THERMAL POLYMERIZATION OF p-ALLYLPHENYL PHENYL ETHER

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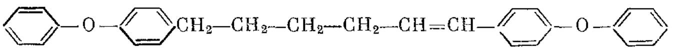
p-Allyl-anisole and -phenetole are well known: their isolation from natural essential oils, their synthesis, and their polymerization have been described. Investigations have been conducted over many years on the thermal transformations of p-allyl-anisole and -phenetole, and the structure of the dimers obtained has been studied [1-5].

The present paper is concerned with the synthesis and thermal polymerization of p-allylphenyl phenyl ether. When this was heated in sealed tubes (200-250°), dimers, trimers, and a small amount of tetramers were obtained. Products of higher molecular weight were not detected. The yields of oligomers depended on the reaction temperature and time (Table 1). The optimum results (65%) were obtained in experiments lasting 100 h at 250°. Under these conditions p-allylanisole is less active. Thus, in the course of 100 h at 250° only 30% conversion of p-allylanisole occurred (Table 2). The thermal polymerization of p-allylphenyl phenyl ether was conducted in tubes filled with air, oxygen, or nitrogen. The results show that the extent to which the process goes depends not only on the reaction temperature and time, but also on the amount of oxygen in the tube (Table 3).

In the fractionation of the thermal-polymerization products (reaction temperatures 200-250°) we isolated unchanged starting substance (fraction I), two dimer fractions, b.p. 295-300° (2 mm) (fraction II) and 300-325° (2 mm) (fraction III), and a glassy residue (fraction IV). From fraction II on standing we isolated a crystalline substance of m.p. 89-90°, and from fraction III – a very small amount of products with m.p. 206-212°. After the separation of the product with m.p. 89-90° the residue was a viscous substance with b.p. 280-283° (3 mm) and f.p. 2°. In the fractions from the experiments conducted at 275° and higher the products of m.p. 89-90° were not detected. Nor were the products of m.p. 206-212° found in experiments conducted at 200°. Judging from the molecular weight, iodine value, and elemental analysis, the compound of m.p. 89-90° and the viscous substance of b.p. 280-283° (3 mm) were dimers with one double bond.

The structure of the dimers was studied by the investigation of oxidation and of the molecular spectra. The near-UV absorption spectrum of the dimer of m.p. 89-90° is in the wavelength range 2700-3200 A and contains a broad absorption band of high intensity (log $\varepsilon > 4.0$) with a maximum at 2625 A. The intensity of this band is about ten times as great as that of the corresponding band of the benzene type in the previously measured spectra of diphenyl ether and p-allylphenyl phenyl ether. This is indicative of the conjugation of the double bond with the benzene ring.

In the oxidation of the dimer of m.p. 89-90° with potassium permanganate in acetone solution we obtained p-phenoxybenzoic and 5-p-phenoxyphenylvaleric acids. On the basis of these data for the solid dimer of m.p. 89-90° we propose the structure of 1,6-bis-p-phenoxyphenyl-1-hexene, analogous to that found earlier for the dimer of p-allylanisole [1].



By the same methods we established an identical structure for the liquid dimer. By its oxidation with potassium permanganate in acetone solution we obtained p-phenoxybenzoic and 5-p-phenoxyphenylvaleric acids, and we determined its absorption spectrum of the near UV. The IR spectra of the solid and liquid dimers were identical, and therefore these compounds are identical in structure. The band at 966 cm^{-1} found for solid dimer indicates the trans form. The liquid dimer is a mixture of cis and trans isomers with respect to the C=C bond (band at 689 cm^{-1}) in which the content of the trans form, judging from the intensity of the band at 966 cm^{-1}, is 25-30%.

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TABLE 1. Thermal Polymerization of p-Allylphenyl Phenyl Ether

Reaction temp., °C	Fraction	Yield, %, in a time, h, of				
		5	10	25	50	100
200	I — unchanged p-allylphenyl phenyl ether	—	98.0	97.0	95.0	—
	II — 295-300° (2 mm)	—	0.75	1.0	2.4	—
	III — 300-325° (2 mm)	—	0.80	1.0	1.6	—
	IV — residue	—	0.45	1.0	1.0	—
250	I	92	87	76	76	35
	II	4	6	9	11	19
	III	2	3	7	4	29
	IV	2	4	8	9	17
250-275	I	—	—	49	26	—
	II	—	—	12	24	—
	III	—	—	12	—	—
	IV	—	—	27	50	—

TABLE 2. Thermal Polymerization of p-Allylanisole at 250° [1]

Fraction	Yield, %, in a time, h, of			
	100	200	238	440
I — unchanged p-allylanisole	70	60	55	20
II — 200-220° (3 mm)	15	17	16	26
III — 220-300° (3 mm)	8	12	12	23
IV — residue	7	9	16	30

EXPERIMENTAL

p-Bromophenyl Phenyl Ether [6]. In the bromination of diphenyl ether in CCl_4 solution at 5-10° we obtained mono- and di-bromo derivatives of diphenyl ether. The monobromo derivative had the following properties: b.p. 166-167.5° (14 mm); n_D^{20} 1.6155; d_4^{20} 1.4209.

p-Allylphenyl Phenyl Ether. p-Allylphenyl phenyl ether was prepared by the Grignard reaction. A three-necked flask was charged with 15.7 g of magnesium turnings and 200 ml of dry ether, and a solution of 160.6 g of p-bromophenyl phenyl ether in 300 ml of dry ether was added with stirring. The bromo compound reacted with magnesium with great difficulty, and it was necessary to apply heat. When the addition of the bromo compound was complete, the mixture was heated further for 2 h in a water bath. It was cooled, and a solution of 53.7 g of allyl chloride in 50 ml of dry ether was added gradually; the mixture was then heated for 2 h. On the next day the organomagnesium complex was decomposed with ice and water, and the mixture was acidified with dilute (1 : 1) hydrochloric acid. The ether layer was separated, filtered from precipitate, and dried over Na_2SO_4. 18 g of a solid product remained on the filter.

When the reaction was conducted with allyl bromide the amount of the solid product was reduced to 2 g. After recrystallization from a mixture of benzene and alcohol it had m.p. 152-154°. Found %: C 85.53; H 5.42; mol. wt. 327.9. $C_{24}H_{18}O_2$. Calculated %: C 85.15; H 5.32; mol. wt. 338.38. The data obtained correspond to 4,4'-diphenoxybiphenyl. The 4,4'-position is confirmed by the IR spectrum (intense band at 830 cm^{-1}).

In the fractionation of the ethereal solution we isolated 73.1 g (54%) of p-allylphenyl phenyl ether and 12.9 g of a solid product (mixture of 4,4'-diphenoxybiphenyl and a substance of unknown structure, m.p. 78-79°). p-Allylphenyl phenyl ether has b.p. 127-130° (2 mm); n_D^{20} 1.5730; d_4^{20} 1.0423. Found %: C 85.82; H 6.68; iodine value 121.57. $C_{15}H_{14}O$. Calculated %: C 85.68; H 6.71; iodine value 120.73.

Dimer of M.p. 89-90°. In the distillation of the polymerization products, crystals immediately began to separate from fraction II. When they had been separated, more solid product came down from the viscous filtrate after long standing at 25-30°. By two crystallizations from acetone we obtained a colorless crystalline compound — 1,6-bis-p-phenoxyphenyl-1-hexene — with m.p. 89-90°. Found %: C 85.61; H 6.83; mol. wt. 394 (cryoscopy); iodine value 62. $C_{30}H_{28}O_2$. Calculated %: C 85.67; H 6.72; mol. wt. 420.52; iodine value 60.36.

TABLE 3. Effect of the Gas Medium on the Thermal Polymerization of p-Allylphenyl Phenyl Ether

Experimental conditions	Fraction	Yield, %, in an atmosphere of		
		oxygen	air	nitrogen
250°	I — unchanged p-allylphenyl phenyl ether	68.5	76	81.5
25 h	II — 274-280° (2 mm)	12.5	9	8.5
	III — 300-325° (2 mm)	6.0	7	8.0
	IV — residue	13.0	8	2.0

Oxidation: A solution of 4 g of $KMnO_4$ in 400 ml of dry acetone was added a little at a time over a period of 12 h to a solution of 4 g of the product of m.p. 89-90° in 100 ml of dry acetone at 0-2° [7]. The precipitated mixture of acids and MnO_2 was filtered off and washed with acetone. The precipitate was suspended in a little water, and SO_2 was passed until the MnO_2 had been decomposed completely. The acid was filtered off, washed with water, and dried. We isolated 3.78 g of a mixture of acids. Separation was effected by repeated boiling with water. We isolated p-phenoxybenzoic acid of m.p. 160-161°, undepressed by admixture of known p-phenoxybenzoic acid, and 5-p-phenoxyphenylvaleric acid of m.p. 59-61°. The latter was identified by its melting point with synthesized 5-p-phenoxyphenylvaleric acid.

3-p-Phenoxyphenyl-1-propanol. 16.5 g of ethyl p-phenoxycinnamate was reduced as a solution in 100 ml of absolute alcohol with 10 g of sodium (Bouveault-Blanc). 100 ml of water was then added to decompose the alkoxide, and water and alcohol were distilled off; the solid residue was treated with hot water. The oily layer formed was separated, washed with water, dried, and distilled. We obtained 6.2 g (44.28%) of 3-p-phenoxyphenyl-1-propanol, b.p. 166-168° (2 mm); n_D^{20} 1.5745.

p-3-Bromopropylphenyl Phenyl Ether. 2.2 g of phosphorus tribromide was added dropwise to a solution of 5.7 g of 3-p-phenoxyphenyl-1-propanol in 20 ml of chloroform, and the mixture was heated for 2 h. The reaction mixture was cooled and decomposed with water, and the organic layer was separated, washed with water, dried, and fractionated. We isolated 2.9 g (40.2%) of the bromo compound, b.p. 184-186° (6 mm); n_D^{20} 1.5855.

5-p-Phenoxyphenylvaleric Acid. 4.8 g of malonic ester was added with stirring to an alcoholic solution of sodium ethoxide (from 0.68 g of sodium and 100 ml of absolute alcohol). 8.7 g of p-3-bromopropylphenyl phenyl ether was added to the cooled solution of the sodiomalonic ester, and the mixture was boiled for 5 h. Precipitated sodium bromide was filtered off. The filtrate was hydrolyzed by boiling it with 4 g of KOH for 3 h, alcohol was driven off, the solid residue was dissolved in water, the solution was washed with ether and acidified with dilute hydrochloric acid, and the acid liberated was extracted with ether. Ether was driven off, and the residue was decarboxylated at 200° with an addition of CuO. After the usual treatment, distillation, and recrystallization from petroleum ether we obtained 2.5 g of 5-p-phenoxyphenylvaleric acid, m.p. 65-66° [8]. Found %: C 75.98; H 6.79; mol. wt. 276.0 (titration). $C_{17}H_{18}O_3$. Calculated %: C 75.53; H 6.71; mol. wt. 270.31.

Liquid Dimer. The viscous product remaining after the separation of the solid dimer of m.p. 89-90° had the following properties: b.p. 280-283° (3 mm); n_D^{20} 1.6102; f.p. 2°; η_{50} 106.7; η_{100} 12.0. Found %: C 85.60; H 6.67; mol. wt. 405 (cryoscopy); iodine value 57.97; $C_{30}H_{28}O_2$. Calculated %: C 85.67; H 6.72; mol. wt. 420.52; iodine value 60.35.

CONCLUSIONS

1. The thermal polymerization of p-allylphenyl phenyl ether was studied.

2. In thermal polymerization at 250° 1,6-bis-p-phenoxyphenyl-1-hexene is obtained in two isomeric forms: a solid dimer — the trans form — and a liquid dimer — the cis form containing 25-30% of the trans isomer. The structure of the dimers was established by investigation of their oxidation and their molecular spectra.

3. The following previously undescribed compounds were synthesized: p-allylphenyl phenyl ether, p-3-bromophenylphenyl phenyl ether, 3-p-phenoxyphenyl-1-propanol, and 4,4'-diphenoxybiphenyl.

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