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Abstract

Full Text

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ON THE POSSIBILITY OF ISOMERIZATION OF THE PHENYL RADICAL IN FREE-RADICAL REACTIONS OF DIPHENYLMERCURY

In a previous communication ([1]), using carbon C^{14} as a label, we showed the absence of isomerization of the phenyl radical in the reactions of photo- and thermal decomposition of benzoyl peroxide in benzene solution. It was of interest to test whether isomerization of the phenyl radical would be observed if other compounds were taken as its source. In the present work we used diphenylmercury (DPM), labeled with carbon C^{14} in the 1,1′-positions of the benzene rings.

The synthesis of DPM was carried out according to the scheme:

$$CH_3{-}C_6H_4^* \longrightarrow COOH{-}C_6H_4^* \longrightarrow COCl{-}C_6H_4^* \longrightarrow CONH_2{-}C_6H_4^* \longrightarrow NH_2{-}C_6H_4^* \longrightarrow I{-}C_6H_4^* \longrightarrow {}^*$$

Photodecomposition was carried out by irradiating solutions of DPM in benzene (molar ratio 1 : 40) with a PRK-2 quartz lamp at a distance of 10 cm at 25–30° for 90 hours.

After completion of the reaction, metallic mercury was filtered off. Benzene was distilled from the filtrate, and then diphenyl was steam-distilled. Diphenyl recrystallized from methyl alcohol had m.p. 69°. A mixed sample gave no depression of the melting point. The experimental results are given in Table 1.

Table 1

DPM, g	Taken into reaction: relative activity of DPM, imp/min	Taken into reaction: benzene, ml	Taken into reaction: molar ratio DPM : benzene	Taken into reaction: Cu metal, g	Relative activity, imp/min: diphenyl	Relative activity, imp/min: benzoic acid after oxidation	Relative activity, imp/min: theoretical activity of benzoic acid in the absence of isomerization	Error, $B_{\text{benz. acid}}/B_{\text{diphen.}}$	
Photodecomposition of diphenylmercury in benzene for 90 hours									
3	970	33	1 : 40		483	876	828	1.81	5.8
3	970	33	1 : 40		486	860	831	1.77	3.5

DPM, g	Taken into reaction: relative activity of DPM, imp/min	Taken into reaction: benzene, ml	Taken into reaction: molar ratio DPM : benzene	Taken into reaction: Cu metal, g	Relative activity, imp/min: diphenyl	Relative activity, imp/min: benzoic acid after oxidation	Relative activity, imp/min: theoretical activity of benzoic acid in the absence of isomerization	Error, $B_{\text{benz. acid}}/B_{\text{diphen.}}$	
Thermal decomposition of diphenylmercury in benzene at 190° for 170 hours									
3	970	16.5	1 : 20	0.6	936	1622	1605	1.73	1.1
3	970	16.5	1 : 20	0.6	920	1588	1577	1.72	1.1

It is known from the literature ([2]) that additions of metal powders Pt, Pd, Ni,

Cu significantly lower the temperature of thermal decomposition of DPM in solvents.

In the case of the reaction in benzene, under these conditions diphenyl is formed exclusively at the expense of DPM radicals ([3]); the solvent—benzene—does not take part in the formation of diphenyl. In this connection we decided to test the possibility of isomerization of the phenyl radical under these conditions as well.

Isolation and purification of biphenyl were carried out in the same way as in the photoreaction. The results of the experiments are given in Table 1. Biphenyl was oxidized with chromic anhydride by the method of (4). To detect possible isomerization of the phenyl radical, the relative activities of biphenyl and of the benzoic acid obtained by its oxidation were compared.

The relative activities were determined with an internal gas-flow counter with an accuracy of 3-4%; for this purpose the samples being measured were burned by the micromethod to CO_2. It may be assumed that isomerization is absent (hydrogen migration does not occur), or that isomerization occurs with migration of the hydrogen atom to the meta position of the benzene ring (a), and with migration of the hydrogen atom to any position of the benzene ring (b). Let us introduce the following conventional notation: A is the relative activity of the substance (imp/min) under the condition that all the activity is concentrated on one carbon atom in the molecule; B is the relative activity of the substance (imp/min) taking into account all carbon atoms in the molecule (the relative activity obtained from the experiment); n is the number of carbon atoms in the molecule. According to the adopted notation, $B = A/n$. For brevity of presentation we do not give the detailed arguments concerning the distribution of relative activities for the various cases; they were set out in the preceding paper (1), and we shall present them as follows:

In the case of absence of isomerization,

$$A_{\text{biphen}} = A_{\text{benz. acid}}; \quad B_{\text{biphen}} = A_{\text{biphen}}/12; \quad B_{\text{benz. acid}} = A_{\text{benz. acid}}/7 = 12B_{\text{biphen}}/7; \quad B_{\text{benz. acid}}/B_{\text{biphen}}$$

For case (a):

$$A_{\text{benz. acid}} = \frac{2}{3}A_{\text{biphen}}; \quad B_{\text{benz. acid}} = \frac{2}{3}A_{\text{biphen}}/7,$$

but since

$$A_{\text{biphen}} = 12B_{\text{biphen}},$$

then

$$B_{\text{benz. acid}} = 1.1 B_{\text{biphen}} \quad \text{and} \quad B_{\text{benz. acid}}/B_{\text{biphen}} = 1.1.$$

For case (b):

$$B_{\text{biphen}} = B_{\text{benz. acid}},$$

since the label is uniformly distributed over all six carbon atoms of the benzene ring, and

$$B_{\text{benz. acid}}/B_{\text{biphen}} = 1.$$

From the data of Table 1 it is seen that, for the photoreaction, the mean error in the ratios of the relative activities of benzoic acid to biphenyl is about 4%, and for the thermoreaction 1.4%, relative to theory. These figures are at the limit of experimental error. On the basis of the data obtained it may be considered that both in photo- and in thermoreactions isomerization of the phenyl radical is not observed, i.e., the reactions proceed as follows:

$$(C_6H_5^*)_2Hg + C_6H_6 \xrightarrow{h\nu} C_6H_5^*{-}C_6H_5 + Hg + C_6H_6^*$$

$$\downarrow \text{ oxidn.}$$

$$\tfrac{1}{2}\, C_6H_5{-}COOH + \tfrac{1}{2}\, C_6H_5{-}{}^*COOH$$

and for catalytic decomposition

$$(C_6H_5^*)_2Hg \xrightarrow{Cu} C_6H_5^*{-}{}^*C_6H_5 + Hg.$$

Migration of the ^{14}C label over the benzene ring does not occur at any stage of the synthesis of diphenylmercury.

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