

**SIDE-PRODUCTS OF ACYLATION OF 1-ACETOXY-2-PHENOXYETHANE WITH PHENYLACETYL CHLORIDE**Ivan LUKÁČ<sup>a</sup>, Marta KAČURÁKOVÁ<sup>a</sup> and Ľubomír MALÍK<sup>b</sup><sup>a</sup> *Polymer Institute, Chemical Research Centre,  
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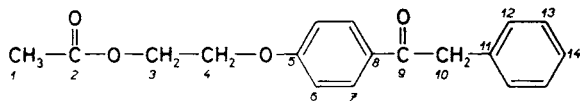
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Acylation of 1-acetoxy-2-phenoxyethane with phenylacetyl chloride in the presence of anhydrous aluminium chloride or tin tetrachloride afforded 1-acetoxy-2-(4-phenylacetylphenoxy)ethane (*I*) as the principal product. In the presence of aluminium chloride 1-[4-(2-acetoxyethoxyphenyl)]-1-chloro-2-phenylethene (*II*), 1,1-di-[4-(2-acetoxyethoxyphenyl)]-2-phenylethene (*III*) and 1-[4-(2-hydroxyethoxyphenyl)]-1-chloro-2-phenylethene (*IV*) were isolated as side-products whereas in the tin tetrachloride-catalyzed reaction only *III* was detected.

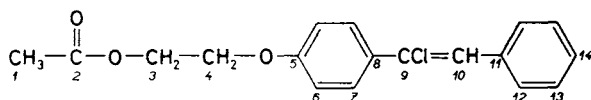
Previously<sup>1</sup> we described the preparation of 1-acetoxy-2-(4-phenylacetylphenoxy)ethane (*I*), an intermediate in the synthesis of polymers containing mono or dicarbonyl groupings<sup>2,3</sup>. Such polymers are cross-linked upon exposure to light and can be used as polymeric sensitizers or, in the case of  $\alpha$ -dicarbonyl compounds, as phosphorescent markers. In repeated preparations of compound *I* by acylation of 1-acetoxy-2-phenoxyethane with phenylacetyl chloride in the presence of aluminium chloride, we encountered difficulties connected with removal of side-products. Therefore, we set out to find an effective method for analytical as well as preparative separation of the acylation products, to study their formation and to identify them. In order to suppress the formation of side-products we decided to apply a milder reagent, tin tetrachloride, instead of aluminium chloride.

The acylation of 1-acetoxy-2-phenoxyethane with phenylacetyl chloride in the presence of anhydrous aluminium chloride or tin tetrachloride afforded compound *I* as the principal product. As further products arising in the presence of anhydrous aluminium chloride we identified 1-[4-(2-acetoxyethoxyphenyl)]-1-chloro-2-phenylethene (*II*), 1,1-di-[4-(2-acetoxyethoxyphenyl)]-2-phenylethene (*III*), and 1-[4-(2-hydroxyethoxyphenyl)]-1-chloro-2-phenylethene (*IV*). In contrast to aluminium chloride which afforded dark-coloured crude product, application of anhydrous tin tetrachloride led to only lightly coloured product. With the latter reagent, compounds *II* or *IV* were not detected; however, compound *II*, if formed, could escape

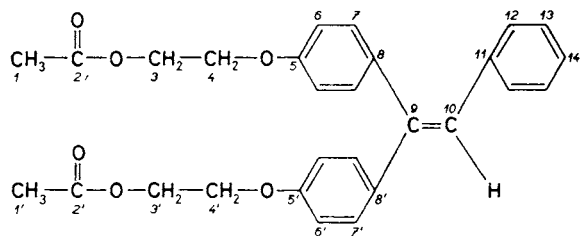
detection in the mother liquors after crystallization of the crude product (which were not further analyzed). Thus, according to the product composition, tin tetrachloride appears to be the better catalyst.



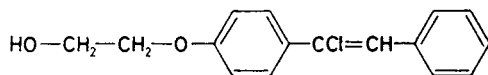
I



II



III



IV

As found already by Gatterman<sup>4,5</sup>, acylation of anisole with propanoyl chloride afforded compounds analogous to *II* and *III*, in addition to the desired 1-(4-methoxyphenyl)-1-propanone (analogous to *I*). Although the product composition indicates that compound *III* arises from *I* via the intermediate *II*, similarly as in the case of 1-(4-methoxyphenyl)-1-propanone<sup>6</sup>, no formation of *II* from *I* was observed either with aluminium chloride or tin tetrachloride under the reaction conditions employed. The product of the type *II* arises probably by direct reaction of 1-acetoxy-2-phenoxyethane with phenylacetyl chloride, isomerized in the reaction medium. When compound *II* was treated with 1-acetoxy-2-phenoxyethane in the presence of tin tetrachloride under the used reaction conditions, compound *III* was detected as the main product, similarly as reported<sup>6,7</sup>.

Separation of the products, particularly *I* from *III*, appeared to be the crucial problem, not only on the preparative but also on the analytical scale. Since compounds *I* and *III* are chemically very similar, they were separated on the basis of different molecular weight rather than chemical behaviour. Analytical separation was achieved by gel chromatography, preparative by distillation. In spite of high boiling and melting point of compound *I*, distillation represents a very efficient procedure of its separation from compound *III* which remains in the distillation residue.

Signals in the  $^{13}\text{C}$  NMR spectra of compounds *I*, *II*, and *III* were assigned to individual carbon atoms on the basis of chemical shifts and multiplicity of signals observed in proton-coupled  $^{13}\text{C}$  NMR spectra with NOE. Thus, *e.g.*, carbon atoms in the positions 8, 8', and 12 were identified using the  $^3J_{\text{C-H}}$  coupling constant of the proton in position 10. The published data for styrene, *cis*- and *trans*-stilbene, and tetraphenylethylene served us for assignment of shifts in the spectrum of 1,1,2-triphenylethylene<sup>8</sup> on the basis of which we assigned the carbon shifts in the spectrum of *III*. No conclusion about the *cis*- or *trans*-configuration of compound *II* can be made since the carbon signals at 131.6 and 132.2 ppm in the proton-coupled spectrum overlap with signals of the proton-bearing carbon atoms.

TABLE I  
Chemical shifts of carbon signals

Carbon atom	Compound <sup>a</sup>			
	<i>I</i>	<i>II</i>	<i>III</i>	
1,1'	20.9	20.8	20.9	20.9
2,2'	170.9	170.8	171.0	171.0
3,3'	62.5	62.6	62.8	62.8
4,4'	66.1	65.9	65.8*	65.9*
5,5'	162.4	158.8	158.1 <sup>o</sup>	157.8 <sup>o</sup>
6,6'	114.3	114.3	114.2	114.6
7,7'	131.0	128.2*	131.6	128.9
8,8'	130.0	132.2 <sup>o</sup>	133.2	136.8
9	192.6	131.6 <sup>o</sup>		141.5
10	45.3	124.4		126.4
11	134.9	135.3		137.7
12	129.4	129.3		129.4
13	128.6	128.0*		127.9
14	126.8	127.7		126.4

<sup>a</sup> Assignment of values denoted\*<sup>o</sup> may be interchanged.

## EXPERIMENTAL

Infrared spectra were measured on an IR-75 spectrometer, UV spectra on a Specord UV-VIS (Zeiss, Jena, G.D.R.) instrument. Proton NMR spectra were taken at 30°C on a Tesla BS 467 (60 MHz) spectrometer in deuteriochloroform with hexamethyldisiloxane as internal standard, <sup>13</sup>C NMR spectra were obtained at room temperature in deuteriochloroform on a JEOL FX-100 instrument with tetramethylsilane as internal standard. Mass spectra were taken on a JMFD 100 (JEOL, Japan) spectrometer. Melting points were determined on a Boetius instrument and are uncorrected.

Purity of the products was followed by thin-layer chromatography on Silufol UV 254 (Kavaliar, Czechoslovakia) in benzene-acetone (93 : 7) and by liquid chromatography (Merckogel PVA 500; 500 × 9 mm column, eluent methanol, detection at 254 nm). In the physico-chemical data given for the compounds,  $V_e$  denote values proportional to elution volume.

## Acylation of 1-Acetoxy-2-phenoxyethane with Phenylacetyl Chloride

a) The acylation in the presence of anhydrous aluminium chloride and the subsequent product isolation were the same as described previously<sup>1</sup>. After crystallization from ethanol, the obtained product contained, in addition to compound *I*, also compounds *III* and *IV*. These were less soluble and were obtained by multiple fractional dissolution in methanol and crystallization from methanol and acetone. The concentrated ethanolic mother liquors from the first crystallization of *I* afforded crystals which on chromatography on silica gel in benzene gave *II* as the first fraction; yield 2–5%. Compound *II* was then purified by crystallization from methanol.

b) Anhydrous tin tetrachloride (40 ml) in dry benzene (40 ml) was added dropwise at 10–15°C to a stirred mixture of phenylacetyl chloride (20 g; 0.13 mol) and 1-acetoxy-2-phenoxyethane (25 g; 0.14 mol) in dry benzene (35 ml). After stirring for 2 h at room temperature, the mixture was poured portionwise into a mixture of ice and conc. hydrochloric acid. The white solid was collected on filter, washed with water and dissolved in chloroform. The chloroform solution was washed with water and concentrated to give a lightly coloured crystalline crude product which after crystallization from methanol contained 10–20% of *III* (in addition to *I*). Compound *I* was isolated by distillation at 208°C/17 Pa.

## Characteristics of the Isolated Compounds

1-Acetoxy-2-(4-phenylacetylphenoxy)ethane (*I*), white crystals, m.p. 93–94°C (ethanol);  $R_F$  0.48,  $V_e$  10.2,

1-[4-(2-Acetoxyethoxyphenyl)]-1-chloro-2-phenylethene (*II*), white crystals, m.p. 86–88°C (methanol);  $R_F$  0.67,  $V_e$  14.7. For  $C_{18}H_{17}O_3Cl$  (316.79) calculated: 68.25% C, 5.41% H; found: 68.20% C, 5.51% H. IR spectrum ( $CHCl_3$ ): 1730  $cm^{-1}$  (C=O, ester). <sup>1</sup>H NMR spectrum:  $\delta$  1.98 (s, 3 H,  $CH_3$ ), 4.18 (m, 4 H,  $CH_2CH_2$ ), 7.22 (m, 10 H, aromatic + C=C—H). Mass spectrum ( $m/z$ ): 316 ( $M^+$ ), 208, 179, 87.

1,1-Di-[4-(2-acetoxyethoxyphenyl)]-2-phenylethene (*III*), white crystals, m.p. 116–118°C (acetone);  $R_F$  0.51,  $V_e$  18.3. For  $C_{28}H_{28}O_6$  (460.53) calculated: 73.03% C, 6.13% H; found: 73.18% C, 6.17% H. IR spectrum ( $CHCl_3$ ): 1720  $cm^{-1}$  (C=O, ester). UV spectrum ( $CHCl_3$ ): 263 nm (4.04), 315 nm (4.16). <sup>1</sup>H NMR spectrum:  $\delta$  2.02 (s, 6 H, 2  $CH_3$ ), 4.20 (m, 8 H, 4  $CH_2$ ), 6.97 (m, 14 H, aromatic + C=C—H). Mass spectrum ( $m/z$ ): 460 ( $M^+$ ), 374, 288, 207, 165, 121, 88.

1-[4-(2-Hydroxyethoxyphenyl)]-1-chloro-2-phenylethene (*IV*), white crystals, m.p. 107–108°C (acetone);  $R_F$  0.27,  $V_e$  9.6. For  $C_{16}H_{15}O_2Cl$  (274.76) calculated: 69.95% C, 5.50% H, 12.90% Cl;

found: 69.85% C, 5.52% H, 12.81% Cl. IR spectrum ( $\text{CHCl}_3$ ): 3 600 (OH free), 3 440 (OH bonded), 1 590 (C—H aromatic)  $\text{cm}^{-1}$ . UV spectrum ( $\text{CHCl}_3$ ): 294 nm.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.95 (s, 1 H, OH), 3.92 (m, 4 H,  $\text{CH}_2\text{CH}_2$ ), 7.20 (m, 10 H, aromatic + C=C—H). Mass spectrum ( $m/z$ ): 274 ( $\text{M}^+$ ), 229, 195, 165, 121, 93, 77.

#### REFERENCES

1. Lukáč I., Zvara I., Kulíčková M., Hrdlovič P.: This Journal 45, 1826 (1980).
2. Hrdlovič P., Lukáč I., Zvara I.: Eur. Polym. J. 17, 1121 (1981).
3. Lukáč I., Zvara I., Hrdlovič P.: Eur. Polym. J. 18, 427 (1982).
4. Gattermann L.: Ber. 22, 1129 (1889).
5. Gattermann L., Erhardt R., Maisch H.: Ber. 23, 1199 (1890).
6. Ziegler E., Gitschthaler K.: Osterr. Chemiker Ztg. 53, 208 (1952).
7. Nagano I. T.: J. Am. Chem. Soc. 77, 1691 (1955).
8. Bremser W., Ernst L., Franke E., Gerhardt R., Hardt A.: *Carbon-13 NMR Spectral Data*. Verlag Chemie, Basle 1981.

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