

SHORT
COMMUNICATIONS

Synthesis of Unsaturated Aldehydes from *m*-Phenoxybenzaldehyde

Yu. V. Popov, T. K. Korchagina, and D. G. Stepochkina

Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia

Received July 10, 2000

Aldehydes constitute an important class of carbonyl compounds which are widely used in synthetic organic chemistry due to their high reactivity. The presence in a single molecule of a carbonyl group, a double C=C bond, and a diphenyl ether moiety gives rise to specific properties of such compounds, especially when these groups are located close to each other [1].

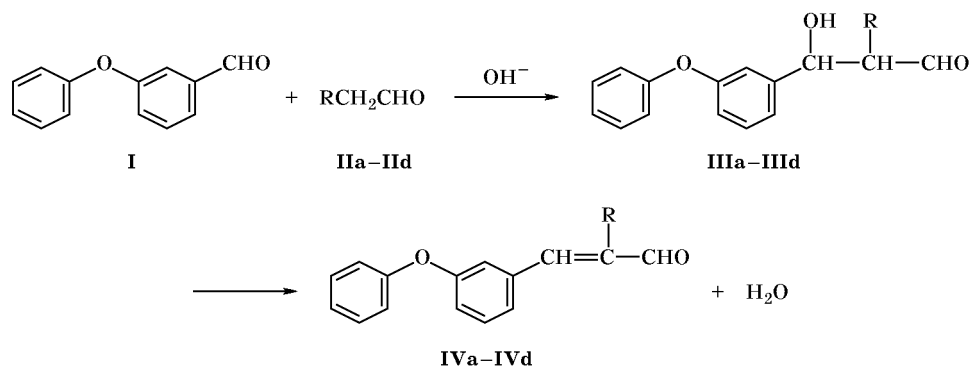
We examined aldol condensation of *m*-phenoxybenzaldehyde (**I**) with various aliphatic aldehydes **IIa–IIId** and obtained unsaturated aldehydes **IIIa–IIId** having a diphenyl ether moiety (Scheme 1). The reactions were carried out in methanol at a molar ratio **I**:**II** of 1:3; the reaction time was 8 h, and a 10% solution of potassium hydroxide in methanol was used as catalyst. In order to prevent self-condensation of the aliphatic aldehyde, it was slowly added to a solution of *m*-phenoxybenzaldehyde and potassium hydroxide in methanol, cooled to 5–7°C, and pH of the medium was continuously monitored. We thus succeeded in obtaining a number of new unsaturated aldehydes **IVa–IVd** in 53–74% yield. The products were isolated by repeated vacuum distillation.

The purity of the products was checked by gas-liquid chromatography. Their structure was confirmed by IR spectroscopy and elemental analysis. The IR spectra of **IVa–IVd** contained characteristic absorption bands at 1620–1640 (C=C) and 1670–1685 cm⁻¹ (C=O), whereas hydroxy group absorption at 3620–3650 cm⁻¹ was lacking. Numerous bands in the region 1440–1490 cm⁻¹ indicated the presence of more than one benzene ring.

2-Ethyl-3-*m*-phenoxyphenyl-2-propenal (**IVb**).

A solution of 2.5 g (0.045 mol) of potassium hydroxide in methanol was added dropwise to a solution of 17.25 g (0.087 mol) of *m*-phenoxybenzaldehyde in 8.71 g (0.272 mol) of methanol, cooled to 5–7°C. A solution of 18.88 g (0.262 mol) of freshly distilled butyraldehyde in 8.71 g (0.272 mol) of methanol was added dropwise over a period of 1 h, maintaining the temperature below 10°C. The mixture was stirred for 8 h, neutralized with glacial acetic acid, and extracted with diethyl ether. The solvent was removed, and the residue was distilled in a vacuum. Yield 16 g (73%), bp 191–192°C (3 mm). Found, %: C 80.63; H 6.51. C₁₇H₁₆O₂. Calculated, %: C 80.93; H 6.35.

Scheme 1.



R = CH₃ (**a**), CH₂CH₃ (**b**), CH₂CH₂CH₃ (**c**), CH(CH₃)₂ (**d**).

2-Methyl-3-*m*-phenoxyphenyl-2-propenal (IVa) was synthesized in a similar way from 17.25 g (0.087 mol) of aldehyde **I**, 17.42 g of methanol, 2.5 g (0.045 mol) of KOH, and 15.22 g (0.262 mol) of freshly distilled propionaldehyde. Yield 11 g (53%), bp 195–196°C (2 mm). Found, %: C 80.90; H 6.02. $C_{16}H_{14}O_2$. Calculated, %: C 80.67; H 5.88.

2-Propyl-3-*m*-phenoxyphenyl-2-propenal (IVc) was synthesized in a similar way from 17.25 g (0.087 mol) of aldehyde **I**, 17.42 g (0.544 mol) of methanol, 2.5 g (0.045 mol) of KOH, and 22.57 g (0.262 mol) of freshly distilled pentanal. Yield 13 g (56%), bp 205–207°C (2 mm). Found, %: C 80.43; H 6.54. $C_{18}H_{18}O_2$. Calculated, %: C 80.90; H 6.74.

2-Isopropyl-3-*m*-phenoxyphenyl-2-propenal (IVd) was synthesized in a similar way from 17.25 g

(0.087 mol) from aldehyde **I**, 17.42 g (0.544 mol) of methanol, 2.5 g (0.045 mol) of KOH, and 22.57 g (0.262 mol) of freshly distilled 3-methylbutanal. Yield 16.7 g (72%), bp 203–205°C (2 mm). Found, %: C 81.25; H 6.14. $C_{18}H_{18}O_2$. Calculated, %: C 80.90; H 6.74.

GLC analysis was performed on a Sigma-300 chromatograph using a 2-m column packed with 15% of SKTFT on Inerton N-AV, injector temperature 270°C. The IR spectra were obtained from solutions in chloroform using a Perkin–Elmer instrument.

REFERENCE

1. Patai, S. and Israeli, Y., *J. Chem. Soc.*, 1960, pp. 2020–2025.