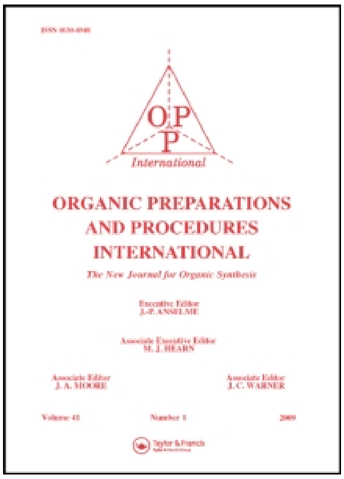

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IMPROVED PREPARATION OF 4-CHLOROMETHYLPHENYL ACETATE

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17.1 Hz, 1H). *Anal.* Calcd. for $C_{17}H_{30}O_3$: C, 72.29; H, 10.70. Found: C, 72.59; H, 10.88.

3b,c,[5] bp 70° (0.45 mmHg); ^{1}H NMR: δ 1.15 (t, J = 7.3 Hz, 6H), 2.53 (t, 2H), 3.30 (t, J = 7.58 Hz, 1H), 4.10 (q, J = 7.3 Hz, 4H), 4.90-5.03 (m, 2H), 5.60-5.70 (ddt, J = 7.2, 10.2 and 17 Hz, 1H).

3b,d,[6] bp 78° (1 mmHg); ^{1}H NMR: δ 1.22 (t, J = 7.3 Hz, 6H), 1.92-2.0 (m, 2H), 2.0-2.13 (m, 2H), 3.35 (t, J = 7.2 Hz, 1H), 4.15 (q, J = 7.3 Hz, 4H), 5-5.1 (m, 2H), 5.70-5.80 (ddt, J = 7.2, 10.2 and 17 Hz, 1H).

4a,c,[5] bp 73° (1.5 mmHg); ^{1}H NMR: δ 1.20 (t, J = 7.3 Hz, 3H), 2.09 (s, 3H), 2.55 (d, J = 7.2 Hz, 4H), 4.15 (q, J = 7.3 Hz, 2H), 4.9-5.0 (m, 4H), 5.45-5.60 (ddt, J = 7.2, 10.2 and 17 Hz, 1H).

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IMPROVED PREPARATION OF 4-CHLOROMETHYLPHENYL ACETATE

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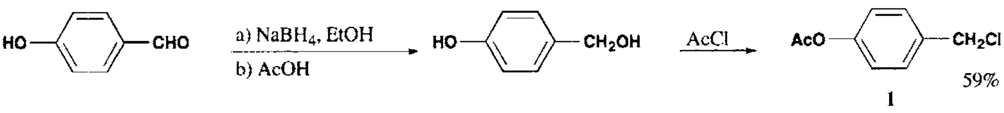
4-Chloromethylphenyl acetate (**1**) is used for the protection of thiols as base-labile 4-acetoxybenzylsulfides.[1] Recently it has been shown that the 4-acetoxybenzyl group is a very useful protective group in the synthesis of unsymmetrically substituted tetrathiafulvalenes.[2,3] Compound **1** is prepared by reaction of 4-hydroxymethylphenol with acetyl chloride,[1] but because a high cost of the starting material and a yield of only 40%, we developed the present synthesis, starting from inexpensive 4-hydroxybenzaldehyde. The aldehyde is reduced with $NaBH_4$ in ethanol to give 4-hydroxymethylphenol, which is treated with acetyl chloride to give **1** The use of a larger amount of acetyl chloride in the last step, increased the yield from 40%[1] to an overall yield of 59%.



1

EXPERIMENTAL SECTION

CAUTION: The reaction between 4-hydroxymethylphenol and acetyl chloride is exothermic and accompanied by a vigorous evolution of HCl.

4-Chloromethylphenyl Acetate.- To a mechanically stirred solution of 122.1 g (1 mole) 4-hydroxybenzaldehyde in 1 L of ethanol cooled to 10°C, was added 25 g (0.66 mole) $NaBH_4$ at such a rate that the temperature remained at 10 -15°. After additional 30 min. stirring, the excess of borohydride was hydrolyzed by cautious addition of acetic acid (approx. 50 mL). The solvent was removed *in vacuo* leaving a mixture of crude 4-hydroxymethylphenol and salts. This solid mixture was added to 600 mL CH_3COCl in small portions (approx. 5 g each) with good stirring and left standing at room temperature overnight. Excess acetyl chloride was removed *in vacuo* leaving an oily residue, which was carefully treated with a saturated $NaHCO_3$ solution until CO_2 evolution ceased. The crude product was taken up in ether, washed with water, dried over $MgSO_4$, concentrated and distilled *in vacuo* to yield 108.8 g (59%) of a colorless liquid, bp. 120-125°/12 mmHg, lit.[1] 104-106°/1.5 mmHg.

^1H NMR ($CDCl_3$): δ 7.3 (d, J= 8.5 Hz, 2 H); 7.0 (d, J= 8.5 Hz, 2 H); 4.5 (s, 2H); 2.2 (s,3H). ^{13}C NMR ($CDCl_3$): δ 169.1; 150.7; 135,0; 129.7; 121.9; 45.5; 20.9.

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