Desulphonylation of α-Nitrosulphones with *N*-Benzyl-1,4-dihydronicotinamide

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Summary A sulphonyl group of α-nitrosulphones is replaced by hydrogen on treatment with *N*-benzyl-1,4-dihydronicotinamide; the reaction proceeds by a non-chain, free-radical process involving one-electron transfer.

1,4-Dihydronicotinamide is a reducing agent which is capable of acting as a good electron donor.[1] Thus, the reaction of α-bromonitroalkanes,[2] α-nitronitriles,[3] or α-nitrocarbonyl compounds[3] with *N*-benzyl-1,4-dihydronicotinamide (BNAH) yields debrominated or denitrated compounds, respectively, *via* one-electron transfer processes. Here we report the one-electron transfer reduction of α-nitrosulphones (**1**) with BNAH, where a sulphonyl group is replaced by hydrogen under mild conditions to give nitroalkanes (**2**) in good yields (equation **1**). Some typical examples are summarized in the Table.

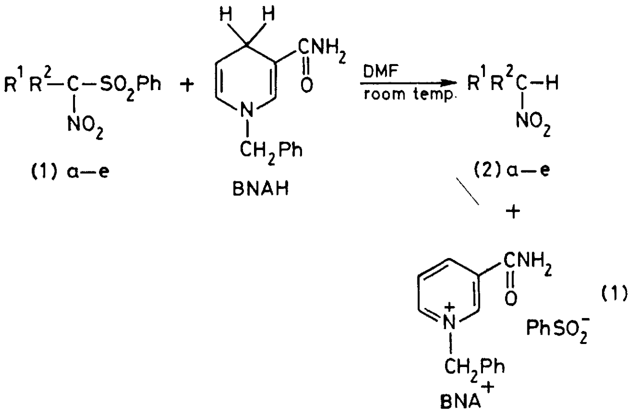

Table. Conversion of α-nitrosulphones (**1**) into nitroalkanes (**2**) with BNAH.[a]

	R^1	R^2	Reaction time/h	Yield of (**2**)/%
a	Me	Me	6	95[b]
b	Me	n-C_6H_{13}	8	65[c]
c	H	n-C_6H_{13}	24	55[c]
d	Et	CH_2CH_2COMe	6	72[c]
e	Et	CH_2CH_2CN	6	75[c]

[a] A mixture of (**1**) (10 mmol) and BNAH (30 mmol) in degassed DMF (30 ml) was stirred under nitrogen at room temperature. [b] Yield determined by g.l.c. [c] Isolated yield.

The conversion of (**1**) into (**2**) was carried out in degassed dimethylformamide (DMF) under nitrogen to prevent the side formation of ketonic products.† In fact the reaction of (**1b**) with BNAH in the presence of oxygen gave octan-2-one in 65% yield. As α-nitrosulphones are readily prepared by nitration of sulphones[4] or alkylation of phenylsulphonylnitromethane,[5] the present method of desul-

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† The reaction of a nitroalkane radical with oxygen gives ketonic products: G. A. Russell, *J. Am. Chem. Soc.*, 1954, **76**, 1595.

phonylation is of synthetic use for the preparation of nitro compounds from sulphones (equation 2).

$$\begin{tikzcd}
R^1CH_2SO_2Ph \arrow[r, "\text{base}", "RONO_2"'] & R^1CH(NO_2)SO_2Ph \arrow[r, "R^2X"] & (\mathbf{1}) \arrow[d] \\
& O_2NCH_2SO_2Ph \arrow[u, "\text{base, } R^1X"'] & (\mathbf{2})
\end{tikzcd} \qquad (2)$$

The particular utility of the present desulphonylation is well demonstrated in the conversion of (**1d**) into (**2d**), where BNAH selectively replaces the sulphonyl group by hydrogen without affecting other groups. In contrast, the usual hydride transfer reagents such as sodium borohydride reduce the carbonyl group in (**1**) selectively without affecting the nitro- or sulphonyl-groups. This suggests that an electron-transfer reaction plays an important role in the present desulphonylation with BNAH.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

(*Received*, 6*th October* 1980; *Com*. 1094.)

[1] A. Ohno, S. Yasui, and S. Oka, *Bull. Chem. Soc., Jpn.*, 1980, **53**, 2651, and references therein.
[2] R. J. Kill and D. A. Widdowson, *J. Chem. Soc., Chem. Commun.*, 1976, 755.
[3] N. Ono, R. Tamura, and A. Kaji, *J. Am. Chem. Soc.*, 1980, **102**, 2851.
[4] W. E. Truce, T. C. Klingler, J. E. Paar, H. Feuer, and D. K. Wu, *J. Org. Chem.*, 1969, **34**, 3104.
[5] P. A. Wade, S. D. Morrow, S. A. Hardinger, M. S. Saft, and H. R. Hinney, *J. Chem. Soc., Chem. Commun.*, 1980, 287.