SYNTHESIS AND SELECTIVE HYDROGENATION
OF DIBENZYLBENzenes AND \( \alpha, \alpha' \)-BIS(BENZYLPHENYL)XYLENES

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In previous investigations [1, 2] we studied the hydrogenation of a number of dibenzylbenzenes at various temperatures and over various catalysts. In the present investigation we have carried out the hydrogenation of dibenzylbenzenes and \( \alpha, \alpha' \)-bis(benzylphenyl)xylenes (compounds containing three and five benzene rings, respectively, linked through methylene groups) over nickel and platinum dioxide at various temperatures.

We synthesized the hydrocarbons by the following schemes:

1. \[
\begin{array}{c}
\text{C}_{6}\text{H}_{4} - \text{CH}_{2} - \text{C}_{6}\text{H}_{4} \\
\text{100-150°}
\end{array}
\]

2. \[
\begin{array}{c}
\text{C}_{6}\text{H}_{4} - \text{C} - \text{C}_{6}\text{H}_{4}
\end{array}
\]

4-Benzylbiphenyl (I), p-dibenzylbenzene (II), and \( \alpha, \alpha' \)-bis-p-benzylphenyl-p-xylene (III) were also prepared by the acylation method in accordance with the following schemes:

3. \[
\begin{array}{c}
\text{C}_{6}\text{H}_{4} - \text{CH}_{2} - \text{C}_{6}\text{H}_{4} \\
\text{C}_{6}\text{H}_{4} - \text{COCl}
\end{array}
\]

4. \[
\begin{array}{c}
\text{C}_{6}\text{H}_{4} - \text{C} - \text{C}_{6}\text{H}_{4}
\end{array}
\]
o-Dibenzylbenzene (IV) was also prepared by organomagnesium synthesis by the scheme:

\[
\begin{align*}
\text{CHOCl} & \quad \text{COCl} & \quad \text{MgBr} \\
\overset{\text{MgBr}}{\text{CHOCl}} & \quad \overset{\text{COCl}}{\text{COCl}} & \quad \rightarrow \\
\end{align*}
\]

By alkylation of diphenylmethane with benzyl chloride we obtained (IV) and (II)—the latter in the larger amount. In the alkylation of biphenyl with benzyl chloride we obtained all three isomers—2-, 3-, and 4-benzylbiphenyls. The separation of the 2-, 3-, and 4-isomers was effected by fractional distillation and crystallization until a constant melting point was attained. One of these, m.p. 85°, was (I), for on oxidation it gave 4-phenylbenzophenone [3, 4]. This hydrocarbon was also obtained by the acylation method (m.p. 86°). The isomer of m.p. 54-56° has been regarded in the literature both as the 2-isomer [4] and the 3-isomer [5]. However, on the basis of the work of Freeman [6], who synthesized 2-benzylbiphenyl (m.p. 54-56°) as follows:

\[
\begin{align*}
\text{CH}_{2} \text{C}_{6} \text{H}_{5} & \quad \text{CHC}_{6} \text{H}_{5} \\
\text{CHC}_{6} \text{H}_{5} & \quad \text{CHC}_{6} \text{H}_{5} \quad \text{dehydrogenation} \\
\end{align*}
\]

it may be considered that the isomer of m.p. 54-56° is 2-benzylbiphenyl (V), which is confirmed by the ultraviolet spectra (Fig. 1), so that the isomer of m.p. 47° is 3-benzylbiphenyl (VI). The contradictory data on the melting points of (V) and (VI) is to be explained to a certain extent by the fact that their structures cannot be confirmed by the oxidation method [as was done in the case of (I)], for their oxidation goes in an extremely complex fashion [6].

The structure of the 2-isomer of m.p. 56° is confirmed by the absence of an ultraviolet absorption maximum at about 252 m\(\mu\). Such a phenomenon is characteristic for ortho-substituted biphenyls and is explained by the disturbance of the coplanarity of the benzene rings of biphenyl [7]. In Fig. 1, we give the ultraviolet spectra of the isomers of m.p. 85 and 47°. The isomer of m.p. 85° gives strong absorption at about 252 m\(\mu\) (\(\epsilon\) 20,000), which indicates the presence of a highly conjugated system characteristic for para isomers of biphenyl derivatives. In the alkylation of \(\alpha,\alpha'-\text{dichloro-p-xylene}\) with diphenylmethane, in addition to (III) its ortho isomer (VII) is formed (Table 1).

The complete hydrogenation of the hydrocarbons was carried out under a pressure of hydrogen in accordance with the scheme:

\[
\begin{align*}
\text{CHCH}_{2} \text{C}_{6} \text{H}_{5} & \quad \text{CHCH}_{2} \text{C}_{6} \text{H}_{5} \\
\overset{\text{Raney nickel}}{\text{C}_{6} \text{H}_{5}} & \quad \overset{\text{C}_{6} \text{H}_{5}}{\text{Raney nickel}} \\
\overset{170-180°}{\text{C}_{6} \text{H}_{5}} & \quad \overset{170-180°}{\text{C}_{6} \text{H}_{5}} \\
\end{align*}
\]

The hydrogenation of hydrocarbons of this type goes in almost quantitative yield, and there is no splitting off of rings such as we observed earlier [8] for hydrocarbons of the alkyltriphenylmethane type, in the hydrogenation of which, under the conditions indicated above, a certain amount of alkylcyclohexylmethanes is always formed. Whereas with the same catalyst but at 100-140° alkyltriphenylmethanes are hydrogenated to alkylcyclohexylphenylmethanes, and 1-p-benzylphenyl-2-phenylethane to 1-p-(cyclohexylmethyl)phenyl-2-phenylethane in about 50% yield, (I) is not hydrogenated at all at 120°, but at 140° it is hydrogenated to 4-(cyclohexylmethyl)biphenyl in 2-3% yield.

(III) is not hydrogenated either at 120° or at 140°, but at 170-180° all five rings are hydrogenated (bands characteristic for aromatic rings are absent from the ultraviolet spectrum). Interesting results were obtained in the hydrogenation of the hydrocarbons at identical temperature and in the same solvents over a platinum catalyst. In the case of (V), (VI), and (I) only one ring is hydrogenated in accordance with the scheme:

\[
\begin{align*}
\text{C}_{6} \text{H}_{5} & \quad \text{C}_{6} \text{H}_{5} \\
\overset{\text{PtO} \_2}{\text{C}_{6} \text{H}_{5}} & \quad \overset{\text{C}_{6} \text{H}_{5}}{\text{C}_{6} \text{H}_{5}} \\
\end{align*}
\]