DENITROSATION OF N-NITROSO-N-BENZYL-*p*-TOLUENESULPHONAMIDE

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ABSTRACT

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

Key words: N-Nitroso-N-benzyl-*p*-toluenesulphonamide, N-benzyl-*p*-toluenesulphonamide, Phenyldiazomethane, NMR.

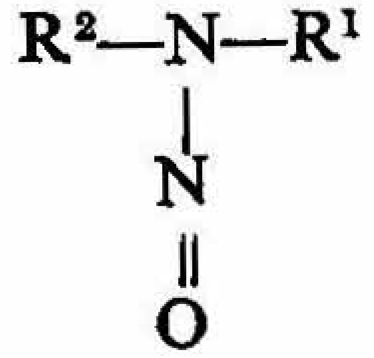
1. INTRODUCTION

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 N–*n*-butyl–N–nitroso-acetamide (I *a*), the denitrosation occurring *via* protonation of the amide nitrogen. Hecht and Kozarich [3] discussed the mechanisms of base induced decomposition of N–nitroso–N–alkylureas (I *b*) and furnished proof for an initial proton abstraction from the urea nitrogen, specifically in the case of N–nitroso–N–methylurea (I *c*), with the generation of a cyanate and diazotate which subsequently gives diazomethane.

2. PRESENT WORK

Recently we had occasion to work with N–nitroso–N–benzyl–*p*–toluenesulphonamide (I *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 (I *d*) [4] [m.p. 89–90°, NMR ($CDCl_3$) : δ 2·39 (3H, *s*, *ar–Me*), 4·91 (2H, s, *ar–CH*$_2$*–*), 7·0–7·3 (7H, m, *ar–H*), 7·72 (2H, d, J 8 Hz, *ar–H*-

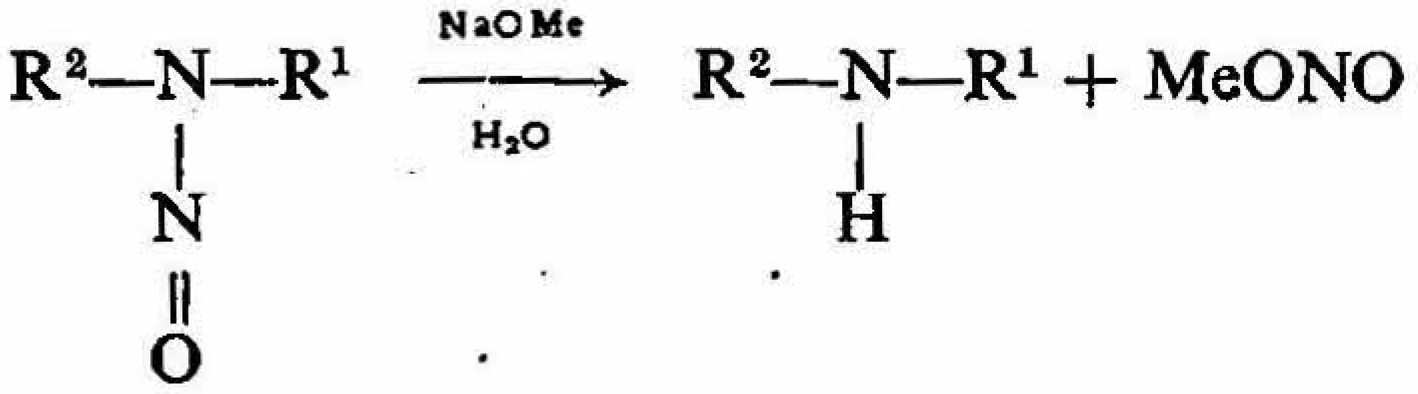
ortho to $-SO_2-$)7], we succeeded in isolating from the organic phase the parent sulphonamide (II) [m.p. 116–117°, m.m.p. undepressed, NMR ($CDCl_3$): δ 2·41 (3H, s, *ar–Me*), 4·08 (2H, d, J 6 Hz, $-NH\text{-}CH_2-$), 5·03 (1H, t, J 6 Hz, $-NH\text{-}CH_2-$), 7·21 (7H, m, *ar–H*), 7·72 (2H, d, J 8 Hz, *ar–H ortho* to–$-SO_2-$)7]. 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 diazohydroxide (Eq. 2).



$$R^2{-}\underset{\substack{|\\ N\\ \|\\ O}}{N}{-}R^1$$

I

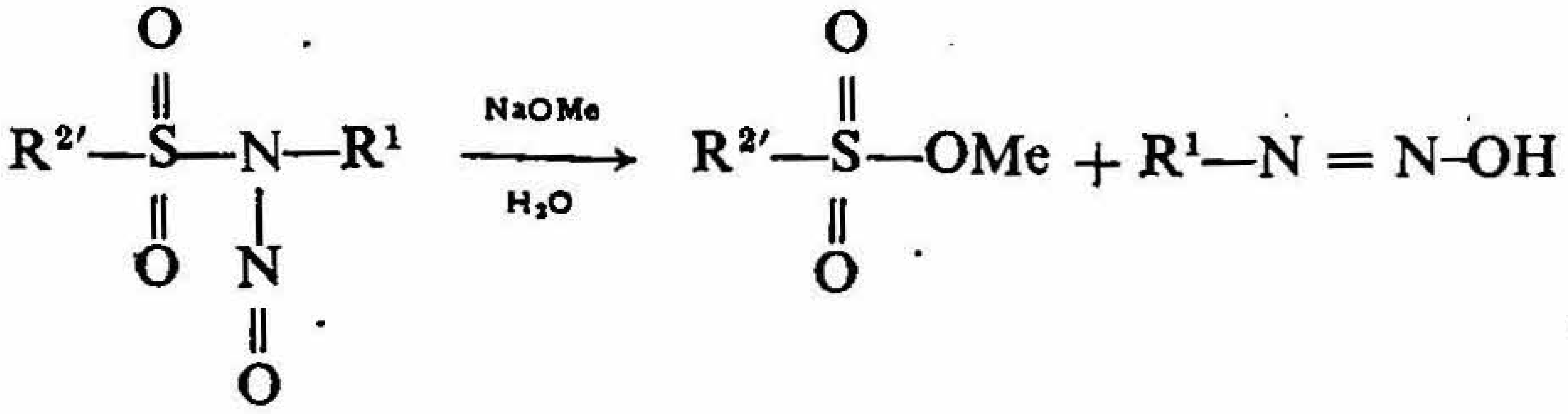
(*a*) $R^1 = n\text{-}Bu$, $R^2 = CH_3CO$
(*b*) $R^1 = CONH_2$, $R^2 = \text{Alkyl}$
(*c*) $R^1 = CONH_2$, $R^2 = Me$
(*d*) $R^1 = CH_2C_6H_5$
$R^2 = p\text{-}CH_3C_6H_4SO_2$



$$R^2{-}\underset{\substack{|\\ N\\ \|\\ O}}{N}{-}R^1 \xrightarrow[H_2O]{NaOMe} R^2{-}\underset{\substack{|\\ H}}{N}{-}R^1 + MeONO \qquad (1)$$

I *d* II

$R^1 = CH_2C_6H_5$, $R^2 = p\text{-}CH_3C_6H_4SO_2$



$$R^{2\prime}{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}\underset{\substack{|\\ N\\ \|\\ O}}{N}{-}R^1 \xrightarrow[H_2O]{NaOMe} R^{2\prime}{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}OMe + R^1{-}N = N{-}OH \qquad (2)$$

$R^1 = CH_2C_6H_5$, $R^{2\prime} = p\text{-}CH_3C_6H_4$.

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

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