

ACYLATION OF 2-PHENOXYETHYL ESTERS OF 2-METHYL- AND 3-PHENYL-2-PROPENOIC ACIDS

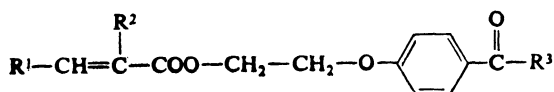
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1-(2-Methyl-2-propenoxyloxy)-2-(4-acylphenoxy)ethanes *II–V* and 1-(3-phenyl-2-propenoxyloxy)-2-[4-(3-chloropropanoyl)phenoxy]ethane (*VI*) were prepared by the Friedel–Crafts acylation, in the presence of anhydrous aluminium chloride, of 2-phenoxyethyl esters of 2-methyl- and 3-phenyl-2-propenoic acids with the corresponding acyl chlorides.

Various active substances, such as stabilizers, dye-stuffs, photocrosslinkers *etc.*, are often incorporated into a polymeric chain as esters of 2-methylpropenoic acid^{1,2}. An aromatic keto group is the active component of many photostabilizing or photosensitizing systems^{1–4}. Aromatic ketones are best accessible by the Friedel–Crafts acylation. However, under the conditions of this reaction a double bond and ester group are often labile. Thus in acylation of active aromatic compounds with 2-propenoic acid in polyphosphoric acid the acylation is accompanied by alkylation, and the double bond disappears⁵. For this reason some analogues of the compounds described herein were previously obtained^{3,6} by acylation of the saturated ester,



	R ₁	R ₂	R ₃
<i>II</i>	H	CH ₃	CH ₂ CH ₂ Cl
<i>III</i>	H	CH ₃	C ₆ H ₅
<i>IV</i>	H	CH ₃	CH ₂ C ₆ H ₅
<i>V</i>	H	CH ₃	CH = CH - C ₆ H ₅
<i>VI</i>	C ₆ H ₅	H	CH ₂ CH ₂ Cl

its hydrolysis and re-esterification with 2-methyl-2-propenoic acid. The present paper shows that in the acylation of an active aromatic compound with acyl chlorides in the presence of anhydrous aluminium chloride the grouping of the 2-methylpropenoic and 3-phenyl-2-propenoic esters remains intact (compounds *II–VI*). This route is easier and even makes it possible to obtain compounds that are not accessible by the original method (*e.g. II* and *VI*).

EXPERIMENTAL

The IR spectra were measured with a spectrometer IR-75 in CCl_4 , the UV spectra with an apparatus Specord UV-VIS (Carl Zeiss, Jena, G.F.R.) in CHCl_3 . The ^1H NMR spectra (60 MHz) were measured at 30°C using a spectrometer Tesla BS 467 (Tesla, Brno, Czechoslovakia), with hexamethyldisiloxane as internal standard in CDCl_3 . The mass spectra were measured with an apparatus JMF D 100 (Jeol, Japan). The purity of the products was tested by thin-layer chromatography on Silufol UV 254 (Kavalier, Czechoslovakia). The melting points, determined on the Boetius stage, are not corrected.

The starting 1-(2-methyl-2-propenoxyloxy)-2-phenoxyethane (*I*) was obtained⁷ by acid-catalysed esterification of 2-phenoxyethanol with 2-methyl-2-propenoic acid in benzene, the reaction water being removed by azeotropic distillation. The mixture was washed with aqueous sodium carbonate and the benzene was distilled off *in vacuo*. The product was freed from a trace of 2-phenoxyethanol by chromatography on silica gel, with light petroleum as eluant. It was a colourless liquid, readily polymerizing. 1-(3-Phenyl-2-propenoxyloxy)-2-phenoxyethane was prepared analogously⁸, m.p. 64°C .

1-(2-Methyl-2-propenoxyloxy)-2-[4-(3-chloropropanoyl)phenoxy]ethane (*II*)

To a suspension of AlCl_3 (15.5 g, 0.12 mol) in CS_2 (10 ml), stirred and cooled in an ice bath, was added 3-chloropropanoyl chloride (12.7 g, 0.1 mol) in CS_2 (20 ml), then 1-(2-methyl-2-propenoxyloxy)-2-phenoxyethane (20.6 g, 0.1 mol) in CS_2 (20 ml) was added dropwise. After all the ester had been added the stirring was continued for 30 min at room temperature, then the mixture was decomposed by being poured cautiously into ice water with HCl. The product was extracted into chloroform and washed with water; the chloroform was distilled off *in vacuo* (without heating). The solid dark residue was dissolved in benzene and purified on a short column of silica gel. The benzene was distilled off *in vacuo* and the product was dissolved in diethyl ether. Freezing gave white crystals (melting at $85.5\text{--}87^\circ\text{C}$), yield 19 g (65%); m.p. $87\text{--}89^\circ\text{C}$ (hexane). IR spectrum: ν_{max} 1660 ($\text{C}=\text{O}$, ketone), 1700 cm^{-1} ($\text{C}=\text{O}$, ester). UV spectrum: λ_{max} 270 nm ($\log \epsilon$ 4.49), 323 nm (2.36). ^1H NMR spectrum: δ 1.88 (s, 3 H, CH_3), 3.30 (t, 2 H, CH_2Cl), 3.80 (t, 2 H, CH_2CO), 4.30 (m, 4 H, $\text{OCH}_2\text{CH}_2\text{O}$), 5.50 (m, 1 H, $\text{CH}_2=\text{C}$), 6.05 (m, 1 H, $\text{CH}_2=\text{C}$), 6.87 (m, 2 H, arom.), 7.85 (m, 2 H, arom.). Mass spectrum: m/e 296 (M^+), 148, 120, 114, 104, 69. For $\text{C}_{15}\text{H}_{17}\text{ClO}_4$ (296.75) calculated: 60.71% C, 5.77% H, 11.95% Cl; found: 61.08% C, 5.89% H, 11.60% Cl.

1-(2-Methyl-2-propenoxyloxy)-2-(4-benzoylphenoxy)ethane (*III*)

Acylation of compound *I* with benzoyl chloride was analogous to the preparation of compound *II*. After extraction into chloroform the extract was washed with aqueous sodium carbonate and water. The chloroform was distilled off *in vacuo*. The product was extracted with cold light petroleum (according to TLC the extract contained the unreacted starting compounds and a small amount of the product). The residue after the extraction was dissolved in benzene and chromatographed on a column of silica gel. The corresponding fraction was distilled *in vacuo* to remove the benzene. The residue was compound *III*, a viscous colourless liquid, yield 43.5%; the product was identical with that obtained previously by a different procedure³.

1-(2-Methyl-2-propenoxyloxy)-2-[4-(phenylacetyl)phenoxy]ethane (*IV*)

Acylation of compound *I* with phenylacetyl chloride was analogous to the preparation of compound *II*. The chloroform extract was washed with water, aqueous sodium carbonate and water. The chloroform was distilled off *in vacuo* and the product was dissolved in diethyl ether. The solu-

tion was boiled with activated carbon, filtered and chilled. The separated solid was collected on a filter and crystallized from light petroleum in a refrigerator; the product (*IV*) melted at 76 to 79°C, yield 23%. After recrystallization from ethanol the m.p. was 79–81°C; the compound was identical with that obtained previously³.

1-(2-Methyl-2-propenoxyloxy)-2-[4-(3-phenyl-2-propenoyl)phenoxy]ethane (*V*)

Acylation of *I* with cinnamoyl chloride was analogous to the preparation of *II*. The reaction mixture was stirred at room temperature for 2 h, then it was decomposed with ice and hydrochloric acid. The product was extracted into chloroform, the extract was washed with water and the chloroform was removed *in vacuo*. The residue was crystallized from light petroleum at a low temperature, from benzene (four times) and finally from methanol; yield 25%, m.p. 90–91°C. IR spectrum: 1 650 (C=O, ketone), 1 700 cm⁻¹ (C=O, ester). UV spectrum: λ_{\max} 317 nm (log ϵ 4.8). ¹H NMR spectrum: δ 1.82 (s, 3 H, CH₃), 4.28 (m, 4 H, OCH₂CH₂O), 5.48 (m, 1 H, CH₂=), 6.05 (s, 1 H, CH₂=), 6.87 (m, 2 H, arom.), 7.40 (m, 7 H, CH=CH—C₆H₅), 7.93 (m, 2 H, arom.). Mass spectrum: *m/e* 336 (M⁺), 207, 148, 129, 120, 69. For C₂₁H₂₀O₄ (336.4) calculated: 74.98% C, 5.99% H; found: 75.1% C, 6.02% H.

1-(3-Phenyl-2-propenoxyloxy)-2-[4-(3-chloropropanoyl)phenoxy]ethane (*VI*)

To a suspension of AlCl₃ (11.2 g, 0.084 mol) in CS₂ (20 ml) was added 3-chloropropanoyl chloride (7.1 g, 0.056 mol) in CS₂ (10 ml), then 1-(3-phenyl-2-propenoxyloxy)-2-phenoxyethane (15 g, 0.056 mol) in CS₂ (30 ml) was added dropwise under a mild reflux. After the latter component had been added the reaction mixture was boiled for another 30 min and decomposed with ice and hydrochloric acid. The product was extracted into chloroform and washed with water. The chloroform was removed *in vacuo* and the residue was crystallized from benzene; yield 10.7 g (53%) of the yellow product, m.p. 93.5–95°C. IR spectrum (CCl₄: CHCl₃ 1 : 1): 1 670 (C=O, ketone), 1 720 cm⁻¹ (C=O, ester). UV spectrum: λ_{\max} 280 nm (log ϵ 4.58), 323 nm (2.48). ¹H NMR spectrum: δ 3.28 (t, CH₂Cl), 3.79 (t, 2 H, COCH₂), 4.37 (m, 4 H, OCH₂CH₂O), 6.38 (d, 1 H, —CH=), 6.92 (m, 2 H, arom.), 7.40 (m, 5 H, arom. and 1 H, —CH=), 7.88 (m, 2 H, arom.). Mass spectrum, *m/e*: 358 (M⁺), 176, 131, 103. For C₂₀H₁₀ClO₄ (358.8) calculated: 66.95% C, 5.34% H, 9.88% Cl; found: 67.26% C, 5.39% H, 9.54% Cl.

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