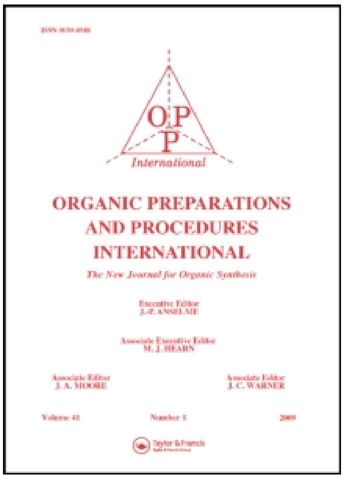

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ONE-POT SYNTHESIS OF NITROSTYRENE OXIDES

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REFERENCES

1. R. P. Skowronski, J. J. Ratto, and L. A. Heredy, Annual Technical Progress Report to DOE, FE-2328-13, 1978, pp. 52-56.
2. N. H. Werstiuk and G. Timmins, Can. J. Chem., 59, 3218 (1981).
3. T. S. Chen, J. Wolinska-Mocydlarz, and L. C. Leitch, J. Labelled Compounds, 6, 285 (1971).
4. The total vapor pressure at 250° was taken as the sum of that for water (576.6 psia) and tetrahydronaphthalene (36.2 psia). The latter value was taken from M. Kara, S. Sung, E. Klinzing, and S. K. Chiang, Fuel, 60, 633 (1981).

ONE-POT SYNTHESIS OF NITROSTYRENE OXIDES

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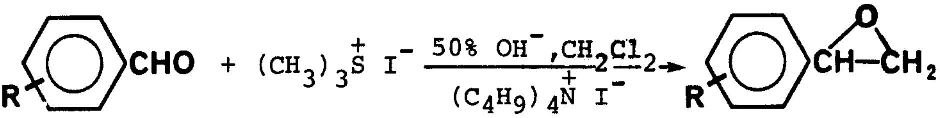
There has been considerable interest in recent years in nitrostyrene oxides and in products derived from them. For instance, o-nitrostyrene oxide has been used as a precursor in the synthesis of o-nitrophenylethylene acetal or ketal, a photoremoveable protective group for aldehydes and ketones.[1,2] It has also been used in the synthesis of benzisoxazolone, an antibacterial and antileukemic agent.[2] A mechanistic study of the ring opening of nitrostyrene oxides was the subject of another series of articles.[3] Nitrostyrene oxides have usually been made *via* lengthy, laborious or costly methods. There are essentially two existing methods for their synthesis in the literature. The first involves the reaction of diazomethane with nitrobenzaldehydes[4] while the second includes α-bromination of nitroacetophenones, reduction of the resulting bromoketones to the corresponding bromohydrins followed by cyclization to epoxides[5,9] with 65-70% overall yield.

The present method, which is modified from a literature procedure,[6] appears to be superior in terms of facility (one-pot reaction, aqueous medium), number of steps (one) and cost; the yields of isolated products are in the same range of that obtained by other methods.



R = *o*, *m*, *p*-NO_2

The purity of the nitrostyrene oxides was checked by GC and NMR. In all cases it was found that the product is more than 92% pure. Chromatography on silica gel using CH_2Cl_2 was very useful in achieving higher purity. The structure of the products was determined by NMR and IR spectroscopy, based on comparison with pertinent data available in the literature. The results were as follows: *p*-nitrostyrene oxide (75% yield), mp. 85-86°; lit.[8] mp. 86°; lit.[3b] mp. 84-85°; lit.[9] mp. 84-86°; *m*-nitrostyrene oxide (73% yield), bp. 104° (0.3 mm Hg); lit.[3a] 103-104° (0.3 mm Hg); *o*-nitrostyrene (65% yield), mp. 64-65°, lit.[1a] mp. 64-65°, lit.[5] mp. 64-65°.

EXPERIMENTAL SECTION

General Procedure.- In a 500 ml round-bottomed flask, equipped with an efficient stirrer and reflux condenser, was placed 200 ml CH_2Cl_2 in which was dissolved 7.50 g (0.049 mol) of the nitrobenzaldehyde[7] and 0.10 g of $(C_4H_9)_4N^+\ I^-$, followed by addition of 10.20 g (0.060 mol) of finely powdered trimethylsulfonium iodide (Aldrich). To this was then added 50 ml of a 50% (w/w) aqueous solution of NaOH. The reaction mixture was stirred and refluxed for 24 hrs. It was then poured into 200 ml of ice-cold water and the organic layer separated. The aqueous layer was further extracted with

CH_2Cl_2 (3 x 50 ml). The combined extracts were washed with water (3 times) and once with a saturated solution of sodium metabisulphite and then water. After drying and evaporation, a solid or a liquid was obtained which was purified accordingly (distillation or chromatography on silica gel using CH_2Cl_2).

REFERENCES

1. a) D. Gravel, J. Herbert and D. Thoraval, Can. J. Chem., 61, 400 (1983); b) J. Hebert and D. Gravel, ibid. 52, 187 (1974).
2. W. Wierenga, A. W. Harrison, B. R. Evans and C. G. Chidester, J. Org. Chem., 49, 438 (1984).
3. a) R. P. Hanzlik and R. B. Westkaemper, J. Am. Chem. Soc., 102, 2464 (1980); b) J. Biggs, N. B. Chapman, A. F. Finch and V. Wray, J. Chem. Soc. [B], 55 (1971).
4. F. Arndt, E. Amende and E. Ender, Monatsh. Chem., 59, 202 (1932); F. Arndt and W. Partale, Ber., 61, 1107 (1928); 61, 1949 (1928).
5. C. O. Guss, J. Org. Chem., 17, 678 (1952).
6. Temperature control in this method was found to be unnecessary, A. I. Vogel "Textbook of Practical Organic Chemistry", 4th Ed., pp. 921-2, Longman, New York, N.Y. (1978). See also M. J. Hatch, J. Org. Chem., 34, 2133 (1969) and A. Merz and G. Markl, Angew. Chem. Int. Ed. Engl., 12, 845 (1973).
7. In case of o-nitrobenzaldehyde, the reaction vessel was protected from light by aluminum foil.
8. A. C. Knipe, J. Chem. Soc. Perkin Trans II, 589 (1973).
9. C. O. Guss and H. G. Mautner, J. Org. Chem., 16, 887 (1951).