SYNTHESIS OF HOMOLOGS OF p-PHENOXYSTYRENE

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Of the derivatives of diphenyl oxide with multiple bonds in the side chain, the following have been described in the lierature: p-phenoxyphenyl-β-acylic acid, p,p'-di-(β-carboxyvinyl)diphenyl oxide [1], o- and p-phenoxystyrenes [2-5], and p,p'-divinyldiphenyl oxide [6]. Homologs of p-phenoxystyrene are unknown.

This communication was devoted to the production of new monomers—homologs of p-phenoxystyrene. Their synthesis was accomplished by dehydration of the corresponding alcohols. For this purpose we produced p-phenoxyphenylmethylcarbinol, p-phenoxyphenylethylcarbinol, p-phenoxyphenylpropylcarbinol, p-phenoxybenzyldimethylcarbinol, p-phenoxyphenyldimethylcarbinol, and p-phenoxyphenylmethylethylcarbinol. Dehydration over $ZnCl_2$ (250-300°; 2-4 mm) converted the carbinols to p-phenoxystyrene, β-methyl-p-phenoxystyrene, β-ethyl-p-phenoxystyrene, β,β-dimethyl-p-phenoxystyrene, α-methyl-p-phenoxystyrene, and α,β-dimethyl-p-phenoxystyrene. The structures of the compounds obtained were confirmed by their UV and IR spectra.

EXPERIMENTAL SECTION

p-Phenoxyphenylmethylcarbinol (I). A solution of 390 g of p-phenoxyphenyl bromide in 400 ml of abs. ether was added dropwise over a period of three hours to 38.2 g of magnesium shavings, after which the mixture was boiled for another hour. When the reaction mass had cooled, a solution of 115 ml of acetaldehyde in 100 ml of ether was added dropwise and the mixture boiled for 0.5 h. The complex was decomposed with a mixture of ice and conc. H_2SO_4 with mixing. After the usual treatment we obtained 183.5 g of a product, b. p. 106-170° (2 mm), representing partially dehydrated (I). The condensation product of the bromide—p,p'-diphenoxydiphenyl, with m. p. 158°, was isolated from the nondistilling residue. A Grignard reaction of 12.15 g of magnesium shavings, 71 g of methyl iodide in a solution of 200 ml of ether, and 99.1 g of p-phenoxybenzaldehyde in a solution of 100 ml of ether produced 86.9 g (81.14%) of partially dehydrated (I); b. p. 157-160° (2.5-3 mm); n_D^{20} 1.5932.

p-Phenoxystyrene (II). A 19-g portion of (I) was added dropwise to 15 g of $ZnCl_2$ (250-300°, 3 mm) over a period of 40 min. As the (II) was formed, it was distilled off. A yield of 13 g (74.7%) of pure (II) was obtained; b. p. 115-117° (2 mm); n_D^{20} 1.6010. The addition of an inhibitor, for example, pyrogallol (0.01 parts by weight) is necessary for distillation and storage.

Into a 0.5-liter Favorsky flask with reflux condenser 20 cm high, we loaded 150 g of dry, powdered p-phenoxyphenyl-β-acrylic acid, 3 g of copper powder, and 1.5 g of pyrogallol, after which the mixture was heated in a stream of nitrogen to 250° (50-100 mm). Distillation of (II) began at this temperature. The crude product was purified by washing with a dilute solution of $NaHCO_3$ and distillation in the presence of 0.1 g of pyrogallol. We obtained 48 g (39.2%) of (II); b. p. 115-120° (3-4 mm); n_D^{20} 1.6017; d_4^{20} 1.0612. Found: C 85.58; H 6.43%; $C_{14}H_{12}O$. Calculated: C 85.68; H 6.16%.

p-Phenoxyphenylethylcarbinol (III) and β-Methyl-p-Phenoxystyrene (IV). A Grignard reaction of 43.6 g of ethyl bromide in 150 ml of abs. ether, 9.73 g of magnesium shavings, and 79.3 g of p-phenoxybenzaldehyde produced 74.4 g (81.5%) of (III), partially dehydrated during distillation. The alcohol isolated contained an admixture of (IV); b. p. 155-160° (1 mm); n_D^{20} 1.5828; d_4^{20} 1.0856. Found: C 79.33; H 6.59%. $C_{15}H_{16}O_2$. Calculated: C 78.92; H 7.06%. The alcohol was dehydrated over $ZnCl_2$ under the conditions described above. From 57.4 g of (III), we obtained 39 g (74.2%) of (IV); b. p. 142-144° (3-3.5 mm); n_D^{20} 1.5983; d_4^{20} 1.0587. Found: C 85.55; H 6.72%. $C_{15}H_{14}O$. Calculated: C 85.68; H 6.71%.

p-Phenoxyphenylpropylcarbinol (V) and β-Ethyl-p-Phenoxystyrene (VI). From 41.7 g of propyl chloride in 150 ml of ether, 12.9 g of magnesium shavings, and 99.1 g of p-phenoxybenzaldehyde in 50 ml of ether, we obtained 92.2 g (76.1%) of crude (V); b. p. 155-158° (2 mm); n_D^{20} 1.5696; d_4^{20} 1.0768. During distillation the alcohol is dehydrated, and hence always contains an admixture of (VI). Found: C 80.43; H 7.55%. $C_{16}H_{18}O_2$. Calculated: C 79.31; H 7.48%.

After dehydration of 85 g of (V) over 65 g of $ZnCl_2$ (250-300°, 3-4 mm), we obtained 73.5 g of crude (VI). After two redistillations, yield 41 g (52.1%) pure (VI); b. p. 127-129° (1 mm); n_D^{20} 1.5960; d_4^{20} 1.0365. Found: C 85.67; H 7.30%. $C_{16}H_{16}O$. Calculated: C 85.68; H 7.19%.

p-Phenoxybenzyldimethylcarbinol (VII) and β,β-Dimethyl-p-Phenoxystyrene (VIII). From 142.14 g of p-phenoxybenzaldehyde in 300 ml of ether, 17.38 g of magnesium shavings, and 40.8 g of absolute acetone, we prepared an organomagnesium compound, which then was decomposed with a mixture of ice and H_2SO_4. The white solid product isolated in the form of a suspension was filtered off and washed on the filter with ether and water; weight 33 g. After washing and drying, the ether was distilled off, and the residue was distilled. Yield 67.7 g (46.6%) (VII); b. p. 152-155° (2 mm); n_D^{20} 1.5680; d_4^{20} 1.0820. Found: C 79.43; H 7.22%. $C_{16}H_{18}O_2$. Calculated: C 79.31; H 7.48%. The residue after distillation (28 g), as well as the filtered product, consists of 1,2-di-(p-phenoxyphenyl)-ethane. After crystallization from toluene: b. p. 252° (3 mm); m. p. 120-121°. Found: C 85.30; H 6.02%. $C_{26}H_{22}O_2$. Calculated: C 85.21; H 6.02%. (VII) was dehydrated over $ZnCl_2$ under the conditions used earlier. The dehydration product was purified by distillation. Yield of (VIII) 71.46%; b. p. 135-138° (2-3 mm); n_D^{20} 1.5850; d_4^{20} 1.0426. Found: C 85.81; H 7.21%. $C_{16}H_{16}O$. Calculated: C 85.68; H 7.19%.

p-Phenoxydiphenyldimethylcarbinol (IX) and α-Methyl-p-Phenoxystyrene (X). From 62.5 g methyl iodide in a solution of 150 ml of ether, 10.7 g of magnesium shavings, and 50.2 g of the methyl ester of p-phenoxybenzoic acid, dissolved in 50 ml of abs. ethyl ether, we obtained 45.6 g of partially dehydrated (IX); b. p. 129-134° (2-3 mm). When it was dehydrated over $ZnCl_2$ (250-300°, 2 mm), we isolated (X) in 78.7% yield; b. p. 133° (1.5 mm); n_D^{20} 1.5921; d_4^{20} 1.0597. Found: C 85.77; H 6.78%. $C_{15}H_{14}O$. Calculated: C 85.68; H 6.71%. To avoid polymerization, the product was distilled in the presence of 0.01 g of pyrogallol.

p-Phenoxyphenylmethylethylcarbinol (XI) and α,β-Dimethyl-p-Phenoxystyrene (XII). From 65.4 g of ethyl bromide in 200 ml of ether, 14.58 g of magnesium shavings, and a solution of 68.5 g of the methyl ester of p-phenoxybenzoic acid in 50 ml of ethyl ether, we obtained (XI), which was subjected without further purification to dehydration over $ZnCl_2$ under the conditions described above. Yield 52.2 g of crude (XII). After purification by distillation, we isolated 42.2 g (62.4%) of the pure product; b. p. 144° (1 mm); n_D^{20} 1.5790; d_4^{20} 1.0305. Found: C 85.66; H 7.39%. $C_{16}H_{16}O$. Calculated: C 85.68; H 8.19%.

CONCLUSIONS

Homologs of p-phenoxystyrene that had not been described in the literature have been synthesized: β-methyl-p-phenoxystyrene, β-ethyl-p-phenoxystyrene, β,β-dimethyl-p-phenoxystyrene, α-methyl-p-phenoxystyrene, and α,β-dimethyl-p-phenoxystyrene.

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