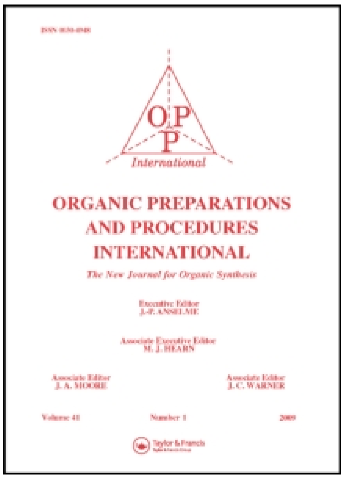

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AN EFFICIENT SYNTHESIS OF N-(2,4-DIFLUOROPHENYL)-N-METHYL-2,4-DINITRO-6-(TRIFLUOROMETHYL)ANILINE

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2-(p-Nitrobenzalazo)-4-(4'-hydroxycoumarin-3'-yl)-5-methylthiazol-2-one (IIIh) in 85% yield as yellow crystals, mp. 305-308°. IR: 3420 (OH), 3000 (CH arom.), 2910 (CH_3), 1675 (CO), 1612 (C=C, arom.) cm^{-1}; nmr: δ 7.3-8.35 (m, 8H arom., NH, CH), 2.20 (s, CH_3); MS: M^+ 422 (100).

Anal. Calcd for $C_{20}H_{14}N_4O_5S$: C, 56.86; H, 3.34; N, 13.26

Found: C, 57.45; H, 3.51; N, 13.27

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AN EFFICIENT SYNTHESIS OF N-(2,4-DIFLUOROPHENYL)-N-METHYL-2,4-DINITRO-6-(TRIFLUOROMETHYL)ANILINE

Submitted by E. V. P. Tao* and H. A. Corbitt
(11/05/84)

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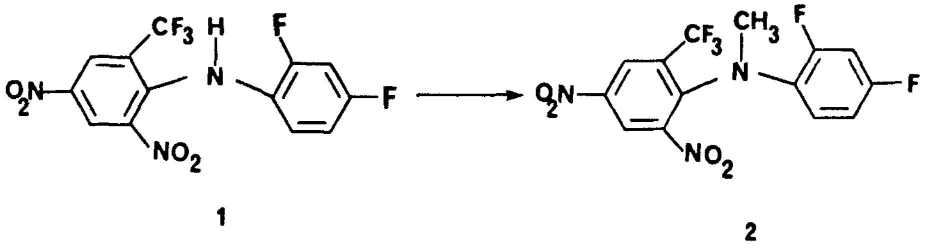
N-(2,4-difluorophenyl)-N-methyl-2,4-dinitro-6-(trifluoromethyl)aniline (2),[1] is a contact miticide which has demonstrated effective control of phytophagus mites on cotton and tree fruits and nuts. Methyl bromide has long been known as a methylating agent;[2] however, it is less known as a methylating agent to convert a secondary aromatic amine to the corresponding tertiary amine as shown below. Until recently there has not been a satisfactory synthesis of 2; either the yield is not high or the process is not economically feasible for large-scale preparation. We now report an efficient synthesis of 2 which utilizes methyl bromide under pressure, gives good yields and is amenable to large scale production.



EXPERIMENTAL SECTION

N-(2,4-Difluorophenyl)-N-methyl-2,4-dinitro-6-(trifluoromethyl)aniline(2).- N-(2,4-Difluorophenyl)-2,4-dinitro-6-(trifluoromethyl)aniline (108.9 g, 64.4% pure, 0.193 mole), sodium carbonate (64 g), and dimethylformamide (150 ml) were placed in a 1 L Chemineer pressure reactor[3] equipped with an air-driven agitator, a baffle, a pressure gauge, a relief port and a sample port. The reaction mixture was cooled to -15°, and methyl bromide (228 g, 2.47 moles) was added as a cold liquid; the reactor was sealed. The reaction mixture was then heated to 95° over a period of 30 min. and was maintained at that temperature for 2 hrs with agitation; the pressure was kept at 120 psig by occasional venting. The reaction mixture was allowed to cool to room temperature and the reactor purged with air in order to remove the remaining methyl bromide. The reaction mixture was poured into water and the product was collected and recrystallized from ethanol to afford 70.6 g, (97%) of 2, mp. 104.5-105.5°.

Anal. Calcd for $C_{14}H_8F_5N_3O_4$: C, 44.58; H, 2.14; F, 25.18; N, 11.14

Found: C, 44.67; H, 2.22; F, 25.26; N, 11.06

NMR (DMSO-d_6): δ 3.26 (s, 3, $N-CH_3$), 7.2 (m, 3, ArH), 8.65, 9.0 (d, 2 meta coupled ArH). Mass spectrum: $M^{+\cdot}$ 377.

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A CONVENIENT, TWO-STEP SYNTHESIS OF BICYCLO[3.3.0]OCT-1(5)-ENE

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(2/1/85)

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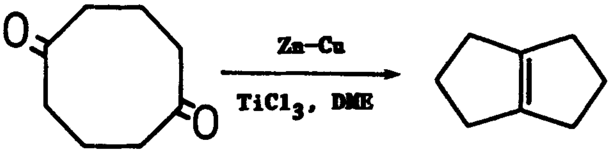
During the course of a collaborative effort on the study of the solid state NMR spectra of alkenes, a sample of bicyclo[3.3.0]oct-1(5)-ene (1) was desired.[1] Although 1 had been prepared by a variety of routes,[2] none of them were convenient. It appeared possible to obtain 1 via a reductive coupling of carbonyl groups.[3] The use of the high dilution procedure of McMurry might allow the conversion of 1,5-cyclooctanedione (2) to 1.[4]



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