

REACTION OF 2-PROPENOIC ACID AND OF DERIVATIVES
OF 1-PHENYL-2-PROPEN-1-ONE
WITH 1-ACETOXY-2-PHENOXYETHANE IN POLYPHOSPHORIC ACID

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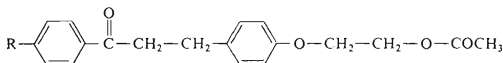
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2-Propenoic acid when reacted with 1-acetoxy-2-phenoxyethane in polyphosphoric acid at room temperature gives intermolecular acylalkylated product *I*. Probably owing to a rapid subsequent reaction the acylated intermediary product could not be detected. Therefore alkylation of a model compound, 1-acetoxy-2-phenoxyethane, with derivatives of 1-phenyl-2-propen-1-one was investigated, which led to compounds *I–IV*.

Phenol ethers in polyphosphoric acid are easily acylated with saturated acids under formation of a single product and in good yields¹. In the reaction with unsaturated acids the formation of several products is possible, in dependence on the structure of phenol ether and the acid used and the reaction conditions. Products of acylation are formed — unsaturated ketones^{2,3}, cyclic products of acylation and intramolecular alkylation², or products of acylation and intermolecular alkylation — 1,3-disubstituted derivatives of propan-1-one².

If 2-propenoic acid and 1-acetoxy-2-phenoxyethane in polyphosphoric acid were used for the reaction at room temperature, the product of acylation and intermolecular alkylation *I* was obtained. The object of our interest was unsaturated ketone which we tried to prepare using a 10-fold excess of 2-propenoic acid. The main product was again compound *I* and only a small amount of polymer. Under the assumption that the first step of the reaction is acylation and the second alkylation, we tried to isolate 1-[4-(2-acetoxyethoxy)phenyl]-2-propen-1-one (*VI*) by means of gel chromatography and ¹H NMR spectroscopy. However, the presence of derivative *VI* in the reaction mixture could not be detected



- I*, R = CH₃COOCH₂CH₂O—
II, R = H
III, R = CH₃
IV, R = C₆H₅

Alkylation with derivative *VI* and other unsaturated ketones confirmed that unsaturated ketone is a possible intermediate in the preparation of substance *I* (products *I-IV*). Lower alkylation yields obtained with derivatives of 2-propen-1-one may be due to polymerization in consequence of their higher concentration in the reaction mixture. However, the relatively long times of alkylation and the fact that an unsaturated ketone could not be detected in the reaction of 2-propenoic acid indicate unambiguously a higher reactivity of the unsaturated ketone formed *in situ*.

EXPERIMENTAL

The IR spectra were measured on an IR-75 and the UV spectra on a Specord UV-VIS instrument in CHCl_3 (Zeiss, Jena, GDR). The ^1H NMR spectra were measured on a 60 MHz BS-467 instrument (Tesla, Brno, Czechoslovakia) at 30°C in CDCl_3 with hexamethyldisiloxane as internal standard. The mass spectra were measured on a JMFD 100 instrument (Jeol, Japan). The melting points were determined on a Boetius apparatus and they were not corrected. The purity of the substances prepared was checked by thin-layer chromatography (Silufol UV-254, Kavalier, Sázava, ČSSR) in chloroform.

1,3-Bis[4-(2-acetoxyethoxy)phenyl]-propan-1-one (*I*)

a) Polyphosphoric acid⁴ (45.0 ml) was added to a mixture of 9 g (0.05 mol) of 1-acetoxy-2-phenoxyethane and 1.8 g (0.025 mol) of 2-propenoic acid and the content of the flask was homogenized and closed. After 48 h standing at room temperature water (250 ml) was added and the separated product was filtered off. It was crystallized from ethanol giving a material with m.p. $97.5-98^\circ\text{C}$, yield 5.5 g (53%). For $\text{C}_{23}\text{H}_{26}\text{O}_7$ (414.5) calculated: 66.54% C, 6.32% H; found: 66.49% C, 6.44% H. IR spectrum (CHCl_3): $\nu_{\text{max}} = 1600$ (C—C arom), 1680 (C=O, ketone), 1740 (C=O, ester), cm^{-1} . UV spectrum: $\lambda_{\text{max}} = 318$ nm ($\log \epsilon = 2.41$) and 272 nm ($\log \epsilon = 4.25$). ^1H NMR spectrum: $\delta = 2.0$ (s, 6 H, $(\text{CH}_3\text{COO})_2$); 3.0 (m, 4 H, COCH_2CH_2); 4.17 (m, 8 H, $(\text{OCH}_2\text{CH}_2\text{O})_2$); 6.95 (m, 6 H, arom.); 7.85 (d, 2 H, arom.). Mass spectrum: $m/e = 414 \text{ M}^+$, 207, 121, 87, 43.

b) 1-Acetoxy-2-phenoxyethane (5 g; 0.028 mol), 2-propenoic acid (20 g; 0.28 mol) and polyphosphoric acid (25 ml) were allowed to react as in the preceding case for 9 days. After decomposition with water the product was extracted with chloroform, dried and concentrated in a vacuum. The residue was extracted with heptane. From the extract 1.59 g (28%) of compound *I* crystallized out. Further 2.52 g were obtained from concentrated mother liquors. The insoluble part weighed 1.04 g, from which 0.5 g of a yellow-red polymer were obtained after dissolution in chloroform and precipitation with methanol, the IR spectrum of which was very similar to that of compound *I*. Probably the polymer consists mainly of poly {1-[4-(2-acetoxyethoxy)phenyl]-2-propen-1-one}. From the mother liquors which were chromatographed on silica gel with *n*-hexane-acetone (95 : 5) 2 g (40%) of the starting 1-acetoxy-2-phenoxyethane were obtained, while elution with hexane-acetone 10 : 3 gave 0.4 g (7%) of compound *I*.

c) Similarly as in case *a*) 2.5 g (0.01 mol) of 1-[4-(2-acetoxyethoxy)phenyl]-2-propen-1-one (*VI*) were reacted with 1.92 g (0.11 mol) of 1-acetoxy-2-phenoxyethane and 25 ml polyphosphoric acid for 48 h. The yield of *I* was 1.8 g (41%).

1-Phenyl-3-[4-(2-acetoxyethoxy)phenyl]propan-1-one (II)

As in the case of substance *I* a mixture of 2.5 g (0.019 mol) of 1-phenyl-2-propen-1-one⁵, 3.4 g (0.019 mol) or 1-acetoxy-2-phenoxyethane and 25 ml of polyphosphoric acid was allowed to react for 20 h. After addition of water the product was extracted with chloroform. After drying and concentration the product was purified on silica gel (3 × 4 cm) in benzene. After concentration of the eluate and crystallization from methanol 1.94 g (31%) of compound with m.p. 48.5 to 50°C were obtained. For C₁₉H₂₀O₄ (312.3) calculated: 73.06% C, 6.45% H; found: 73.80% C, 6.65% H. IR spectrum (CCl₄): ν_{\max} = 1 595 (C—C, arom), 1 680 (C=O) ketone, 1 730 (C=O ester) cm⁻¹. UV spectrum: λ_{\max} = 322 nm (log ϵ = 1.91) and 281 nm (log ϵ = 3.30). ¹H NMR spectrum: δ = 1.98 (s, 3 H, CH₃CO); 2.96 (m, 4 H, COCH₂CH₂); 4.08 (m, 4 H, OCH₂CH₂O); 6.83 (m, 4 H, arom.); 7.33 (m, 3 H, arom.); 7.83 (m, 2 H, arom.). Mass spectrum: m/e = 312 M⁺, 207, 193, 133, 121, 119, 105, 93, 77, 43.

1-(4-Methylphenyl)-3-[4-(2-acetoxyethoxy)phenyl]propan-1-one (III)

Similarly as in the case of compound *I* 5 g (0.034 mol) of 1-(4-methylphenyl)-2-propene-1-one⁶, 6.16 g (0.034 mol) of 1-acetoxy-2-phenoxyethane and 50 ml of polyphosphoric acid were allowed to react for 7 days. After addition of water the product was extracted with chloroform. After drying, concentration and crystallization from ethanol 8.9 g (81%) of substance were obtained, m.p. 81–82°C. For C₂₀H₂₂O₄ (326.2) calculated: 73.58% C, 6.80% H; found: 73.99% C, 6.99% H. IR spectrum (CCl₄): ν_{\max} = 1 605 (C—C, arom.), 1 680 (C=O, ketone), 1 750 (C=O, ester) cm⁻¹. UV spectrum: λ_{\max} = 320 nm (log ϵ = 2.15) and 256 nm (log ϵ = 4.28). ¹H NMR spectrum: δ = 2.08 (s, 3 H, COCH₃); 3.04 (m, 4 H, COCH₂CH₂); 4.21 (m, 4 H, OCH₂CH₂O); 7.0 (m, 6 H, arom.); 7.83 (d, 2 H, arom.). Mass spectrum: m/e = 326 M⁺, 133, 129, 91, 43.

1-(4-Biphenyl)-3-[4-(2-acetoxyethoxy)phenyl]propan-1-one (IV)

It was obtained as substance *I*. From 2 g (0.01 mol) of 1-(4-biphenyl)-propen-1-one⁷, 1.73 g (0.01 mol) of 1-acetoxy-2-phenoxyethane and 25 ml of polyphosphoric acid a product was obtained which was crystallized from heptane, affording, 1.1 g (29%) of compound *IV*, m.p. 94 to 96°C. For C₂₅H₂₄O₄ (388.5) calculated: 77.30% C, 6.23% H; found: 77.37% C, 6.34% H. IR spectrum (CCl₄): ν_{\max} = 1 605 (C—C, arom.), 1 680 (C=O, ketone); 1 740 (C=C, ester) cm⁻¹. UV spectrum: λ_{\max} = 290 nm (log ϵ = 4.54). ¹H NMR spectrum: δ = 2.43 (s, 3 H, CH₃CO); 3.5 (m, 4 H, COCH₂CH₂); 4.62 (m, 4 H, OCH₂CH₂O); 7.3 (m, 4 H, arom.); 7.88 (m, 7 H, arom.); 8.33 (d, 2 H, arom.). Mass spectrum: m/e = 388 M⁺, 345, 181, 153, 104, 43.

1-[4-(2-Acetoxyethoxy)phenyl]-3-chloropropan-1-one (V)

3-Chloropropanoyl chlorid (17.6 g; 0.14 mol) in 18 ml of carbon disulfide was added under stirring and cooling to a mixture of 22.2 g (0.17 mol) of anhydrous aluminum chloride in 23 ml of carbon disulfide. 1-Acetoxy-2-phenoxyethane (25 g; 0.14 mol) in 25 ml of carbon disulfide was then added to the mixture which was refluxed for 30 min. After cooling it was poured onto ice acidified with hydrochloric acid, extracted with chloroform, and the extract was washed 4 times with water. After drying over anhydrous sodium sulfate and concentration in a vacuum the residue was extracted with a hot mixture of 20 ml of ether and 500 ml of hexane. On cooling at -70°C a product was obtained which was recrystallized from n-hexane to afford 19 g (51%) of a compound with m.p. 45–46°C. For C₁₃H₁₅ClO₄ (270.7) calculated: 57.68% C, 5.59% H, 13.1% Cl; found: 57.86% C, 5.92% H, 12.54% Cl. IR spectrum (CHCl₃): ν_{\max} = 1 600 (C—C, arom.), 1 680 (C=O, ketone), 1 730 (CO, ester) cm⁻¹. UV spectrum: λ_{\max} = 277 nm (log ϵ =

= 4.15). ^1H NMR spectrum: δ = 2.03 (s, 3 H, CH_3COO); 3.33 (t, 2 H, $\text{CO}-\text{CH}_2-$); 3.83 (t, 2 H, CH_2-Cl); 4.25 (m, 4 H, $\text{OCH}_2\text{CH}_2\text{O}$); 6.89 (d, 2 H, arom.); 7.87 (d, 2 H, arom.). Mass spectrum: m/e = 273, 270 M^+ , 234, 220, 131, 120, 104, 87, 43.

1-[4-(2-Acetoxyethoxy)phenyl]-2-propen-1-one (VI)

5 g (0.018 mol) of 1-[4-(2-acetoxyethoxy)phenyl]-3-chloropropan-1-one, 15 ml of methanol and 2.72 g (0.028 mol) of anhydrous potassium acetate were refluxed for 10 min. The methanolic solution was diluted with water, extracted with chloroform, the extract was dried and concentrated in a vacuum. The product was purified chromatographically on silica gel (3×15 cm) using benzene-light petroleum (75 : 25) for elution. Yield, 2.5 g (58%) of an easily polymerizing liquid. ^1H NMR spectrum: δ = 2.05 (s, 3 H, CH_3COO); 4.25 (m, 4 H, $\text{OCH}_2\text{CH}_2\text{O}$); 5.75 (d, 1 H, $\text{CH}_2=$); 6.28 (d, 1 H, $\text{CH}_2=$); 6.83 (t, 1 H, $=\text{CH}-$); 7.08 (d, 2 H, arom.); 7.89 (d, 2 H, arom.).

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