

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

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

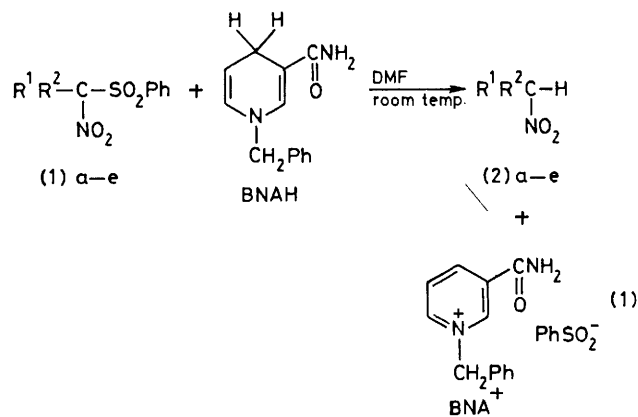
1,4-DIHYDROPYRIDINAMIDE is a reducing agent which is capable of acting as a good electron donor.¹ Thus, the reaction of α -bromonitroalkanes,² α -nitronitriles,³ or α -nitrocarbonyl compounds⁴ with *N*-benzyl-1,4-dihydropyridinamide (BNAH) yields debrominated or denitrated

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 ₆ H ₁₃	8	65 ^c
c	H	n-C ₆ H ₁₃	24	55 ^c
d	Et	CH ₂ CH ₂ COMe	6	72 ^c
e	Et	CH ₂ CH ₂ CN	6	75 ^c

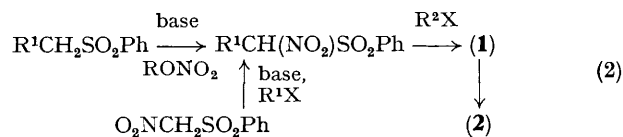
^a A mixture of (**1**) (10 mmol) and BNAH (30 mmol) in degassed DMF (30 ml) was stirred under nitrogen at room temperature. ^b Yield determined by g.l.c. ^c Isolated yield.



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 sulphones⁴ or alkylation of phenylsulphonylnitromethane,⁵ the present method of desul-

[†] 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).



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.

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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.