THE REACTION BETWEEN BENZOTRIAZOLE AND DIARYLNITRILEIMINES

Revannuru Venkatachaliah Venkataratnam
Regional Research Laboratory, Hyderabad 500 007, India
José Elguero*
Instituto de Química Médica, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain

Abstract—The reaction between benzotriazole and diarylnitrileimines yielded the arylhydrazones of 1- and 2-benzotriazole. The structures were established through detailed studies by $^1$H and $^{13}$C nmr spectroscopies.

1,3-Dipoles can react with N-unsubstituted azoles in two ways: either to give a cycloaddition product by reaction with a formal double bond or an N-substituted derivative by electrophilic attack on the nitrogen. Both possibilities have been observed.

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The first reaction was observed mainly with pyrroles and indoles (generally N-substituted). A few reactions of other ring systems described in literature are: i) the reaction of 1-methylindazole with a nitrileimine (Eq. 1), ii) the reaction of NH-imidazoles with benzonitrile oxide (Eq. 2), iii) the reaction of benzotriazole with diarylnitrileimines (Eq. 3).

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{C} \\
\end{array}
\quad + \quad \begin{array}{c}
\text{C} \\
\text{H} \\
\text{C} \\
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{C} \\
\end{array}
\quad \text{N} \\
\text{H} \\
\text{C} \\
\end{array}
\]

(Eq. 1)

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{C} \\
\end{array}
\quad + \quad \begin{array}{c}
\text{Ac} \quad \text{C} = \text{N} \quad \text{N} \quad \text{Ph} \\
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{C} \\
\end{array}
\quad \text{N} \\
\text{H} \\
\text{C} \\
\end{array}
\]

(Eq. 2)
The second reaction has not been systematically studied (except for the N-methylation of azoles with diazomethane), but some examples can be found in the literature (Eq. 3 and 4).

\[
\begin{align*}
\text{NC} & \text{Ph} + \text{Ph-C}=\text{N}-\text{N}-\text{Ph} \\
\text{H}_2\text{N} & \text{N} \\
\end{align*}
\]

As shown in Eq. 3, Sayanna et al.\(^4\) reported that reactions of benzotriazole \(^\dagger\) with diarylnitrileimines \(^\ddagger\) afforded cycloadducts \(3\) and 1-substituted products \(4\). However, the structure of compound \(3\) is quite unexpected: it is the first example of a tetrazolo[1,2-a]benzotriazole,\(^1\) which is non-aromatic and possesses four linked sp\(^3\) nitrogens. Taking into account that in the reaction of \(1\) with \(2\) there is possible an alternative structure for compound \(3\), namely the 2-substituted isomer \(5\), the nmr \((^{1}H, ^{13}C)\) spectroscopic study of the products obtained in the reaction was carried out.

\[
\begin{align*}
\text{a, X = Y = H} & \\
\text{b, X = H, Y = Me} & \\
\text{c, X = H, Y = NO\(_{2}\)} & \\
\text{d, X = Me, Y = H} & \\
\end{align*}
\]

The spectra were recorded in dimethyl sulfoxide at 300 MHz for the proton and 75 MHz for the carbon-13 (Varian XL-300); all values are in ppm from internal TMS (\(\delta\) scale).
The complexity of the aromatic protons does not prevent the observation of the AA' BB' system characteristic of a 2-substituted benzotriazole which is only consistent with structure $\frac{5}{4}$.

The carbon-13 nmr spectra definitely prove that the compounds resulting from the reaction of benzotriazole $\frac{1}{4}$ with diarylnitrileimines $\frac{2}{3}$ are positional isomers $\frac{4}{3}$ and $\frac{5}{3}$; the chemical shifts of the N-substituents are almost identical. The assignment of the heterocyclic carbons is based on literature results for benzotriazoles carrying other substituents on the nitrogen. The chemical shifts found for compounds $\frac{4}{3}$ and $\frac{5}{3}$ are closely to those of N-methyl derivatives $\frac{5}{6}$ and $\frac{6}{7}$, respectively.

Table 1. Proton chemical shifts

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Table 2. Carbon-13 chemical shifts

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*Assignments can be reversed
Carbon C_8 appears around 130 ppm, much higher than standard ketone phenylhydrazones (around 160 ppm), due to the effect of the benzotriazole. A similar shielding is observed when acetone (ΔC=O: 205.1 ppm) is compared with 1-acetylbenzotriazole (ΔC=O: 169.3 ppm).

In conclusion, we can assert that, with the possible exception of imidazoles (Eq. 2), N-unsubstituted diazoles, triazoles and tetrazoles react with 1,3-dipoles as nucleophiles and not as dipolarophiles.

Compounds 4a and 5a are formally phenylhydrazones of 1- and 2-benzoylbenzotriazole. It is interesting to notice that, since acylation of azoles under thermodynamic control is known to give only 1-acylbenzotriazoles, compounds 5 are derivatives of a new class of compounds, the 2-acylbenzotriazoles.

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REFERENCES


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