The Reaction of 1,3-Disubstituted Triazenes with Phenyl Isocyanide. \(N^1\)-Aryldiazoformaldridines

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Triazenes attract some interest in the literature, especially with regard to tautomerism, 1,2 and Z/E isomerism. 3 Recently the thermal 4 and photochemical 5 decomposition of triazenes have been studied. As a result of our interest in this field 6 we now report a new reaction for 1,3-disubstituted triazenes, namely the reaction with phenyl isocyanide with formation of the hitherto unknown \(N^1\)-aryldiazoformaldridines (2).

\[
R^1-N=N-NH-R^2+PhNC \rightarrow \\
R^1-N=N-NCH=\Phi
\]

\( 1a-e \) 2a-e

<table>
<thead>
<tr>
<th>Compound</th>
<th>( R^1 )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Ph</td>
<td>Ph</td>
</tr>
<tr>
<td>b</td>
<td>p-CH(_2)C(_6)H(_5)</td>
<td>Me</td>
</tr>
<tr>
<td>c</td>
<td>p-CH(_3)C(_6)H(_4)</td>
<td>p-CH(_2)C(_6)H(_4)</td>
</tr>
<tr>
<td>d</td>
<td>Ph</td>
<td>PhCH(_2)</td>
</tr>
<tr>
<td>e</td>
<td>p-CH(_3)C(_6)H(_4)</td>
<td>PhCH(_2)</td>
</tr>
</tbody>
</table>

The reactions were carried out at room temperature with equivalent amounts of phenyl isocyanide and triazene, catalyzed with copper(I) chloride. After 1-12 h the isocyanide had disappeared. Light petroleum was added and the products separated as yellow crystals in good yields after cooling at -20 °C overnight. The products could be recrystallized from benzene/light petroleum.

The \(N^1\)-aryldiazoformaldridines (2) are stable compounds at room temperature and in neutral solution at elevated temperature up to 80 °C. On treatment with catalytic amounts of acid the \(N^1\)-aryldiaz-o-N\(^2\)-aryldiazoformaldridines (2a,2c) decomposed very fast. Decomposing 2a in benzene solution with a few drops of acetic acid gave an almost quantitative yield of \(N^1\)-diphenylformamidine. Acid catalysed decomposition of 2b resulted in tarry materials and 2d was quite stable upon this treatment.

The structure of the \(N^1\)-diazoformaldridines (2) could be settled by \(^1H\) and \(^13C\) NMR spectroscopy. For 2b, 2d and 2e there are two possibil-

The presence of only one set of signals in the \(^1H\) and \(^13C\) NMR spectra indicated that only one isomer was formed. To distinguish between the possibilities A and B we used the "p-toly method". 7 By means of this method the \(^1H\) NMR chemical shift values for the p-tolylamino and the p-tolyldiazido group were established as \( \delta \) 2.41 and 2.32 respectively for 2c. For 2b and 2e the methyl signals are found at \( \delta \) 2.33 and 2.35 indicating that the structure must be a B type.

From the \(^13C\) NMR spectra the same structure could be established by observing the quaternary carbons atoms. From the \(^13C\) NMR data of 2c and of 3,3-dimethyl-1-p-tolytl-triazene 8 the chemical shifts for the two types of p-tolyl groups could be established. The p-tolyldiazido group is found at \( \delta \) 146.5 and 138.5 and the p-tolylamino group at \( \delta \) 138.7 and 133.7. For 2b the two quaternary carbon atoms corresponding to the p-tolyl group are found at \( \delta \) 146.7 and 138.3 and for 2e at \( \delta \) 146.3 and 138.3. The amino type p-tolyl group is not seen in the spectra of 2b and 2e which is also why the \(^13C\) NMR spectra indicate that the structure is a B type.

**Experimental.** The instrumental equipment is reported earlier. 9 \(^13C\) NMR spectra were recorded on a Bruker WH 90 apparatus. Melting points are uncorrected. All the triazenes have been prepared in accordance with a previously published procedure. 4 Attempted preparation of 3-methyl-1-phenyltriazene gave a 1:1 mixture of the triazene and 3-methyl-1,5-diphenylpentaaazide. This compound was therefore omitted and instead 3-methyl-1-p-tolytltriazene (1b), which was formed without contamination of pentaaazide was used.

\(N^1\),\(^2\)-Diphenyl-N\(^1\)-phenylidyiacomadidine 2a. A solution of phenyl isocyanide (50 mmol) and copper(I) chloride (1 mmol) in benzene (100 ml) was stirred at room temperature with 1,3-diphenyltriazene (50 mmol) for 2 h, i.e. until the phenyl isocyanide was consumed. Light petroleum (150 ml) was added and the mixture left at -20 °C overnight. The precipitate was filtered off giving 91 % of a yellow powder. The product could be recrystallized from a mixture of benzene and light petroleum.

Preparaton of N-Acylformimidates.
Reaction of Carboxamides with Triethyl Orthoformate

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Several reports on the synthesis of N-acyl-
formimidates by reaction between triethyl orthoformate and amides have appeared in the literature.1-7 For the carboxamides1,8 more
extensive work has shown the structural assignment to be wrong.2-7 The compounds formed were trisacrylanamethanes and not
N-acylformimidates. For the reaction of sul-
fonylamides8 and phosphonylamides4 with triethyl orthoformate the corresponding formi-
midates were actually formed.

N-Acylamides have previously been syn-
thesized by alkylation of the silver salts of
diacylamines8 and by acylation8,10 of the
Corresponding imidates; no formimidate has
been reported. We have reinvestigated the
reaction between carboxamides and triethyl
orthoformate in order to prepare the hitherto
unknown N-acylformimidates and report here
the preparation of the formimidates listed in
Scheme 1. Attempts to prepare ethyl N-
benzoylformimidate 2d by benzoylation of
O-ethyl formimidate11,12 were unsuccessful.

\[
\begin{align*}
RCONH_2 + HC(OClH_3)_2 & \rightarrow \\
RCON = OClH_3 + 2C_2H_4OH
\end{align*}
\]

\[1a \rightarrow k\]

\[\begin{array}{ll}
a & RClH_3 \\
b & ClCH_2CH_2Cl \\
c & ClC_2H_2 \\
d & C_2H_4 \\
e & o-FClH_4
\end{array} \]

\[\begin{array}{ll}
a & o-CiClH_4 \\
b & g-CiClH_4 \\
c & p-CiClH_4 \\
d & o-BrC_2H_4 \\
e & o-CHClC_2H_4
\end{array} \]

\[\begin{array}{ll}
a & 2,6-Cl_2C_2H_4 \\
b & 2,4-Cl_2C_2H_4 \\
c & 2,3-Cl_2C_2H_4 \\
d & 2,2-Cl_2C_2H_4 \\
e & 0-CiClC_2H_4
\end{array} \]

Scheme 1.

Results. The reactions were carried out by
refluxing the amide with excess orthoester and a
few drops of concentrated sulfuric acid
distilling off ethanol while it was formed.
Evaporation of excess orthoester and sub-
sequent distillation gave the acylformimidates
in yields ranging from 11 to 90%. It turned
out that the electronegativity of the substituent
in 1 strongly influenced the reaction pathway
and the yield of formimido. Thus benzamide
gave a yield of 33% and o-fluorobenzamide
a yield of 73%. The same was observed with