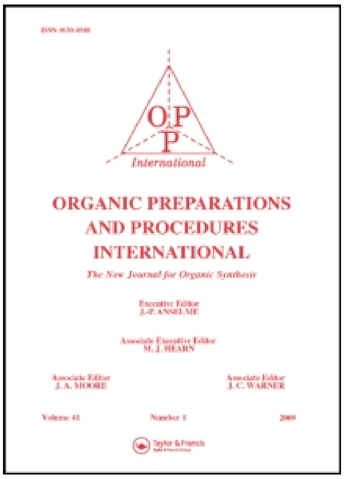

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SYNTHESIS OF NITROALKANES FROM BROMOALKANES BY PHASE-TRANSFER CATALYSIS

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SYNTHESIS OF NITROALKANES FROM BROMOALKANES BY PHASE-TRANSFER CATALYSIS

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1-Nitropropane, an intermediate for ethambutol, is usually manufactured by the vapour phase nitration of propane, which unfortunately is hazardous and leads to the formation of various side-products depending on the reaction conditions.[1] The recent use of nitrite form of basic anion exchange resin for the synthesis of 1-nitropropane, from the corresponding bromide, involves long reaction periods and low selectivity.[2] A number of methods for the nitrite displacement with phase-transfer catalyst (PTC), crown ethers, polyethylene glycols and tetraalkylammonium salts, have been reported; the selectivity for nitrooctane varied between 20% and 70% depending upon the reaction conditions and PTC employed.[3-5]

For the synthesis of nitroalkanes from bromoalkanes and sodium nitrite, using chloroform as solvent, the liquid-liquid rather than liquid-solid mode of operation was required and it was necessary to maintain alkaline conditions by the addition of 0.4M sodium carbonate. Several PTC were tried and tetrabutylammonium hydrogen sulfate (TBAHS) worked best; of a number of solvents tried, chloroform was found to be the best. The main by-product formed was the alkyl nitrite and hydrolysis to the alcohol was negligible. Thus in 6 hrs, with TBAHS as PTC, the yield of 1-nitropropane was 62% and 23% of unreacted 1-bromopropane was recovered; propyl nitrite was detected to the extent of 14%. Under the same contitions as for 1-bromopropane, the yield of 1-nitrobutane was 57% with 26% recovery of unreacted 1-bromobutane. By contrast, with 1-chlorobutane, under similar conditions as above, no reaction to 1-nitrobutane occurred. 1-Nitrohexane was obtained in 45% yield and 39% of unreacted 1-bromohexane was recovered. Further, with 2-bromopropane the rate was relatively low and the yield of 2-nitropropane was 24% and the recovery of unreacted 2-bromopropane was 65%.

EXPERIMENTAL SECTION

1-Nitropropane.- The reaction was conducted in a fully baffled mechanically agitated glass contactor of 100 ml capacity provided with a glass impeller at 31°. To an aqueous phase solution (60 ml) of sodium nitrite (25 g, 0.36 mol) and sodium carbonate (2.55 g, 0.024mol), an organic phase consisting of 1-bromopropane (10 ml, 0.11 mol) and TBAHS (1.12g, 3.3 mmol) in chloroform (10 ml) was added. The reaction mixture was stirred at a constant speed of agitation of 1500 rev/min. The progress of the reaction was monitored by analysing samples from the organic phase by gas-liquid chromatography; an s.s. column, 3.2 mm dia. x 2 meter long, packed with 10% SE-30 on Chromosorb-W, was used with nitrogen, as a carrier, on a "Chemito" gas chromatograph. After 6 hrs, the reaction mixture was worked up and the residue was distilled to yield 6.0 g (61% yield) of 1-nitropropane, bp. 55°/40 mm. The product was structurally confirmed through an FT-IR (Bruker, IFS 88) and ^{1}H-NMR (Varian EM-360L, 60 MHz).

^{1}H-NMR data.- 1-Nitropropane, (CCl_4) : δ 1.0 (3H, t, CH_3), δ 2.0 (2H, m,$CH_2CH_2NO_2$), δ 4.3 (2H, t, CH_2NO_2). 2-Nitropropane, (CCl_4): δ 1.6 (6H, d, 2-CH_3), δ 4.6 (1H, m, CH). 1-Nitrobutane, (CCl_4): δ 1.0 (3H, t, CH_3), δ 1.1-2.1 (4H, m, CH_2CH_2), δ 4.39 (2H, t, CH_2NO_2). 1-Nitrohexane, (CCl_4) : δ 0.9 (3H, t, CH_3), δ 1.0-2.2 (8H, m, $(CH_2)_4$), δ 4.33 (2H, t, CH_2NO_2).

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