Palladium-Catalyzed Decomposition of Azide. Formation of Benzonitrile from Benzyl Azide

Hiroshi Hayashi, Atsuyoshi Ohno, and Shinzaburo Oka*

Received November 11, 1975

Palladium metal catalyzes the decomposition of benzyl azide affording benzonitrile, benzylamine, and benzyldienebenzylamine. The presence of a suitable hydrogen-acceptor improves the yield of benzonitrile at the sacrifice of benzylamine, whereas the yield of benzyldienebenzylamine remains constant. A plausible scheme has been proposed for the reaction.

INTRODUCTION

The azide group possesses many qualities that enable it an excellent starting group for organic synthesis. It can be introduced into organic moiety by several convenient methods, even in the presence of various other functional groups. The dipolar character and the reactivity (or instability) of the azide group make it react in a variety of fashions. However, surprisingly little is known on its application to organic syntheses except for the syntheses of amines by reduction, carbonyl compounds by acid-catalyzed decomposition, and heterocyclic compounds by 1,3-dipolar addition. Some other transformations are restricted to azides of limited structures.

In the course of our studies on the chemistry of the azide group, we have found that a primary azide can be transformed into the corresponding nitrile by catalytic aid of palladium metal under such a mild condition as below 80°C in neutral solutions. In this paper will be reported the procedure and reaction condition. A brief discussion on the mechanism will also be presented.

It should be emphasized that the present procedure provides a method to obtain various nitriles without elongating the skeletal carbon-chain.

RESULTS

When a mixture of benzyl azide (1) and a catalytic amount of palladium black in benzene was refluxed for 30 min, benzonitrile (2), benzylamine (3), dibenzylamine (4), and benzyldienebenzylamine (5) were obtained in 43, 29, 2, and 27% yields, respectively.

\[
\text{PhCH}_2\text{N}_3 \xrightarrow{\text{Pd}^0/\text{PhH}} \text{PhCN} + \text{PhCH}_2\text{NH}_2 + (\text{PhCH}_2)_2\text{NH} + \text{PhCH} = \text{NCH}_2\text{Ph} \quad (1)
\]

The same, but a little bit slower, reaction took place at temperatures as low as 40°C provided the mixture was set under an atmosphere of nitrogen. Ethanol could be substituted for benzene, whereas amines retarded the reaction appreciably. High-dilution technique,
Table I. Palladium-Catalyzed Decomposition of 1a.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp., °C</th>
<th>Reaction Time, hr</th>
<th>Conv., %b</th>
<th>Yield of Product, %c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>40</td>
<td>1.5</td>
<td>100</td>
<td>43</td>
</tr>
<tr>
<td>Benzene</td>
<td>reflux</td>
<td>0.5</td>
<td>100</td>
<td>43</td>
</tr>
<tr>
<td>Benzene</td>
<td>reflux</td>
<td>0.25</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>Ethanol</td>
<td>reflux</td>
<td>0.5</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>reflux</td>
<td>2.0</td>
<td>96</td>
<td>42</td>
</tr>
<tr>
<td>n-Butylamine</td>
<td>reflux</td>
<td>2.0</td>
<td>84</td>
<td>29</td>
</tr>
</tbody>
</table>

a Method A. b Consumed 1. c Based on 1 used. d Method B. e 99.5%.

Table II. Effect of Hydrogen-Acceptors.

<table>
<thead>
<tr>
<th>Con</th>
<th>Yield of Products, %b</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMethodon</td>
<td>2 35 AII2</td>
</tr>
<tr>
<td>PhCH=CH2</td>
<td>B87 61 226 40</td>
</tr>
<tr>
<td>cis-PhCH=CHPh</td>
<td>100 56 629 32</td>
</tr>
<tr>
<td>trans-PhCH=CHPh</td>
<td>100 63 723 33</td>
</tr>
<tr>
<td>CH3COCH=CHPh</td>
<td>A100 52 30 10</td>
</tr>
<tr>
<td>CH3COCH=CHPh</td>
<td>B100 61 27 25</td>
</tr>
<tr>
<td>HOC(CH3)2C≡CC(CH3)2OH</td>
<td>A100 63 9 23 35(2)c</td>
</tr>
<tr>
<td>HOC(CH3)2C≡CC(CH3)2OH</td>
<td>B100 76 0 22 57(3)c</td>
</tr>
<tr>
<td>PhC≡CPh</td>
<td>A99 69 0 24 49(4)c</td>
</tr>
<tr>
<td>PhC≡CPh</td>
<td>B97 75 0 24 59(4)c</td>
</tr>
</tbody>
</table>

a Consumed 1. b Based on 1 used. c Numbers out of and in parentheses are yields of cis- and trans-isomers, respectively.

Table III. Palladium-Catalyzed Decomposition of 1 in the Presence of Aminea.

<table>
<thead>
<tr>
<th>Azide</th>
<th>Amineb</th>
<th>A Method</th>
<th>Conv., %a</th>
<th>Yield of Products, %d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>—</td>
<td>A</td>
<td>100 41 30 16 10 2 1 29</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>Hf</td>
<td>A</td>
<td>99 58 23 15 13 2 1 31</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>Hf</td>
<td>B</td>
<td>93 57 24 14 12 2 1 29</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>—</td>
<td>A</td>
<td>100 44 30 1 3 9 19 32</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>Hf</td>
<td>A</td>
<td>98 51 20 1 2 12 19 34</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>Hf</td>
<td>B</td>
<td>90 51 19 1 2 11 17 31</td>
</tr>
</tbody>
</table>

a 8, Cl-CH=CH-NH2: 9, Cl-CH=CN: 10, CH=CH=NCH2-Cl: 11, Cl-\(\text{Cl}^-\)
-CH=CH-NH2: 12, Cl-CH=CH=NCH2-Cl: 13, Cl-CH2-N3.
b 0.5 mmol. c Consumed azide. d Based on azide used.

employed to avoid unnecessary bimolecular reaction of 1, did not alter the yields of products. The results are summarized in Table I.

Since, formally, the present reaction is composed of the disproportionation of the
intermediate benzyl nitrene and successive side-processes, the yield of 2 is expected not to exceed 50% under the present condition. In the presence of a suitable hydrogen-acceptor, however, the yield of 2 may be improved at the sacrifice of the yields of amine-products. Among many compounds investigated, those listed in Table II appeared to be good hydrogen-acceptors. Mono-substituted acetylenes and some olefins such as 1,1-dicyano-2-phenylethylene, 1,1-diacetyl-2-phenylethylene, and trans-1,2-dicyanoethylene prevented the decomposition of 1 almost completely. Table II also shows that the high-dilution technique is effective when the reaction is run in the presence of a hydrogen-acceptor. As is shown in Table III, the coexistence of an amine in the reaction mixture causes large decrease of the effect of the hydrogen-acceptor.

**DISCUSSION**

There is little doubt that a complex, 6, might be formed initially by the interaction between 1 and palladium metal. The retardation of the reaction by the presence of mono-substituted acetylenes or electron-deficient olefins may be accounted for by strong interaction between these compounds and palladium preventing the azide from coordination.

The successive processes may be obvious:

\[ 1 + \text{Pd} \rightarrow \text{PhCH}_2\text{N} = \text{N} \quad \rightarrow \text{N}_2 \quad \rightarrow \text{PhCH}_2\text{N} \text{Pd} \]

\[ \text{6} \]

of mono-substituted acetylenes or electron-deficient olefins may be accounted for by strong interaction between these compounds and palladium preventing the azide from coordination.

The successive processes may be obvious:

\[ 6 \rightarrow \text{PhCN} \rightarrow \text{PdH}_2 \]

\[ \text{A} \rightarrow \text{AH}_2 \rightarrow \text{Pd} \quad \text{(A: hydrogen-acceptor)} \]

\[ \text{3} \rightarrow \text{Pd} + \text{N}_2 \]

\[ 6 + 3 \rightarrow 5 + \text{Pd} + \text{NH}_3 \]

\[ 3 \rightarrow 5 \text{ and 4} \]

The fact that an acetylenic compound used for a hydrogen-acceptor is reduced to the cis-olefin predominantly supports the process in Eq. 4, which is the catalytic hydrogenation of the acceptor. The reaction in Eq. 6 is obvious from the results shown in Table III, and that in Eq. 7 is known. Thus, an excellent hydrogen-acceptor is the compound which has larger susceptibility to catalytic hydrogenation than 1 but has less facility of coordination to palladium (0) than 1.

It is important to emphasize that, as is shown in Tables I and II, the yield of 5 remains constant (~25%) whole under a variety of reaction conditions, where the yield of 3 changes widely (0–30%). The results cannot be accounted for by reactions in Eqs. 3-7 by themselves, where 3 is proposed to be the precursor of 5. Instead, it is reasonable to expect another process for the appearance of 5.

Juday and Adkins proposed the intermediate formation of a dimer of the imine to account for the formation of a Schiff base from Raney nickel hydrogenation of aromatic nitrile. Under the present condition, the results are best interpreted by assuming a
trimer of 6, which is in equilibrium with the monomer, for a precursor of 5 (Eqs. 8 and 9).

\[
\frac{[(\text{PhCH}_2\text{N})\text{Pd})_2]}{7} \rightleftharpoons 3 \ (\text{PhCH}_2\text{N})\text{Pd} \quad (8)
\]

\[
7 \rightarrow 2 + 5 + 3\text{Pd} + \text{NH}_3 \quad (9)
\]

Let us assume \( K = (3 \times 2)^3 / 1 = 216 \, \text{(mol/l)}^9 \) for the equilibrium in Eq. 8, then the maximum yields of 2, 3, and 5 are calculated to be 44, 33, and 22\%, respectively, in the absence of a hydrogen-acceptor and those of 2, A\text{H}_2, and 5 to be 78, 67, and 22\%, respectively, in the presence of a hydrogen-acceptor, A. The calculated values are in good agreement with those observed experimentally. Of course, the value of the equilibrium constant assumed above has no real meaning because the rates of reactions from 6 and 7 have to be taken into account. The value, instead, suggests that the contribution of 6 is about twice as important as that of 7.

Consequently, in order to improve the yield of 2 more than 80\% one has to look for a condition which shifts the equilibrium toward right-hand side and the research is in progress to this end.

**EXPERIMENTAL**

**Materials.** Benzyl azide (bp 86–87°C/20 mmHg (lit.\(^{10}\) 82.5°C/16.5 mmHg), \( n_\text{D}^{14} 1.5407 \)), p-chlorobenzyl azide (bp 80–82°C/1.5 mmHg, \( n_\text{D}^{15} 1.5600 \)), and diphenylacetylene (mp 60–61°C (lit.\(^{12}\) mp 60–61°C)) were prepared according to the literature, respectively. Solvents were purified by distillation prior to the use. Other reagents were obtained from commercial sources and used without further purification.

**Procedure. Method A.** A mixture of benzyl azide (2.0 mmol) and palladium black (10 mg) in benzene (4.0 ml) was refluxed for 30 min or stirred for 1.5 hr at 40°C under an atmosphere of nitrogen. It was necessary to exclude air from the system when the reaction was carried out without refluxing, otherwise no reaction took place even after 12 hr.

To the reaction mixture were added 200 mg of biphenyl as an internal standard, 4 ml of ether, and 10 ml of water. The ether extract was subjected to VPC analyses on Yanagimoto G 1800 with a column of Silicon DC-200 (Im, 150°C, \( \text{H}_2 0.4 \, \text{kg/cm}^2 \)) or BDS (Im, 120°C, \( \text{H}_2 0.2 \, \text{kg/cm}^2 \)).

**Method B.** Into a refluxing mixture of palladium black (10 mg) and benzene (4.0 ml) was infused benzyl azide (2.0 mmol) over a period of 2 hr. The whole mixture was refluxed for additional 15 min and the products were analysed as described above.

In some experiments 100 mg of palladium on charcoal was employed in place of palladium black yielding similar results. Ethanol could be substituted for benzene, but amines were not good solvents for the reaction (Table I).

**Identification of Products.** In a typical run 3.3 g (0.02 mol) of p-chlorobenzyl azide was added to a refluxing mixture of 2,5-dimethyl-3-hexyne-2,5-diol (2.8 g, 0.02 mol) and palladium black (0.1 g) in benzene (20 ml) over a period of 1 hr and the whole mixture was refluxed for additional 10 min. The reaction mixture was filtered and the filtrate was washed with four 25 ml portions of water. The organic layer was dried over CaCl\(_2\) and the solvent was evaporated in vacuo. The residue was distilled at a bath temperature
Palladium-Catalyzed Decomposition of Azide

of 95°C under a pressure of 20 mmHg.

The distillate was recrystallized from cyclohexane giving 1.6 g (60% yield) of p-chlorobenzonitrile: mp 91-93°C (lit.\textsuperscript{13} mp 89-91°C).

The unvolatile substance was recrystallized from n-hexane giving 0.5 g (20% yield) of N-(p-chlorobenzyliden)p-chlorobenzylamine: mp 58-60°C (lit.\textsuperscript{14} mp 62-65°C).

The water layers were combined and extracted with 50 ml of ether. The ether layer was washed with three 25 ml portions of water and dried over CaCl\textsubscript{2}. The solvent was evaporated in vacuo and the residue was recrystallized from benzene yielding 1.0 g (40% yield) of cis-2,5-dimethyl-3-hexene-2,5-diol: mp 68-69°C (lit.\textsuperscript{13} mp 68-69°C).

REFERENCES

(7) We do not specify the structure of the complex. It may be represented by one of 6a-6c or by equilibrium(s) between two or three of them.

\[
\begin{align*}
\text{PhCH}_{2}\text{N} \rightleftharpoons \text{Pd} \quad \text{PhCH} = \text{N} \rightleftharpoons \text{PdH} \quad \text{PhCH} \rightleftharpoons \text{NH} \\
\text{Pd} \\
6a & 6b & 6c
\end{align*}
\]