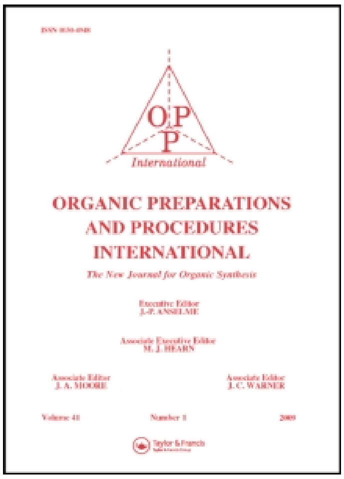

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3-CHLOROMETHYL-2,4,6-TRIMETHYLBENZOIC ACID

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3-CHLOROMETHYL-2,4,6-TRIMETHYLBENZOIC ACID

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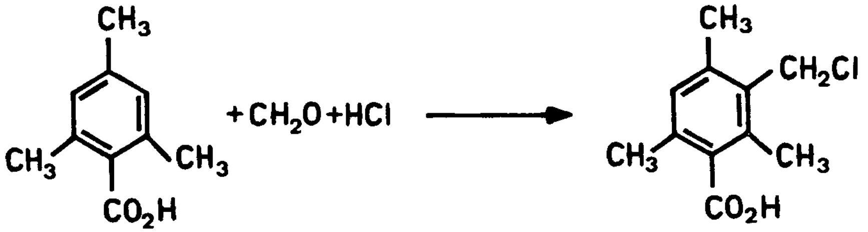
Attempted preparation of the title compound[1] from mesitoic acid by means of a standard chloromethylation method[2] used routinely with mesitylene resulted in formation of 3-hydroxymethyl-2,4,6-trimethylbenzoic acid. Rapid hydrolysis of the chloromethyl group evidently occurred during the mildly basic aqueous wash stage incorporated in the work-up procedure.[2] Direct formation of the hydroxymethyl derivative in this way was actually quite convenient as it was required for experiments on the attachment of the 2,4,6-trimethylbenzyl moiety to chloromethylated polystyrene supports.

3-Chloromethyl-2,4,6-trimethylbenzoic acid, mp. 200-201.5°, was readily obtained by the action of concentrated hydrochloric acid on the hydroxymethyl compound. The conversion was accompanied by a substantial downfield shift (0.3 ppm) of the benzylic proton resonance and by the disappearance of the strong hydroxyl band at 3410 cm^{-1}.



These observations suggest that a compound in the literature purported to be 3-chloromethyl-2,4,6-trimethylbenzoic acid (mp. 206°),[3] and prepared from mesitaldehyde by successive chloromethylation and oxidation steps involving aqueous basic conditions, is in reality the hydroxymethyl acid (mp. 207-208°). A more recent reference[1] to the chloromethyl acid, formed by direct chloromethylation of mesitoic acid and its hydrolysis to the hydroxymethyl derivative, gives melting points for both compounds which are much lower than those obtained here.

EXPERIMENTAL

Melting points are uncorrected.

3-Hydroxymethyl-2,4,6-trimethylbenzoic Acid.- Mesitoic acid (1.3 g) was chloromethylated as described in Organic Syntheses.[2] After 6 hrs., at 80-85°, the reaction mixture was diluted with water, the crude product treated with 1M sodium bicarbonate, and the filtered solution acidified with hydrochloric acid. The average yield over numerous runs was 1.16 g. (75%). This material was washed with hot ethyl acetate and recrystallized from ethanol/cyclohexane, mp. 207-208°, lit.[1] 137-138°; IR (KBr): 3410 (OH), 1690 cm^{-1} (CO_2H); 60 MHz NMR (DMSO-d_6): δ 2.19, 2.29, 2.32, s, CH_3 groups assigned in positional order 4,6,2; 4.47, s, CH_2; 6.87, s, arom. H.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.2; O. 24.8.

Found: C, 67.8; H, 7.3; O, 24.8.

3-Chloromethyl-2,4,6-trimethylbenzoic Acid.- The hydroxymethyl acid (200 mg.) was shaken with cold concentrated hydrochloric acid (5 ml) and ether (5 ml). Filtration from a litle suspended solid, if necessary, and removal of the ether under vacuum gave the chloromethyl acid (197 mg.; 90%), which was recrystallized from acetonitrile, mp. 200-201.5°, lit.[1] 178-179°); IR (KBr); 1695 cm^{-1} (CO_2H); 60 MHz NMR (DMSO-d_6): δ2.23, 2.33, 2.37, s, CH_3; 4.78, s, CH_2; 6.97, s, arom. H.

Anal. Calcd. for $C_{11}H_{13}ClO_2$: C, 62.1; H, 6.1; Cl, 16.7.
Found: C, 62.4; H, 6.4; Cl, 16.6.

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SYNTHESIS OF p-BIS(DIMETHYLHYDROXYSILYL)BENZENE

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p-Bis(dimethylhydroxysilyl)benzene is a convenient precursor for the synthesis of poly(tetramethyl-p-silphenylene-polysiloxane),[1] reported to be more stable than polydimethylsiloxane both to atmospheric oxidation and degradation at elevated temperatures.[2] However, methods involving Grignard re-