Chemistry

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Abstract

Full Text

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Reaction of Diphenyl with tert-Butyl Peroxide

When tert-butyl peroxide decomposes in hydrocarbons having mobile hydrogen atoms—for example, in diphenylmethane—abstraction of these atoms by active radicals gives stable benzyl-type radicals. As a result of recombination of the latter, reaction of the dimers with the peroxide, etc., the polymer polydiphenylmethylene is formed (1), which, in the course of chain growth, undergoes methylation at the benzene rings (2).

In the present work we investigated, under the same conditions, the behavior of hydrocarbons that do not have mobile hydrogen atoms, in particular diphenyl. In the products of the reaction of the latter with tert-butyl peroxide at 200° there were found compounds of three types: oligomers with molecular weight 380–400, a polymer in the form of a yellow powder soluble in benzene, with m.p. 100–120°, molecular weight up to 6000 (ebullioscopically in benzene), and individual methylation products. The latter are a mixture of isomeric monomethyldiphenyls, which, according to gas-liquid chromatography data (Fig. 1), contains predominantly 4-methyl-diphenyl (53%), 28% of the *m*-isomer, and 19% of the *o*-isomer.

Homolytic methylation of benzene and its derivatives during decomposition of acetyl peroxide was studied by Schwarz et al. (3), and during decomposition of tert-butyl peroxide by Kovli and Waters (4).

The conversion of diphenyl in the initial stages of the reaction with tert-butyl peroxide, which in this process decomposes mainly into methyl radicals and acetone, may be represented by the following scheme, analogous to the arylation scheme according to Iliel et al. (5).

$$\mathrm{Ph{-}Ph} + \mathrm{CH_3^{\bullet}} \longrightarrow \mathrm{(I)} \longrightarrow \mathrm{Ph{-}Ph{-}CH_3} \quad \mathrm{(II)}$$

As methylated diphenyls accumulate in the reaction mixture, the attack of free radicals formed during peroxide decomposition is directed predominantly at the mobile α-hydrogen atoms of the methylene group. This is indicated, in particular, by the increase in the tert-butyl alcohol : acetone ratio in the course of the reaction, observed according to gas-liquid chromatography data. The polymer is apparently formed as the result of repeated processes of methylation

Fig. 1. Chromatogram of diphenyl methylation products

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Fig. 2. Change in the composition of the reaction mixture during polyrecombination of diphenyl

Figure 2: Fig. 2. Change in the composition of the reaction mixture during polyrecombination of diphenyl

of the products of recombination of methyldiphenyl radicals, abstraction of a hydrogen atom from part of the methyl groups, etc.

(III)

For the polymer, found, %: C 91.68; H 7.05
For structure III ($C_{31}H_{30}$), calculated, %: C 92.48; H 7.51

The low melting point of the polymer is apparently connected with its branched structure and the presence of dimethylene bridges in the *m*-position, since a polymer of regular structure,

$$-CH_2-Ph-Ph-CH_2-$$

has m.p. 530° (6).

The IR spectrum of the polymer shows absorption corresponding both to CH_2 groups (2920, 2860 cm^{-1}) and to CH_3 groups (2960 cm^{-1}), as well as absorptions corresponding to a trisubstituted benzene ring (770, 700 cm^{-1}). In the NMR spectrum of a benzene solution of the polymer, chemical shifts of $50 \cdot 10^{-7}$ and $60 \cdot 10^{-7}$ were found, which can be assigned, respectively, to the protons of α-CH_3, α-CH_2, and β-CH_3 groups.

The yield of polymer as a function of the amount of peroxide introduced into the reaction is shown in Fig. 2 (curve 1). In the same figure, curve 3 represents the yield of oligomers—the by-products of the reaction.

Fig. 1. Chromatogram of diphenyl methylation products

Fig. 2. Change in the composition of the reaction mixture during polyrecombination of diphenyl: **1** —content of polymeric product in the mixture, **2** —monomer content, **3** —oligomer content

Investigation of the oxidation products of the oligomers gives grounds to regard them as products of recombination of cyclohexadienyl radicals (5) of type I—primary methylation products—and of their subsequent transformation into dimethyl derivatives of quaterphenyl, for example *m*-phenyl-4-diphenylbenzene

(IV) and its isomers. The dicarboxylic acids corresponding to these hydrocarbons were isolated as a mixture from the products of oxidation of the oligomers with chromic anhydride in acetic acid.

Similarly, at a consumption of 1.5 or more moles of peroxide, polymers were obtained from diphenyl oxide (mol. wt. 3000, m.p. 160-177°) and benzophenone (mol. wt. $> 15\,000$, m.p. 205-215°). The IR spectra and elemental-analysis data also indicate the structure of the polymer chain from compounds methylated beforehand, as well as methylation of the chain during its growth. Thus, the polymer from diphenyl oxide may be represented by the following probable structure:

(V)

For the polymer found, %: C 85.38; H 6.03
For the structure ($C_{15}H_{14}O$) calculated, %: C 85.71; H 6.67

Experimental Part

Diphenyl was recrystallized from alcohol, m.p. 70.5–71°. The reaction of diphenyl and other compounds with tert-butyl peroxide (purity 99.5% by chromatography) was carried out in a nitrogen atmosphere at 200°. The peroxide was added dropwise with stirring ([1]). From the reaction mixture, unreacted diphenyl was distilled off in vacuo together with the methylation products. The latter were concentrated in the alcoholic mother liquor after recrystallization of the diphenyl recovered from the reaction, distilled in vacuo, and analyzed on gas–liquid chromatographs.

The isomers were identified by adding to the mixture pure methyldiphenyls, synthesized at the Institute of Organic Chemistry of the Academy of Sciences of the USSR, corresponding to literature data and kindly provided by E. P. Kaplan.

The residue after distillation of diphenyl was dissolved in benzene, and the polymer was reprecipitated with methanol. Oligomers were isolated from the filtrate after distillation of the solvents in the form of a yellow product with m.p. 80–90° (after recrystallization from alcohol). Oxidation of the oligomers with chromic anhydride in acetic acid gave organic acids with molecular weight 400 (cryoscopically in benzene) and neutralization equivalent 195 (average value), which is close to the corresponding values for acids corresponding to hydrocarbon IV and its isomers. (For $C_{26}H_{18}O_4$, molecular weight 394, neutralization equivalent 195.) The corresponding values for diphenyldicarboxylic acids are 210 and 370.

Polymers from diphenyl oxide and benzophenone were isolated after dissolving the reaction mixture in benzene and reprecipitation with methanol.

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Note: Figure translations are in progress. See original paper for figures.