DENITROSATION OF N-NITROSO-N-BENZYL-\textit{p-}TOLUENESULPHONAMIDE

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Received on October 13, 1973 and in revised form on February 12, 1974.

Abstract

\textit{N}-Nitroso-\textit{N}-benzyl-\textit{p}-toluenesulphonamide (\textit{I} \textit{d}), a precursor for phenyl-
diazomethane undergoes denitrosation with sodium methoxide to furnish \textit{N}-benzyl-
\textit{p}-toluenesulphonamide (\textit{II}), which is a wasteful side reaction not recorded by earlier
workers [4]. The N.M.R. data of \textit{I} \textit{d} and \textit{II} are given.

Key words: \textit{N}-Nitroso-\textit{N}-benzyl-\textit{p}-toluenesulphonamide, \textit{N}-benzyl-\textit{p}-toluenesulphona-
mide, Phenyl diazomethane, NMR.

1. Introduction

\textit{N}-Nitroso compounds have attracted attention from the preparative
point of view for obtaining diazoalkanes and, in recent years, because of
their intense carcinogenic nature [1]. The mechanism of decomposition
of these compounds under acid and base catalysis has also excited interest
and was the subject of two recently reported communications. Berry and
Challis [2] demonstrated deamination and denitrosation in the acid catalysed
decomposition of \textit{N}-n-butyl-\textit{N}-nitroso-acetamide (\textit{I} \textit{a}), the denitrosation
occurring via protonation of the amide nitrogen. Hecht and Kozarich [3]
discussed the mechanisms of base induced decomposition of \textit{N}-nitroso-\textit{N-}
alkylureas (\textit{I} \textit{b}) and furnished proof for an initial proton abstraction from the
urea nitrogen, specifically in the case of \textit{N}-nitroso-\textit{N}-methylurea (\textit{I} \textit{c}),
with the generation of a cyanate and diazotate which subsequently gives
diazomethane.

2. Present Work

Recently we had occasion to work with \textit{N}-nitroso-\textit{N}-benzyl-\textit{p-}tolu-
enesulphonamide (\textit{I} \textit{d}) in connection with the preparation of the dibenzyl
ester of a substituted malonic acid. In our experiment to generate phenyl
diazomethane (by the action of sodium methoxide in ether) from the nitroso-
sulphonamide (\textit{I} \textit{d}) [4] \textit{m.p.} 89-90°, NMR (\textit{CDCl}_3) : 8 2.39 (3H, \textit{s}, \textit{ar-Me}),
ortho to $-\text{SO}_2-$), we succeeded in isolating from the organic phase the parent sulphonamide (II) [m.p. 116-117°, m.m.p. undepressed, NMR (CDCl$_3$): $\delta$ 2.41 (3H, s, ar-Me), 4.08 (2H, d, J 6 Hz, $-\text{NH-CH}_2-$), 5.03 (1H, t, J 6 Hz, $-\text{NH-CH}_3-$), 7.21 (7H, m, ar-H), 7.72 (2H, d, J 8 Hz, ar-H ortho to $-\text{SO}_2-$)]. Nucleophilic attack on the nitrogen of the nitroso moiety [5] leading to II (Eq. 1) was not reported by the earlier workers [4]. Attack on the sulphonyl group would give phenyldiazomethane, via the diazo-hydroxide (Eq. 2).

\[
\begin{align*}
R^2 - N - R^1 & \xrightarrow{\text{NaOMe}} R^2 - N - R^1 + \text{MeONO} \\
\text{(1)}
\end{align*}
\]

(a) $R^1 = n-$Bu, $R^2 = $CH$_3$CO
(b) $R^1 = $CONH$_2$, $R^2 = $Alkyl
(c) $R^1 = $CONH$_2$, $R^2 = $Me
(d) $R^1 = $CH$_2$C$_6$H$_5$, $R^2 = $p-$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$

\[
\begin{align*}
R^2 - N - R^1 & \xrightarrow{\text{H}_2\text{O}} R^2 - N - R^1 + \text{MeONO} \\
\text{(2)}
\end{align*}
\]

Thus, in the preparation of phenyldiazomethane from I d, the undesired reaction represented by equation 1 also occurs concomitantly, along with the normal reaction represented by equation 2. The benzyl esters formed by the in situ esterification with phenyldiazomethane produced by this method would therefore be contaminated with $N$-benzyl-$p$-toluenesulphonamide (II),

3. Conclusion

Thus, in the preparation of phenyldiazomethane from I d, the undesired reaction represented by equation 1 also occurs concomitantly, along with the normal reaction represented by equation 2. The benzyl esters formed by the in situ esterification with phenyldiazomethane produced by this method would therefore be contaminated with $N$-benzyl-$p$-toluenesulphonamide (II),
4. ACKNOWLEDGEMENT

One of us (G.U.D.) thanks the Council of Scientific and Industrial Research, New Delhi, India, for a Junior Research Fellowship.

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