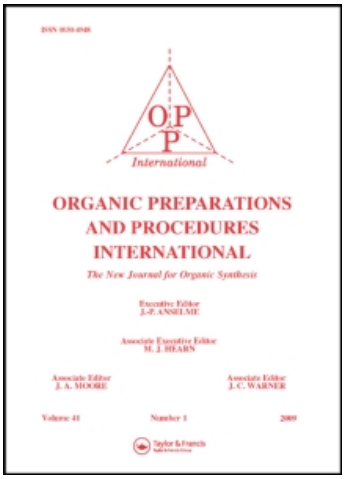

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IMPROVED HIGH-YIELD CONVERSION OF DINITROMESITYLENE TO NITROMESIDINE

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OPPI BRIEFS

IMPROVED HIGH-YIELD CONVERSION OF DINITROMESITYLENE TO NITROMESIDINE

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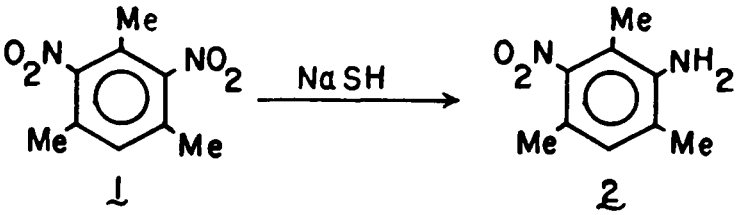
Nitromesidine (2), a key intermediate in many conversions, is not commercially available. Reported procedures for the reduction of one nitro group of dinitromesitylene (1) use mild reducing agents such as hydrogen sulfide and ammonia[1] or sodium polysulfide.[2] Although yields of 90% and 95% have been reported, prolonged reaction times (2 days[1] or 50 hrs[3]) are required. In addition, the formation of elemental sulfur is undesirable since it is difficult to remove by filtration because it is often formed in a colloidal state.[3] Although the procedure[2] using polysulfide takes less time (2 hrs for the polysulfide addition followed by 3.5 hrs reflux), only a moderate yield of 78% was obtained. Adams et al.[4] used sodium



1 2

hydrosulfide for the reduction of one of the nitro groups of dinitrobenzene. We report the application of this reagent for the conversion of dinitromesitylene to nitromesidine (2) in excellent yield and purity, in relatively short reaction times.

EXPERIMENTAL SECTION

^1H NMR (60 MHz) spectra were obtained in $CDCl_3$ with a Perkin-Elmer R-12B instrument. ^{13}C NMR spectra were determined on a JEOL FX90Q spectrometer using TMS as internal standard. Mass spectra were recorded with a Finnigan 1020 automated GC/MS system. Melting points are corrected and were taken with a Fisher hot-stage apparatus calibrated against pure recrystallized standards using a Büchi mp apparatus. IR spectra were obtained using a Perkin-Elmer 1320 instrument.

Reduction of Dinitromesitylene (1) to Nitromesidine (2).- Dinitromesitylene (1)[3] (18 g, 0.090 mol) was dissolved in 90 ml of hot ethanol in a 3-necked flask equipped with a condenser, dropping funnel, magnetic stirring bar, and a septum for removal of samples to monitor the reaction. Methanolic sodium hydrosulfide solution, prepared[4] from 49.5 g (0.21 mol) of $Na_2S \cdot 9H_2O$ in 90 ml of water and 18.25 g (0.22 mol) of oven-dried sodium bicarbonate, was added over a period of 1 hr followed by reflux for 3 hrs; the reaction mixture was then cooled and stirred at room temperature for 0.5 hr. During the period of reflux, the reaction was monitored by GC/MS with samples obtained with a syringe through the septum. The solvent was removed by distillation until drops of an immiscible liquid were observed to float on the solvent in the flask. The reaction mixture was cooled and poured into 300 ml of cold water. The yellow precipitate of nitromesidine (15.6 g., ca. 100%) was collected, washed with water to remove sodium hydrosulfide, and dried on the suction filter for about 2 hrs. GC/MS on this sample showed the absence of 1 and of any other products. Further purification was carried out by dissolving the sample in toluene and adding concentrated hydrochloric acid dropwise until no more white precipitate of amine hydrochloride was observed to form. The hydrochloride was collected and dried on the suction filter, transferred to a flask, and treated with 30% aqueous ammonia to liberate the free amine. The solid nitromesidine was then collected and dried on the Büchner funnel to yield 15 g (97%) of

yellow fluffy crystals, mp. 71-72°, lit.[3] 71-72.5°.

Nitromesidine (2) showed the following spectral properties: ^1H ($CDCl_3$): δ 2.03 (3 H, s, ring CH_3); 2.13 (6 H, s, ring CH_3), 3.63 (2 H, s, NH_2); 6.73 (1 H, s, ring H); ^{13}C NMR($CDCl_3$): δ 12.30, 16.52, 17.55 (ring methyls); 112.85, 117.83, 123.84, 130.07, 141.62 (aromatic ring carbons). Mass spectrum (70 ev): m/e 180 (M^+, 100%), 163 (55%), 148 (4%), 135 (40%), 118 (48%), 108 (47%), 91 (52%), 77 (25%), 65 (23%); IR (KBr): 3360, 3430 (m N-H str); 1640 (b, N-H bend); 1310 (w, C-N); 1520, 1370 (sh, $C-NO_2$) cm^{-1}.

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1,2-DINITROCYCLOHEXENE

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Previously, only five examples of isolated 1,2-dinitroalkenes had been reported: 1,2-dinitroethene (1a),[1] 2,3-dinitro-2-butene (1b),[2] 3,4-