Short Communications

Structure and Decomposition of Aryldiazoureas

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Since 1888 it has been known that 1,3-disub-
stituted triazenes react with isocyanates under
formation of diazoureas.1 The reaction has been
widely used in determination of the tautomeric
structure of triazenes. The proposed mechanism was
that the isocyanate reacted at the nitrogen with the
hydrogen atom and that the structure of the
diazourea could be established from analysis of the
decomposition products, i.e. the N,N'-disubstituted
urea as depicted in Scheme 1 reaction path A.
Argumentation of that type has long been known to
be unreliable and we will here show that in this
case the decomposition products depend on how
the decomposition is carried out.

Results. N-Aryldiazoureas are formed by reaction
of phenyl isocyanate with equivalent amounts of
triazene at room temperature in toluene or light
petroleum solution.

\[
R - NH - N = N - Ar + PhNCO \rightarrow
\]

1a-c

\[
R - N = N = N - N = N - CO - NHPh
\]

2a-c

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>p-CH_{3}C_{6}H_{4}</td>
<td>p-CH_{3}C_{6}H_{4}</td>
</tr>
<tr>
<td>b</td>
<td>C_{6}H_{5}C_{2}</td>
<td>p-CH_{3}C_{6}H_{4}</td>
</tr>
<tr>
<td>c</td>
<td>CH_{3}</td>
<td>p-CH_{3}C_{6}H_{4}</td>
</tr>
<tr>
<td>d</td>
<td>C_{6}H_{5}OCOCH_{2}</td>
<td>p-CH_{3}C_{6}H_{4}</td>
</tr>
</tbody>
</table>

The structure of the N-aryldiazoureas 2 could be
established from the $^{13}$C NMR spectra by observing

the quaternary carbon atoms in the p-tolyl group.
From compound 2a and 3,3-dimethyl-1-p-tolyl-
triazene the chemical shifts for the two types of
p-tolyl groups could be established. The p-tolyl diazourea
is formed at $\delta$ 146.3 and 138.8 and the p-
tolylamino group at $\delta$ 139.3 and 132.6. For 2b the
two quaternary carbon atoms in the p-tolyl group
are found at $\delta$ 146.2 and 139.1, for 2c at $\delta$ 146.7
and 138.9 and for 2d at $\delta$ 145.8 and 139.5. The amino
type p-tolyl group is not seen in the spectra and thus
the structure for the diazoureas must be N-alkyl-N-
aryldiazo-N'-phenylurea as shown for 2b-d.

The "p-tolyl method"2 where discrimination
between p-tolylamino and p-tolylamino is based on
the $^1$H NMR chemical shift of the p-methyl group
turned out to be less useful here because the chemical
shifts of the two types of methyl groups were of
approximately the same value.

The decomposition of the N-aryldiazoureas was
carried out in refluxing benzene with equivalent
amounts of acetic acid and diazourea. Only the
ureas formed were isolated and characterized. In
case the urea after reaction path B was formed,
in contrast to our expectations from the structure 2.

\[
RNH - CONHPh \rightarrow R - N = N = N = CO - NHPh
\]

Scheme 1.

Decomposition of 2b in aqueous hydrochloric
acid,1 however, follows path A giving small amounts
of N-benzyl-N'-phenylurea and no N-phenyl-N'-
p-tolyl-urea. From these findings the structure was
established as 2b.1 Decomposition studies of that
type can thus only be used in structure determina-
tion when the mechanism of the decomposition is
fully understood. In this case, it seems possible that
the phenyl isocyanate is split off first and the
triazene decomposed afterwards. This is supported
by the fact that a smell of phenyl isocyanate has been
noticed3 from the decomposition mixture and
when the decomposition is carried out in refluxing
xylene without acetic acid an IR absorption at 2300
\text{cm}^{-1} is seen, corresponding to the phenyl iso-
cyanate. Finally, when the decomposition of 2b is
carried out in benzene with equivalent amounts of
aniline and two equivalents of acetic acid 66% of
N,N'-diphenylurea and 13% N-phenyl-N'-p-tolyl-
urea are formed.
The reason why no N-alkyl-N'-phenylureas are
formed in the decomposition carried out in benzene
with acetic acid may be explained by the fact that the
alkyl group reacts with acetic acid with ester forma-
tion5 when the triazene is decomposed.
(Scheme 2).
\[
\begin{align*}
\text{R} - \text{N} - \text{N} &= \text{N} - \text{C}_6\text{H}_4\text{CH}_3 \\
\text{CONH} - \text{Ph} \\
\text{RNH} - \text{N} &= \text{N} - \text{C}_6\text{H}_4\text{CH}_3 + \text{PhNCO} \\
\text{RNH} - \text{N} &= \text{N} - \text{C}_6\text{H}_4\text{CH}_3 + \text{HAc} \\
\text{R} - \text{Ac} + \text{N}_2 + \text{H}_2\text{N} - \text{C}_6\text{H}_4\text{CH}_3
\end{align*}
\]
Scheme 2.

**Experimental.** The experimental equipment was
reported earlier.6 All the aryldiazoureas have been
prepared in accordance with a previously published
procedure.1

**General procedure for decomposition of N-aryl-
diazoureas.** The diazourea (0.01 mol) was refluxed
in benzene (50 ml) with acetic acid (0.01 mol) until
the diazourea had disappeared (TLC). The reaction
mixture was cooled in ice and the N-phenyl-N'-p-
tolylurea filtered off.

120 °C (d) 1H NMR (CDCl₃): δ 2.33 (3 H, s), 2.38
(3 H, s), 6.87 - 7.72 (13 H, m), 8.56 (1 H, s) gave 84 %
yield of N-phenyl-N'-p-tolylurea in the decom-
position.

120 °C. 1H NMR (CDCl₃): δ 2.36 (3 H, s), 5.36
(2 H, s), 6.92 - 7.69 (14 H, m), 8.42 (1 H, s) gave 62 %
yield of N-phenyl-N'-p-tolylurea in the decom-
position.

95 °C. 1H NMR (CDCl₃): δ 2.39 (3 H, s), 3.48
(3 H, s), 6.90 - 7.70 (9 H, m), 8.42 (1 H, s) gave 53 %
of N-phenyl-N'-p-tolylurea in the decom-
position.

N'-Ethoxycarbonylmethyl-N-phenyl-N-p-tolyl-
diazourea 2d. M.p. 88 °C. 1H NMR (CDCl₃): δ 1.23
(3 H, t), 2.37 (3 H, s), 4.15 (2 H, q), 4.86 (2 H, s),
6.87 - 7.73 (9 H, m), 8.35 (1 H, s) gave 75 % of
N-phenyl-N'-p-tolylurea in the decomposition.

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13C NMR facilities.

Ges. 21 (1888) 1016.
2. Iwamura, H., Albert, K. and Rieker, A. Tetra-
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Chem. Ges. 21 (1888) 2557.

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