

A PRACTICAL AND CONVENIENT SYNTHESIS OF THE  
 NITROETHYLENE TRANSFER REAGENT, 2-NITROETHYL PHENYL SULFOXIDE

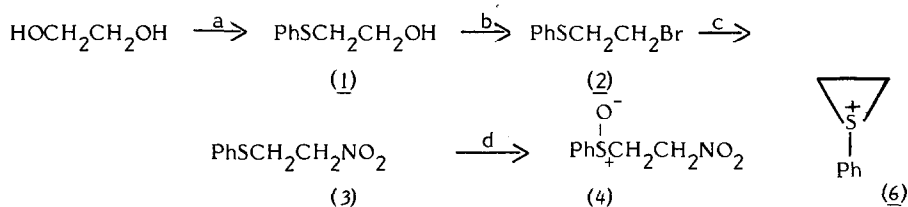
S. Ranganathan\*, D. Ranganathan\* and S.K. Singh

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India.

ABSTRACT: A safe and practical route to the nitroethylene transfer reagent, 2-nitroethylphenyl sulfoxide, involving sodium nitrite-DMSO, for the introduction of the nitro function, is described.

We report the successful outcome of prolonged efforts to delineate a safe and practical pathway for nitroethylene generation<sup>1</sup>. The potential of nitroethylene as a versatile reagent for organic synthesis is finding increasing application<sup>2</sup>. Presently, all the methods available for nitroethylene preparation are directly or indirectly related to 2-nitroethanol, whose preparation from nitromethane and paraformaldehyde is grossly inefficient and unless utmost care is taken, can result in explosion<sup>3</sup>.

The nitroethylene transfer reagent, 2-nitroethylphenylsulfoxide (4) has now been prepared by employing sodium nitrite to introduce the nitro function and 4-<sup>t</sup>butyl iodoxybenzene<sup>4</sup> to bring about the facile and uncomplicated oxidation of the resulting 2-nitroethylphenylsulfide<sup>5,6</sup>:

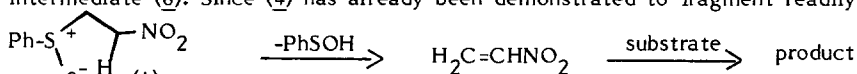


a.i. 45% HBr, reflux 8h (30%); ii. PhSH, 20% NaOH, reflux 1h (88%). b. PBr<sub>3</sub>, rt (81%).  
 c. NaNO<sub>2</sub>, DMSO rt 8h, (72%). d. 4-<sup>t</sup>BuPhIO<sub>2</sub>-TFA, PhH, rt 12h (90%).

The optimum conditions for the (2) → (3) change were determined as a result of experiments which are summarized below :

PhSCH <sub>2</sub> CH <sub>2</sub> X + MNO <sub>2</sub> → PhSCH <sub>2</sub> CH <sub>2</sub> NO <sub>2</sub> (3) + PhSCH <sub>2</sub> CH <sub>2</sub> ONO (5) <sup>7</sup>					(3)%	(5) %
MNO <sub>2</sub>	X	eq(mmol)	solvent	conditions		
AgNO <sub>2</sub>	Br	2	ether	14 h, rt	63	20
AgNO <sub>2</sub>	Cl <sup>8</sup>	2	ether	14 h, rt	39	58
NaNO <sub>2</sub>	Br	2	ether	14 h, rt/5 h reflux	0	0
NaNO <sub>2</sub>	Br	2	benzene	12 h, rt/5 h reflux	0	0 <sub>9</sub>
NaNO <sub>2</sub>	Br	5	DMF	24 h, rt	62	0 <sub>9</sub>
NaNO <sub>2</sub>	Br	5	DMSO	8 h, rt	72	0

The absence of the nitrite (5) in the  $\text{NaNO}_2$ -DMF/DMSO reaction is somewhat surprising<sup>10</sup> and it is likely that, under these conditions, the nitro compound (4) is formed by the opening of the intermediate (6). Since (4) has already been demonstrated to fragment readily and quantitatively



to nitroethylene<sup>1</sup> on benzene reflux, the facile route described should further encourage the use of nitroethylene in organic synthesis.

#### REFERENCES AND NOTES

1. S. Ranganathan, D. Ranganathan and A.K. Mehrotra, *J. Am. Chem. Soc.*, **96**, 5261(1974); S. Ranganathan, D. Ranganathan and R. Iyengar, *Tetrahedron*, **32**, 961(1976); S. Ranganathan, D. Ranganathan and A.K. Mehrotra, *Synthesis*, 289(1977); D. Ranganathan, C.B. Rao, and S. Ranganathan, *J. Chem. Soc., Chem. Commun.*, 975(1979); D. Ranganathan, C.B. Rao, S. Ranganathan, A.K. Mehrotra and R. Iyengar, *J. Org. Chem.*, **45**, 1185(1980); D. Ranganathan, S. Ranganathan, C.B. Rao and K. Kesavan, *Synthesis*, 884(1980); D. Ranganathan, S. Ranganathan and S. Bamezai, *Tetrahedron Lett.*, 2789(1982); D. Ranganathan, S. Ranganathan, S. Bamezai, S. Mehrotra and P.V. Ramachandran, *J. Chem. Res. (S)*, 78(1983).
2. For recent applications of nitroethylene, please see : A.G.M. Barrett and G.G. Graboski, *Chem. Rev.*, **86**, 751(1986); E.J. Corey and A.G. Myers, *J. Am. Chem. Soc.*, **107**, 5574(1985); N. Ono, A. Kamimura, H. Miyake, I. Hamamoto and A. Kaji, *J. Org. Chem.*, **50**, 3692(1985); E.E. Van Tamelen and S.R. Zawacky, *Tetrahedron Lett.*, **26**, 2833(1985); S. Piettre, Z. Janouski, R. Merenyi and H.G. Viehe, *Tetrahedron*, **41**, 2527(1985); R.M. Cory, P.C. Anderson, M.D. Bailey, F.R. McLaren, R.M. Renneboog and B.R. Yamamoto, *Can. J. Chem.*, **63**, 2618(1985); S. Kurokawa and A.G. Anderson Jr., *Bull. Chem. Soc., Japan*, **58**, 367(1985); A. Korgesaar, N. Johanson and I. Annus, *Chem. Abstr.*, **104**, 33787p (1986); A. Korgesaar, T. Tensing and M. Nechaeva, *Chem. Abstr.*, **104**, 33788g(1986).
3. The Organic Synthesis procedure (W. Noland, Coll. Vol. V, p.833) calls for the generation of nitromethane conjugate base in ~10 fold excess of  $\text{MeNO}_2$ , followed by reaction with para formaldehyde and isolation of the product by co-distillation with Ph-O-Ph, for uniform heat distribution. We have used this procedure extensively and, inspite of all precautions, on three occasions explosions resulted, either during or after the distillation. This is to be contrasted with our equally wide use of nitroethylene, where, on no occasion there was hazard.
4. S. Ranganathan, D. Ranganathan and S.K. Singh, *Tetrahedron Lett.*, 4955(1985).
5. The usual oxidizing agents such as m-Cl PBA and peracids gave mixtures.
6. 2-Nitroethyl Phenyl Sulfoxide(4) :  $\text{PhSCH}_2\text{CH}_2\text{OH}$ (1) :  $\text{HOCH}_2\text{CH}_2\text{OH}$ (960 mmol) +  $\text{HBr}$ (48% aq, 50 ml), reflux 8 h, distil off 50 ml, neutralize  $\text{Na}_2\text{CO}_3$ , saturate  $\text{Na}_2\text{SO}_4$ , extract  $\text{Et}_2\text{O}$ , dry ( $\text{MgSO}_4$ ) and distil to give 30%  $\text{BrCH}_2\text{CH}_2\text{OH}$ , bp 149-150°.  $\text{BrCH}_2\text{CH}_2\text{OH}$ (500 mmol) +  $\text{PhSH}$ (500 mmol) + 20% aq.  $\text{NaOH}$  (120 ml), reflux 1 h, cool, separate oily layer, extract  $\text{CHCl}_3$ , combined organic extracts, dry, evaporate and distil to afford, 88% of (1), bp 135°/8 torr; nmr :  $\delta$  ( $\text{CCl}_4$ ) : 2.93(t), 3.11-3.81(m), 7.16(m).  $\text{PhSCH}_2\text{CH}_2\text{Br}$ (2) : Add, in drops,  $\text{PBr}_3$  (10 mmol) to stirred, neat (1) (30 mmol); after 1 h rt, admix with cold water, extract ( $\text{Et}_2\text{O}$ ), dry, evaporate and distil to give 81% of (2), bp 120-122°/0.05 torr; nmr :  $\delta$   $\text{CDCl}_3$  : 3.2-3.5(m), 7.2(m).  $\text{PhSCH}_2\text{CH}_2\text{NO}_2$ (3) : To stirred, dry  $\text{NaNO}_2$  (18 mmol) in dry DMSO (20 ml), add over 0.5 h, solution of (2) (356 mmol) in dry DMSO (15 ml). After 5 h, admix with cold water (40 ml), extract ( $\text{Et}_2\text{O}$ ), dry, evaporate, chromatograph on silica gel and elute with hexane :  $\text{PhH}$ :7:3 to give 72% (3), bp 130°/0.3 torr; nmr :  $\delta$   $\text{CDCl}_3$  : 3.28(t), 4.35(t), 7.6(m). 2-Nitroethyl phenyl sulfoxide(4) : Stirred mixture of (3) (1 mmol) + 4- $\text{t-BuPhIO}_2$ (1 mmol) + dry  $\text{PhH}$ (10 ml) + TFA (0.2 ml) leave rt 12 h, filter, evaporate, chromatograph on silica gel and elute with  $\text{PhH}$ : $\text{EtOAc}$ : 4:1 to give 96% of (4) mp 64°; nmr :  $\delta$   $\text{CDCl}_3$  : 3.5(m), 4.7(m), 7.8(m).
7. Elutes after (3); nmr :  $\delta$  ( $\text{CDCl}_3$ ) : 3.06(t), 4.8(t), 7.25(m).
8. Prepared from (1) and  $\text{SOCl}_2$  in 96% yield; nmr :  $\delta$   $\text{CDCl}_3$  : 2.9-3.2(m), 3.4-3.7(m), 7.2(m).
9. Blank experiments have shown that the nitrite (5), if formed, would have survived the reaction conditions.
10. N. Kornblum, H.O. Larson, R.K. Blackwood, D.D. Mooberry, E.P. Olivetto and G.E. Graham, *J. Am. Chem. Soc.*, **78**, 1497(1956).

(Received in UK 13 April 1987)