Chemistry

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Abstract

Full Text

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ON THE ORDER OF ADDITION OF LITHIUM TO DIPHENYL

A. D. Petrov and T. I. Chernysheva (^{1}) showed that, in the reaction of trimethylchlorosilane and tributylchlorosilane with dilithium dihydrodiphenyl, in the first case monotrimethyldisilyldihydrodiphenyl is formed, and in the second, dibutyldisilyldihydrodiphenyl.

In our condensation of dilithium dihydrodiphenyl with alkyl halides (^{2}) (*n*-butyl-, *n*-hexyl-, sec.-octyl-, 2-ethylhexyl-, *n*-nonyl-, and *n*-decyl bromides), both monoalkyldihydrodiphenyls and dialkyldihydrodiphenyls were obtained. However, the question of the site of addition of lithium to diphenyl, and consequently also of the most probable positions of the alkyl substituents in the alkyldihydrodiphenyls, remained unclear. According to Schlenk and Bergmann (^{3}), addition of lithium to diphenyl occurs in the 1,4-position:

$$\mathrm{Ph{-}Ph} + 2\,\mathrm{Li} \longrightarrow \mathrm{Li{-}C_6H_4{-}C_6H_4{-}Li}$$

According to spectral analysis (^{4}), for the mono- and dialkyldihydrodiphenyls and dihydrodiphenyls obtained by us, addition of lithium to diphenyl takes place predominantly in the 2,5-position:

$$\mathrm{Ph{-}Ph} + 2\,\mathrm{Li} \longrightarrow \mathrm{Li{-}C_6H_4{-}C_6H_4{-}Li}$$

In the present work we attempted to prove the site of addition of lithium to diphenyl in two ways: by oxidation of dihydrodiphenyl with SeO_2 and by condensation of dilithium dihydrodiphenyl with benzyl bromide, leading to readily identifiable terphenyls. If addition of lithium proceeds in the 1,4-position, then, as a result of addition of one phenyl radical, we should have obtained *p*-terphenyl with m.p. 210°. If, however, addition of lithium proceeds in the 2,5-position, then we should have obtained *o*- or *m*-terphenyls with melting points of 56° and 84°, respectively.

The first route of proof proved unsuccessful: oxidation of dihydrodiphenyl with SeO_2 gave neither the expected products—neither phenylcyclohexadienone

$$\mathrm{C_6H_5{-}C_6H_7{=}O}$$

nor phenylquinone

$$C_6H_5{-}C_6H_3(=O)_2$$

and the dihydrodiphenyl was reduced to diphenyl

$$C_6H_5{-}C_6H_7 \xrightarrow{SeO_2} C_6H_5{-}C_6H_5$$

analogously to the oxidation of 9,10-dihydroanthracene described by Badger (5).

In the reaction of benzyl bromide with dilithium dihydrodiphenyl in ether medium, followed by dehydrogenation of the product over Pd on charcoal, there was ob-

obtained in 6–15% yield as a mixture of terphenyls. By the method we developed for separating the still residues from the pyrolysis of benzene (6), we isolated *o*- and *p*-terphenyls

$$\begin{gathered}\text{biphenyl} \xrightarrow{2\text{Li}} \text{lithiated biphenyl derivatives} + \text{lithiated biphenyl derivatives} \xrightarrow{C_6H_5Br} \\ \longrightarrow p\text{-terphenyl} + \text{hydrogenated } o\text{-terphenyl derivative} \xrightarrow{\text{Pd}} \\ \longrightarrow p\text{-terphenyl} + o\text{-terphenyl}\end{gathered}$$

We were unable to isolate *m*-terphenyl. Apparently, in this case we have a known analogy with the bromination of toluene, where, as is known, only the *o*- and *p*-isomers are likewise formed (7). Depending on the temperature of the experiment, one or another terphenyl predominated; at a reaction temperature of 30°, 50% *o*-terphenyl is formed, while at 0° the *p*-isomer predominates.

Infrared spectra were recorded for the terphenyls obtained on a UR-10 instrument in the region 400–700 cm^{-1} with a KBr prism and in the region 700–1400 cm^{-1} with a NaCl prism*. For *o*-terphenyl the following bands were found: 500 strong, 525 strong, 560 medium, 615 medium, 708 medium, 745–455 strong, 785 medium, 810 strong, 845 medium, 880 strong, 900 medium, 920 medium, 955 strong, 980 strong, 1015 medium, 1080 medium, 1110 strong, 1160 strong, 1185 strong. For *p*-terphenyl the following bands were found: 460, 618, 690, 750, 840, 910, 1010, 1030, 1050, 1080, 1130, 1180.

Thus, it may be considered that the addition of lithium to biphenyl proceeds both at the 1,4-position and at the 2,5-position (possibly the latter compound is formed as a result of isomerization of the former)*.

Experimental Part

Oxidation of dihydrodiphenyl with SeO_2. Preparation of dihydrodiphenyl. Into a flask filled with nitrogen were placed 77 g of biphenyl, 400 ml of absolute ether, 7 g of finely cut lithium, and glass beads. The flask was closed with a stopper and shaken on a shaker for 100 h. The reaction flask was then placed in an ice-water bath and, through a dropping funnel, first alcohol and then water were added; the ethereal solution was separated, washed successively with water, and dried. After removal of the solvent and freezing-out of unreacted biphenyl, the resulting (15 g) liquid dihydrodiphenyl was distilled. It had b.p. 84–85° at 4 mm; freezing point −5°; n_D^{20} 1.5603; D_4^{20} 0.9925. MR found 50.91, for $C_{12}H_{10}$ MR calculated 51.08.

Three grams of dihydrodiphenyl, 2 g of SeO_2, and 6 ml of nitrobenzene were taken. The mixture was heated in a flask with a reflux condenser. At 50° darkening began; at 80° the reaction proceeded vigorously and the temperature rapidly rose to 125°. The reaction mass was then heated for 2 h at 150°. The product was extracted with ether and filtered from Se. After removal of the solvent

The product was steam-distilled; the separated crystals, recrystallized from C_2H_5OH, had m.p. 68°.

Found, %:	C 92.81; 92.64;	H 6.45; 6.40
$C_{12}H_{10}$%. Calculated, %:	C 93.51;	H 6.42

Reaction of dilithium dihydrodiphenyl with bromobenzene. Into a flask filled with nitrogen were placed 77 g of diphenyl, 500 ml of absolute ether, and 8 g of finely cut lithium. Shaking on a rocking apparatus was continued for 100 hr. Then, at 0°, 157 g of bromobenzene was added. After the usual work-up and removal of the ether, the product was distilled on a column. The following were obtained (in grams): benzene 25, bromobenzene 55, diphenyl 57, and terphenyls 12.5 (11%). In experiments in which bromobenzene was added to dilithium dihydrodiphenyl at −15°, −30°, the yield of terphenyls was 5-8 g (5-8%). At 35° the yield of terphenyl was 13 g (12%).

Dehydrogenation of terphenyls. Into a flask with a long neck, equipped with a stirrer and thermometer, were placed 10 g of terphenyl and 2.1 g of Pd on carbon (Pd content 20%). The flask was placed in a Wood' s-metal bath and heated to 300–335°. Heating was continued for 40 min. After cooling, the crystalline product was extracted with 50 ml of benzene at 50°.

Separation of terphenyls. To separate the terphenyls, the products of several parallel experiments were combined. The entire mass was dissolved in benzene at 60°. On cooling the benzene, crystals separated; these were recrystallized

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* The infrared spectra were determined by E. D. Lubuzh, to whom the authors express their gratitude.

twice from benzene and had m.p. 203–205°. The mother liquor after isolation of *p*-terphenyl and the benzene extract after recrystallization were combined. The benzene was distilled off; after one day the remaining oily mass crystallized. These crystals were recrystallized from alcohol; they had m.p. 70–72° and, according to spectral analysis, were diphenyl, sometimes with a small impurity of *p*-terphenyl. From the alcoholic mother liquor, after removal of diphenyl, the alcohol was distilled off; a clear yellow, readily mobile liquid remained in the flask, freezing point +5°. After standing in a refrigerator for 3-5 days, this liquid crystallized. The crystals, recrystallized from alcohol, had m.p. 52°; they were *o*-terphenyl.

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