

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

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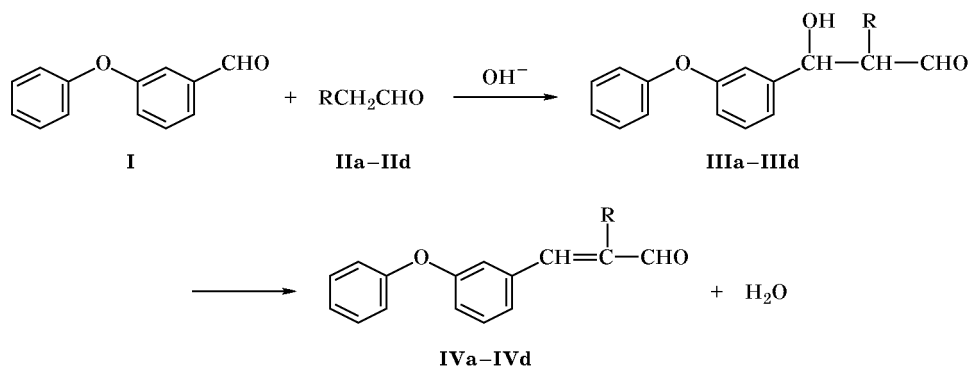
Aldehydes constitute an important class of carbonyl compounds which are widely used in synthetic organic chemistry due to their high reactivity. The presence in a single molecule of a carbonyl group, a double C=C bond, and a diphenyl ether moiety gives rise to specific properties of such compounds, especially 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–IIIId** 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. C₁₆H₁₄O₂. 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. C₁₈H₁₈O₂. 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. C₁₈H₁₈O₂. 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.