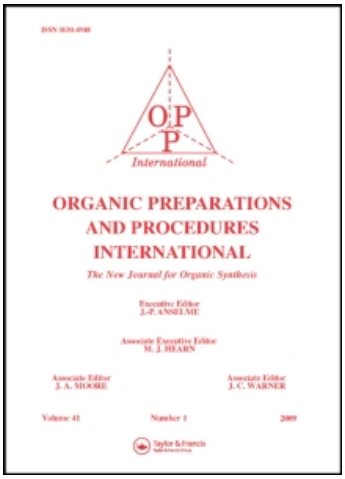

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AN IMPROVED PROCEDURE FOR THE PREPARATION OF ARYLOXIRANES

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18. Aldrich Catalogue-Hand Book of Fine Chemicals, 1991-92.

19. H. Firouzabadi and I. Mohammadpour Baltork, *Bull. Chem. Soc. Jpn*, **65**, 1131 (1992).

20. E. I. Tinyakova, E. K. Khrennikova and B. A. Dolgoplosk, *Zhur. Obschei Khim.*, **28**, 1632 (1958).

21. J. Drabowicz and M. Mikolajczyk, *Synthesis*, 32 (**1980**).

22. M. T. Rogers and T. W. Campbell, *J. Am. Chem. Soc.*, **69**, 2039 (1947).

23. V. I. Cohen, *J. Org. Chem.*, **42**, 2510 (1977).

24. A. Krief, A. F. De Mahieu, W. Dumont and M. Trabelsi, *Synthesis*, 131 (**1988**).

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AN IMPROVED PROCEDURE FOR THE PREPARATION OF ARYLOXIRANES

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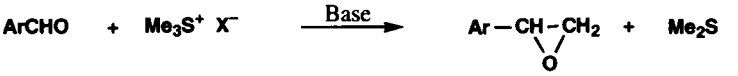
Oxiranes are reactive and versatile synthetic intermediates,[1] conveniently prepared by reaction of aldehydes and ketones with dimethylsulfonium methylide. While a method for generating the ylide under strong acid conditions has recently been reported,[2] strongly basic conditions are more usual.



The original method in which the ylide was generated from trimethylsulfonium iodide with sodium hydride in anhydrous dimethyl sulfoxide,[3] was subsequently applied to a range of aromatic and heteroaromatic aldehydes to prepare intermediates in the synthesis of antimalarials.[4] Success has since been reported for phenyloxirane with conc. aqueous sodium hydroxide as base in two-phase systems, both with[5] and without[6] a phase-transfer catalyst. In aqueous conditions, the sulfonium salt counterion is stated to be important in ylide generation, with better results with the chloride (though less convenient to prepare) than iodide.[7] Under phase-transfer conditions, the sulfonium chloride gave a 60% yield of *p*-nitrophenyloxirane[8] and 15% yield of the 4-pyridinyl analog.[9]

In our hands, the phase-transfer reaction with trimethylsulfonium *iodide* and aqueous sodium hydroxide was quite successful when applied to benzaldehyde. With the more reactive 4-nitrobenzaldehyde, however, the Cannizzaro reaction was competitive and 4-nitrobenzyl alcohol

was even the main product under some variations of these reaction conditions. Nucleophilic hydroxide was therefore undesirable and we turned to potassium *tert*-butoxide as the base and homogeneous reactions in *tert*-butyl alcohol as solvent. Experimentally, this was more convenient than the original sodium hydride-dimethyl sulfoxide method, the Cannizzaro reaction was repressed and 4-nitrophenyloxirane was readily isolated. We have also applied these conditions to two other potentially sensitive aldehydes and obtained 4-oxiranyl-8-nitroquinoline and an improved yield of 4-oxiranylpyridine. We therefore recommend this experimentally simple use of the easily obtained sulfonium iodide for the generation of aryloxiranes.

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded at 300 MHz, in $CDCl_3$ solvent, with TMS as internal standard.

4-Nitrophenyloxirane.- A mixture of 4-nitrobenzaldehyde (0.45 g, 2.9 mmol) and trimethylsulfonium iodide[10] (1.2 g, 5.8 mmol) in *tert-b*utyl alcohol (60 mL) was stirred and heated to 60°. Potassium *tert*-butoxide (3.5 M in *tert*-butyl alcohol, 4 mL, 1.4 mmol) was added within 1 min and the mixture was heated and stirred for a further 2 hrs. It was then cooled in ice and neutralized with 1M hydrochloric acid, the solvent was evaporated under reduced pressure, the semi-solid residue was dissolved in cold water (25 mL) and extracted with ether (3 x 25 mL). The extracts were dried ($MgSO_4$) and the solvent removed to give the oxirane (0.26 g, 53%), mp. 79-81° (from ether), lit.[11] mp. 79-81°; lit.[8] mp. 84-85°. ^{1}H NMR: δ 2.76 (dd, *J* = 5.5, 2.5 Hz, 1H, H-β), 3.23 (dd, *J* = 5.5, 4.2 Hz, 1H, H-β'), 3.94 (dd, *J* = 4.2, 2.5 Hz, 1H, H-α), 7.42 + 8.19 (d+ d, *J* = 6.8 Hz, 4H, ArH).

Also prepared by this method were:

4-Oxiranylpyridine, isolated as an oil (49%), with ^{1}H NMR in accord with that reported:[9] δ 2.76 (dd, *J* = 5.6, 2.4 Hz, 1H, H-β), 3.19 (dd, *J* = 5.6, 4.2 Hz, 1H, H-β'), 3.84 (dd, *J* = 4.2, 2.4 Hz, 1H, H-α), 7.21 (dd, *J* = 4.5, 1.5 Hz, 2H, H-3,5), 8.56 (dd, *J* = 4.5, 1.5 Hz, 2H, H-2,6).

8-Nitro-4-oxiranylquinoline, (49%), mp. 119-120° [from light petroleum (bp. 90-110°)]; ^{1}H NMR: δ 2.77 (dd, *J* = 5.7, 2.5 Hz, 1H, H-β), 3.37 (dd, J = 5.7, 4.1 Hz, 1H, H-β'), 4.49 (dd, *J* = 4.1, 2.5 Hz, 1H, H-α), 7.50 (d, *J* = 4.5 Hz, 1H, H-3), 7.67 (dd, *J* = 8.6, 7.6 Hz, 1H, H-6), 8.02 (dd, *J* = 7.6, 1.1 Hz, 1H, H-5), 8.31 (dd, *J* = 8.6, 1.1 Hz, 1H, H-7), 9.20 (d, *J* = 4.5 Hz, 1H, H-2).

Anal. Calcd for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.73; N, 12.96. Found: C, 61.03; H, 3.31; N, 13.31

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REFERENCES

1. A. S. Rao, S. K. Paknikar and J. G. Kirtane, *Tetrahedron*, **39**, 2323 (1983).

2. J. Forrester, R. V. H. Jones, P. N. Preston and E. S. C. Simpson, *J. Chem. Soc. Perkin Trans. 1*, 1937 (**1993**).

3. E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

4. W. G. Duncan, W. T. Colwell, C. R. Scott and D. W. Henry, *J. Med. Chem.*, **11**, 1221 (1968).

5. A. Merz and G. Märkl, *Angew. Chem. Inter. Eng. Ed.*, **12**, 845 (1973).

6. M. J. Hatch, *J. Org. Chem.*, **34**, 2133 (1969).

7. M. Rosenberger, W. Jackson and G. Saucy, *Helv. Chim. Acta*, **63**, 1665 (1980).

8. M. M. Kayser and P. Morand, *Can. J. Chem.*, **58**, 302 (1980).

9. K. Kloc, E. Kubicz and J. Mlochowski, *Heterocycles*, **22**, 2517 (1984).

10. H. J. Emeléus and H. G. Heal, *J. Chem. Soc.*, 1126 (**1946**).

11. W. Wierenga, A. W. Harrison, B. R. Evans and C. G. Chidester, *J. Org. Chem.*, **49**, 438 (1984).

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SYNTHESIS OF ALDIMINES BY DEOXYGENATION OF NITRONES

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Aldimines are an important class of organic compounds[1] and perusal of the literature reveals that the preferred route for the synthesis of aldimines involves the condensation of aldehydes with ammonia or amines. However, this method is sensitive to the pH of the reaction medium and substituent effects. For example, it is difficult to obtain aldimines from the condensation of 4-methoxybenzaldehyde with amines or 4-nitroanilines with aldehydes. Hence, any method that does not depend upon these factors is worthy of examination. As a continuation of our work on the chemistry of nitrones,[2] it was proposed to synthesize the aldimines through the deoxygenation of α,N-diaryl nitrones. Perusal of the literature reveals that the selective deoxygenation of nitrones and heteroaromatic N-oxides has been the subject of considerable interest and several methods are available on the reduction of the N-O bond in these systems.[3] Triphenylphosphine has been used to reduce the N-O bond of the aldonitrones to yield the aldimines in 90% yield;[3c] the promised detailed procedures never appeared.[4] Related material supplied by Prof. Horner reported that attempts to deoxygenate α-(4-methoxyphenyl)-N-phenylnitrone with an equimolar quantity of triphenylphosphine by