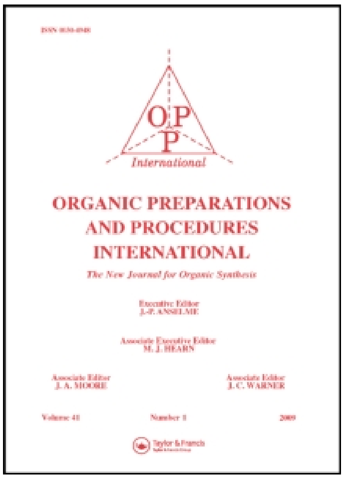

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2,4,6-TRICHLORO-*m*-TOLUIDINE

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2,4,6-TRICHLORO-m-TOLUIDINE

Submitted by
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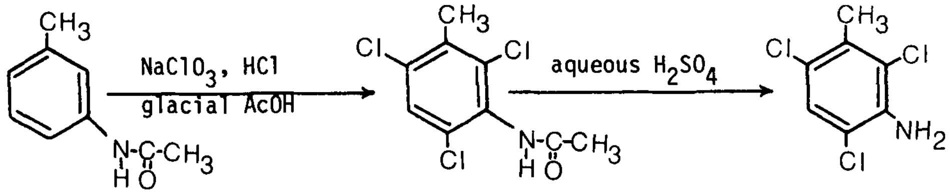
2,4,6-Trichloro-m-toluidine (III) is a useful intermediate in preparing a series of herbicides. Cohen and Dakin[1] claimed to have prepared III by the hydrolysis of 2,4,6-trichloro-m-acetotoluidide (II) obtained from the chlorination of I with sodium chlorate (2 moles chlorate/mole I) in glacial acetic acid. However, the product they obtained was not fully characterized. When their procedure was repeated, only a dichlorinated acetotoluidide was obtained. We wish to report the synthesis of 2,4,6-trichloro-m-acetotoluidide (II) and also 2,4,6-trichloro-m-toluidine (III).



I II III

EXPERIMENTAL

Melting points were determined on a Büchi melting point apparatus with a calibrated thermometer. Ir spectra were measured with a Beckman Model IR-8 grating spectrometer. Nmr spectra were recorded on a Varian Model T-60 spectrometer with tetramethylsilane as an internal standard. Elemental analyses were performed by PCR, Inc., Gainesville, Florida.

2,4,6-Trichloro-*m*-acetotoluidide (II). - To a stirred solution of *m*-acetotoluide (10 g, 0.067 mole) dissolved in 200 ml of glacial acetic acid, 25 ml of conc. hydrochloric acid (0.29 mole) was carefully added. To this solution maintained at 15-25° was added, dropwise, a solution of sodium chlorate (26 g, 0.24 mole) dissolved in 30 ml of water. The solution was stirred for 3 hrs. at room temperature. Upon addition of 500 ml of cold water, 2,4,6-trichloro-*m*-acetotoluidide precipitated; the product was recrystallized from alcohol. Yield: 9.0 g (53%) mp. 180-181° (lit.[2] 181°), (lit.[3] 192°); nmr ($CDCl_3$) δ 1.62(s,1,-NH-[4]), 2.2(s,3,-CH_3), 2.42(s,3,-CH_3), 7.2(s,1, aryl); ir(KBr) 1670 cm^{-1} (C=O).

Anal. Calcd. for $C_9H_8NOCl_3$: C 42.80, H 3.17, N 5.55, Cl 41.96

Found: C 42.58, H 3.14, N 5.56, Cl 40.74

2,4,6-Trichloro-*m*-toluidine (III). - 2,4,6-trichloro-*m*-acetotoluidide (II) (5 g, 0.020 mole) was heated to reflux with 75 ml of 50% aqueous sulfuric acid solution for 4.5 hrs. On cooling, a white preicpitate was obtained. This precipitate was filtered, dissolved in 25% aqueous alcohol and made basic with 25% aqueous NaOH solution. A pale brown solid was obtained and was recrystallized from alcohol to yield 1.8 g (42.8%) of white crystals, mp. 71-72° (lit.[1] 77-78°), (lit.[3] 85°); nmr ($CDCl_3$) δ 2.2(s,3,-CH_3), 4.4(s,2,-NH_2[4]), 7.2(s,1, aryl); ir (KBr) 1270, 1620, 3280, 3400 cm^{-1} (Ar-NH$_2$).

Anal. Calcd. for $C_7H_6NCl_3$: C 39.93, H 2.85, N 6.66, Cl 50.59
Found: C 39.80, H 2.83, N 6.82, Cl 50.18

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*To whom inquiries should be sent.

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4. Exchanges with D_2O.

THE SYNTHESIS OF SOME NEW 3-METHYL-2-PYRAZOLIN-5-ONES

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A number of new N-substituted 3-methyl-4-arylhydrazono-2-pyrazolin-5-ones (II) have been prepared by the reaction of ethyl 2,3-dioxobutyrate 2-arylhydrazones (I)[1] with 4-phenylsemicarbazide, benzylsulfonylhydrazine[2] and 4-acetamidobenzenesulfonylhydrazine[3] respectively.