69–70°C) was prepared in 15·5% yield following the procedure described for the preparation of *Ib*, but the reaction mixture was heated under reflux for 2 h. For $C_{17}H_{16}O_4$ calculated: 71·82% C, 5·67% H; found: 71·54% C, 5·79% H. IR Data ($CCl_4$): $\nu_{max}$ = 920, 935, 1040, 1070, 1150, 1170, 1200, 1250, 1280, 1305, 1315, 1410, 1440, 1500, 1570, 1600 (C—C arom.), 1650 (C=O, ketone), 1750 (C=O, ester), 2970 $cm^{-1}$. UV Data ($CHCl_3$): $\lambda_{max}$ = 287 nm (log $\varepsilon$ = 4·28, 342 nm (log $\varepsilon$ = 2·68). $^1$H-NMR Data ($CDCl_3$): $\delta$ = 2·0 (s, 3 H, $CH_3COO$), 4·25 (m, 4 H, O—$CH_2CH_2$—O), 6·92 (m, 2 H, aromatic), 7·62 (m, 7 H, aromatic). Mass spectral data: *m/e* = 284 [$M^+$], 241, 197, 181, 169, 165, 153, 152, 147, 141, 133, 121, 115, 105, 87, 77, 43.

1-Acetoxy)-2-(4-phenylacetylphenoxy)ethane (*Id*)

A solution of phenylacetyl chloride (15·5 g, 0·1 mol) in carbon disulphide (30 ml) followed by a solution of 1-acetoxy-2-phenoxyethane (18 g, 0·1) in carbon disulphide (15 ml) was added with stirring at 0°C to aluminium chloride (14·7 g, 0·11 mol). The mixture was stirred at room temperature for 1 h, the reaction was terminated by very slow addition of ice and 10% HCl, and the product was extracted with diethyl ether (200 ml). The ethereal extract was washed with water, cold 5% NaOH and water (twice). A product separated from the aqueous layer, mainly from the first extraction and, after concentration of the ethereal phase, the two parts were combined, decolorized with charcoal and crystallized from ethanol (100 ml, twice) to give the title compound (5·2 g, 17·5%), m.p. 93–94°C. For $C_{18}H_{18}O_4$ (298·3) calculated: 72·47% C, 6·08% H; found: 72·07% C, 6·19% H. IR Data ($CCl_4$): $\nu_{max}$ = 960, 985, 1055, 1170, 1210, 1315, 1370, 1450, 1505, 1575, 1600 (C—C, arom.), 1675 (C=O, ketone), 1740 (C=O, ester), 2950 $cm^{-1}$. UV Data ($CHCl_3$): $\lambda_{max}$ = 274 nm (log $\varepsilon$ = 4·28) and 317 nm (log $\varepsilon$ = 2·56). $^1$H-NMR Data ($CDCl_3$): $\delta$ = 2·00 (s, 3 H, $CH_3COO$), 4·20 (m, 6 H, O—$CH_2CH_2$—O and $CH_2CO$), 7·08 (m, 2 H, aromatic), 7·21 (s, 5 H, aromatic), 7·96 (m, 2 H, aromatic). Mass spectral data: *m/e* = 298 [$M^+$], 207, 165, 121, 91, 87, 43. The same material was obtained (41%) following the procedure described for the preparation of *Ia*, except for the prolonged reaction time (30 days); in the beginning of the reaction the mixture was homogenized and heated to 50°C.

2-(4-Acetylphenoxy)-1-hydroxyethane (*IIa*)

A solution of NaOH (9 g, 0·225 mol) in water (30 ml) was added to a solution of *Ia* (14 g, 0·063 mol) in 30 ml ethanol. The mixture was heated under reflux for 10 min, diluted with water and extracted with chloroform. The extract was washed with water, dried with $MgSO_4$, concentrated and the residue was crystallized from diethyl ether, to give the title substance (9·6 g, 85%)-m.p. 65–67°C, ref.[3] 73–74°C, ref.[4] 66°C, ref.[5] 68–69°C. IR Data ($CHCl_3$ : $CCl_4$): $\nu_{max}$ = 840, 920, 960, 1 040, 1 080, 1 120, 1 180, 1 230, 1 260, 1 310, 1 360, 1 420, 1 450, 1 510, 1 580, 1 600 (C—C, arom.), 1 680 (C=O, ketone), 2 340, 3000, 3 460 (—OH assoc.), 3 600 (—OH free) $cm^{-1}$. UV Data ($CHCl_3$): $\lambda_{max}$ = 270 nm (log $\varepsilon$ = 4·48), 323 nm (log $\varepsilon$ = 2·48). $^1$H-NMR Data ($CDCl_3$): $\delta$ = 2·45 (s, 3 H, $CH_3CO$), 2·60 (s, 1 H, OH), 3·98 (m, 4 H, —$OCH_2CH_2O$—), 6·84 (m, 2 H, aromatic), 7·85 (m, 2 H, aromatic). Mass spectral data: *m/e* [$M^+$], 165, 121, 93, 65, 43.

1-Hydroxy-2-(4-propanoylphenoxy)ethane (*IIb*)

The substance was prepared as described for the preparation of *IIa*. Yield 89%, m.p. 38–39°C For $C_{11}H_{14}O_3$ (194·2) calculated: 68·02% C, 7·27% H; found: 67·21% C, 7·29% H. IR Data ($CCl_4$): $\nu_{max}$ = 740, 850, 920, 960, 1 045, 1 080, 1 180, 1 230, 1 260, 1 310, 1 350, 1 420, 1 460, 1 510, 1 610 (C—C arom.), 1 690 (C=O, ketone), 2 340, 2940, 3 500 (—OH assoc.), 3 640 (—OH free) $cm^{-1}$. UV Data $CHCl_3$: $\lambda_{max}$ = 269 nm (log $\varepsilon$ = 4·44), 313 nm (log $\varepsilon$ = 2·36). $^1$H-NMR Data ($CDCl_3$): $\delta$ = 1·12 (t, 3 H, $CH_3$), 2·65 (s, 1 H, OH), 2·83 (q, 2 H, —$COCH_2$), 3·98 (m, 4 H, —$OCH_2CH_2O$—), 6·88 (m, 2 H, aromatic), 7·90 (m, 2 H, aromatic). Mass spectral data: *m/e* = 194 [$M^+$], 165, 121, 93.

2-(4-Benzoylphenoxy)-1-hydroxyethane (*IIc*)

The substance was obtained following the procedure described for the preparation of *IIa*. M.p. 79–80°C (from n-heptane), ref.[1] m.p. 83°C, ref.[2] 87–88°C, yield 91%. IR Data ($CCl_4$ : $CHCl_3$): $\nu_{max}$ = 740, 840, 920, 935, 1 030, 1070, 1 150, 1 170, 1 215, 1 250, 1 280, 1 300, 1 315, 1 415, 1 505, 1 600 (C—C arom.), 1 650 (C=O, ketone), 3010, 3460 (—OH assoc.), 3610 (—OH free) $cm^{-1}$. UV Data ($CHCl_3$): $\lambda_{max}$ = 286 nm (log $\varepsilon$ = 4·36), 339 nm (log $\varepsilon$ = 2·64). $^1$H-NMR Data ($CDCl_3$): $\delta$ = 2·52 (s, 1 H, OH), 3·97 (m, 4 H, —$OCH_2CH_2O$—), 6·90 (m, 2 H, aromatic), 7·62 (m, 7 H, aromatic). Mass spectral data: *m/e* = 242 [$M^+$], 165, 138, 121, 105.

2-(4-Phenylacetylphenoxy)-1-hydroxyethane (*IId*)

For the working procedure see the preparation of *IIa*. M.p. 97–98°C (from n-heptane), yield 83%. For $C_{16}H_{16}O_3$ (256·3) calculated: 74·98% C, 6·29% H; found: 74·83% C, 6·38% H. IR Data ($CCl_4$ : $CHCl_3$ = 1 : 1): $\nu_{max}$ = 740, 910, 980, 1030, 1070, 1 170, 1210, 1250, 1305, 1415, 1450, 1505, 1600 (C—C arom.), 1670 (C=O, ketone), 3010, 3460 (—OH assoc.), 3600 (—OH free) $cm^{-1}$. UV Data ($CHCl_3$): $\lambda_{max}$ = 276 (log $\varepsilon$ = 4·33), 323 nm (log $\varepsilon$ = 2·52). $^1$H-NMR Data ($CDCl_3$): $\delta$ = 2·33 (s, 1 H, OH), 3·93 (m, 4 H, —$OCH_2CH_2O$—), 4·18 (s, 2 H, —$CH_2CO$—), 6·84 (m, 2 H, aromatic), 7·24 (s, 5 H, aromatic), 7·96 (m, 2 H, aromatic). Mass spectral data *m/e* = 256 [$M^+$], 165, 121, 104, 93, 91, 77, 76.

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