N-Methyl-*N*-phenyl-*N*′-methylsulphinylhydrazine: Preparation and Decomposition

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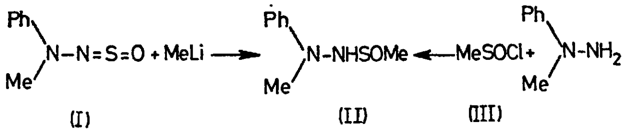
Summary The reaction of methyl-lithium with the hydrazine (I) gives the *N*-methylsulphinylhydrazine (II) which decomposes to 1,4-dimethyl-1,4-diphenyl-2-tetrazene (IV) and formaldehyde *N*-methyl-*N*-phenylhydrazone *via* the *N*-nitrene; fragmentation of (II) gives *N*-methylaniline·

As part of our study[1] of compounds of the type R^1R^2–N=S=O, we have investigated the reaction of MeLi with the hydrazine (I) and now report our preliminary results. By analogy with previous work on the RN=S=O system,[2] MeLi added to the N=S=O bond of the hydrazine (I) at room temperature to give an 87% yield of the methylsulphinylhydrazine (II), m.p. 101—102° (decomp.); ν_{max} 3100 and 1080—1020 cm^{-1}, τ 6·36 (3H, MeSO), 6·68 (3H, MeN), 3·88 (1H, exchangeable), and 2·5—3·2 (5H, ArH). Its structure was conclusively established by the elemental analysis and by authentic synthesis from *N*-methyl-*N*-phenylhydrazine and methanesulphinyl chloride (III). When the reaction of MeLi and (I) was carried out in ether at reflux, the yield of (II) decreased to 38%; the tetrazene (IV), identical in all respects with an authentic sample, was isolated (*ca.* 5%): in addition, a red oil consisting largely of formaldehyde *N*-methyl-*N*-phenylhydrazone and *N*-methylaniline was formed.



Compound (IV) can be viewed as arising from the elimination of methanesulphenate ion to yield the corresponding *N*-nitrene in a manner analogous to the Bamford–Stevens and the Carpino reactions.[3] Similarly, the formation of the hydrazone is readily accounted for *via* a *N*-nitrene–hydrazone rearrangement.[4] In a separate experiment, it was found that triethylamine at reflux was sufficient to induce the elimination of methanesulphenic acid from (II). *N*-Methylaniline (9%) and formaldehyde *N*-methyl-*N*-phenylhydrazone (40%) were also the major products when (II) was heated under reflux in ethanol for 3 h; in addition, (V) and traces of the tetrazene were formed.

Since control experiments showed that the decomposition of the tetrazene was not the source of *N*-methylaniline, fragmentation of (II) perhaps *via* tautomeric form (IIa)[5] (Scheme) may account for its formation.† The formation of (V) remains obscure at this time although it has been established that air oxidation is *not* occurring.

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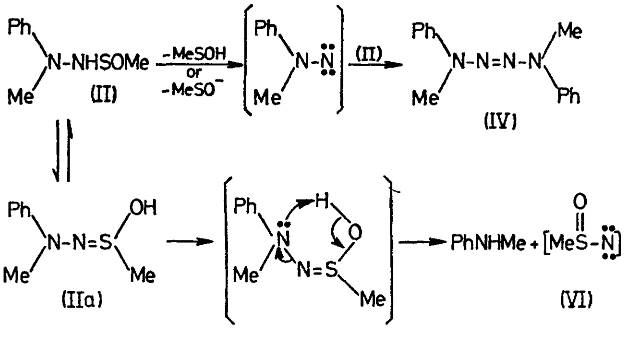

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† Products directly traceable to methanesulphinyl nitrene (T. J. Maricich, *J. Amer. Chem. Soc.*, 1968, **90**, 7181; *Tetrahedron Letters*, 1971, 729; M. Kobayashi and A. Yamamoto, *Bull. Chem. Soc. Japan*, 1966, **39**, 2733; H. C. Buchholt and A. Senning, *Acta Chem. Scand.*, 1970, **24**, 2255) have not yet been identified.

[1] K. F. Cerny, M. A. Feingold, and J.-P. Anselme, 163rd American Chemical Society Meeting, Boston, Massachusetts, April 1973, Org. No. 122.

[2] A. Schönberg, A. Stephenson, H. Kaltschmidt, E. Peterson, and H. Schulten, *Ber.*, 1933, **66**, 237.

[3] (a) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 1958, 4735; (b) L. A. Carpino, *J. Amer. Chem. Soc.*, 1957, **79**, 4427.

[4] G. Koga and J.-P. Anselme, *J. Org. Chem.*, 1970, **35**, 960; D. M. Lemal, F. Menger, and E. A. Coats, *ibid.*, 1964, **86**, 2395. Although the 'normal' product of the diazene–hydrazone rearrangement should be formaldehyde phenylhydrazone, this type of hydrazone (*NN*-disubstituted) is apparently the major (if not sole) product of the rearrangement of dibenzylamino nitrene; see also D. M. Lemal in 'Nitrenes,' ed., W. Lwowski, Interscience, New York, 1970, p. 389, footnote.

[5] We have adduced evidence for the existence of the iminomethanesulphinic acid form in the case of *N*-dibenzylaminoiminomethanesulphinic acid (S. Mataka and J.-P. Anselme, unpublished results).