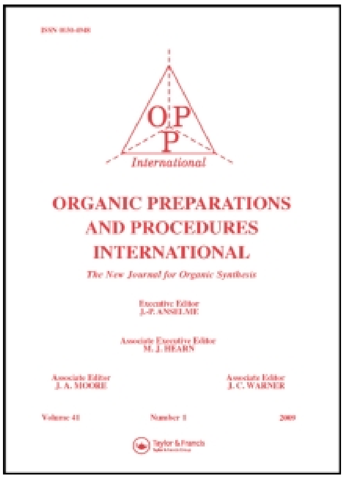

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AN IMPROVED SYNTHESIS OF 5-HYDROXYPENTANAL

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AN IMPROVED SYNTHESIS OF 5-HYDROXYPENTANAL[†]

Submitted by (03/21/88)

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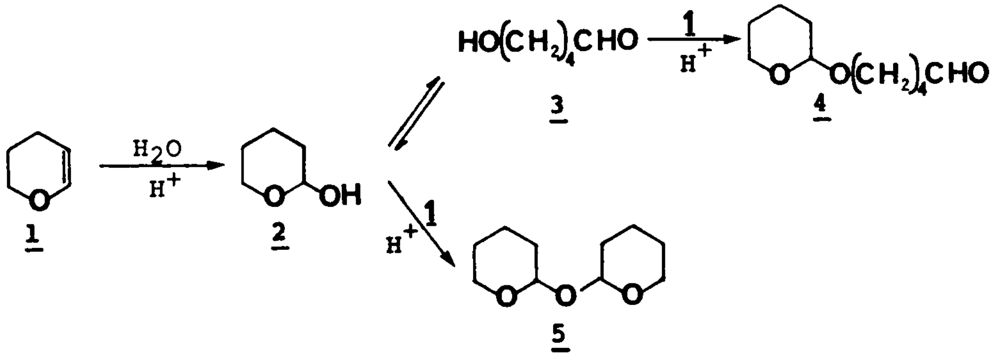
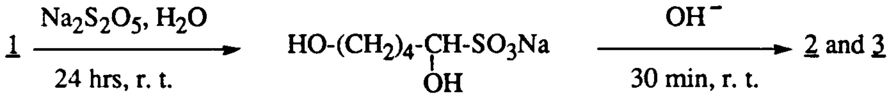
5-Hydroxypentanal (3) is a useful starting material for the synthesis of insect pheromones 5-alken-1-yl acetates and 5-alken-1-ols,[1] by virtue of the possibility of the Wittig condensation of its carbonyl function. It has been synthesized[2] by acid-catalyzed hydration of 3,4-dihydro-2H-pyran (1). The reaction mixture was reported to contain 3 and its lactol form, the 2-hydroxytetrahydropyran (2). The Wittig condensation of the crude mixture thus obtained, however, resulted in rather low yield of the desired 5-alken-1-ols, and a significant amount of their THP ether could also be isolated from the reaction mixture. We therefore reexamined this hydration and found that four products were formed. As a result of the acid-catalyzed hydration of 1, the 2-hydroxytetrahydropyran (2) was formed primarily which equilibrated with its open chain form, the 5-hydroxypentanal (3). The acid-catalyst (conc. hydrochloric acid), however, promotes not only the addition of water to the C-C double bond of 1, but also that of the OH groups in 3 and 2, thus resulting in the protected compounds 2-(2-tetrahydropyranyloxy) tetrahydropyran (5), and 5-(2-tetrahydropyranyloxy)pentanal (4). The ratio of 4 + 5 to 3 + 2 depends on the amount of acid used. Increasing its amount led to higher proportion of protected compounds (4 and 5). It proved impossible, however, to avoid the formation of side-products totally by decreasing the amount of the catalyst.We now report our modification which significantly decreases the amount of protected compounds 4 and 5.



Instead of hydrochloric acid, we use sodium metabisulfite which gives sodium bisulfite in aqueous solution. The medium is sufficiently acidic (pH about 4) to catalyse the addition of water, but only moderately that of the OH groups. In addition, the sodium bisulfite converts 3 to its bisulfite adduct (6) as the sole product of the reaction. On treatment with sodium hydroxyde, adduct 6 furnishes a mixture of 2 and 3. This two-step reaction represents an efficient method for the preparation of 3 containing only 2% of protected compounds 4 and 5.



$$1 \xrightarrow[\text{24 hrs, r. t.}]{Na_2S_2O_5,\ H_2O} HO\text{-}(CH_2)_4\text{-}\underset{OH}{CH}\text{-}SO_3Na \xrightarrow[\text{30 min, r. t.}]{OH^-} 2 \text{ and } 3$$

6

EXPERIMENTAL SECTION

The proportions of compounds in the end-product were determined by ^1H- (100 MHz) and^{13}C-NMR (25.5 MHz) in VARIAN XL-100 spectrometer (solvent: $CDCl_3$ internal standard: TMS) and GC in PERKIN ELMER F22 instrument with CPWAX 57CB capillary column (25 m x 0.22 mm i. d.) and FID detector (Column at 150°C, temp. of detector and injector: 200°C), carrier: N_2, 2.7 ml/min, split 1:100. The GC and NMR measurements gave the same ratio of compounds.

5-Hydroxypentanal (3).- To a solution of sodium metabisulfite (10.5 g; 0.055 mol) in water (30 ml) 3,4-dihydro-2H-pyran (1; 10 ml; 0.109 mol) was added dropwise at room temperature under stirring. The resulting mixture was stirred for 24 hrs at 25°C and evaporated in vacuo to yield a white powder (6; 21 g; 0.102 mol; Anal: calcd for $C_5H_{11}O_5SNa$: C, 29.1; H, 5.3; O, 38.8; S, 15.5; found: C, 29.0; H, 5.4; O, 38.0; S, 15.0). Compound 6 was then dissolved in 10% NaOH solution (60 ml) and stirred for 30 min at 25°C. The resulting mixture was extracted with ether (3 x 100 ml) and the organic extract was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by distillation to yield 10.0 g as a colourless liquid which contains 97% of 3 (87% yield), 1% of 2, 1% of 4 and less than 1% of 5, bp. 100-110°/16 torr.

2-Hydroxytetrahydropyran (2), R_t: 2.7 min; ^1H-NMR: δ 4.80 (m, 1H, -OCHO-); 3,3-3.95 (m, 2H, $-OCH_2-$); 1.30-1.90 (m, 6H, $-(CH_2)_3-$); ^{13}C-NMR: δ 19.5 (C^3), 25.3 (C^4), 30.9 (C^2), 62.3 (C^5), 98.8 (C^1).

5-Hydroxypentanal (3), R_t: 6.6 min; ^1H-NMR: δ 9.81 (t, J = 2 Hz, 1H, -CHO); 3.4-3.7 (m, 2H, $-OCH_2-$); 3.0 (brs, 1H, -OH); 2.4 (m, 2H, $-CH_2C{=}O$); 1.35-1.85 (m, 4H, $-(CH_2)_2-$; ^{13}C-NMR: δ 29.2 (C^3), 32.0 (C^4), 43.6 (C^2), 63.7 (C^5), 202.5 (C^1).

5-(2-Tetrahydropyranyloxy)pentanal (4), R_t: 3.9 min; ^1H-NMR: δ 9.8 (t, J = 2 Hz, 1H, -CHO); 4.54 (m, 1H, -OCHO-); 3.3-3.9 (m, 4H, $2x\text{-}CH_2O-$); 2.54 (m, 2H, $-CH_2C = O$); 1.3-1.9 (m, 10H, $-(CH_2)_3-$ + $-(CH_2)_2$); ^{13}C-NMR: δ 19.1 ($C^{3'}$), 25.5 ($C^{4'}$), 29.2 (C^3), 30.4 ($C^{2'}$), 33.9 (C^4), 43.6 (C^2), 63.3 ($C^{5'}$), 67.0 (C^5), 98.5 ($C^{1'}$), 202.5 (C^1).

2-(2-Tetrahydropyranloxy)tetrahydropyran (5), R_t: 3.5 min; ^1H-NMR: δ 4.93 (m, 2H, -OCHOCHO); 3.3-3.8 (m, 4H, $2x\text{-}OCH_2-$); 1.3-1.9 (m, 12H, $2x\text{-}(CH_2)_3-$); ^{13}C-NMR: δ 19.7 (C^3), 25.5 (C^4), 30.4 (C^2), 62.8 (C^5), 94.5 (C^1).

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A SIMPLE SYNTHESIS OF (+)-trans-VERBENYL PROPIONATE, A PHEROMONE ANALOG OF AMERICAN COCKROACH USING LEAD(IV) PROPIONATE[†]

Submitted by (03/21/88)

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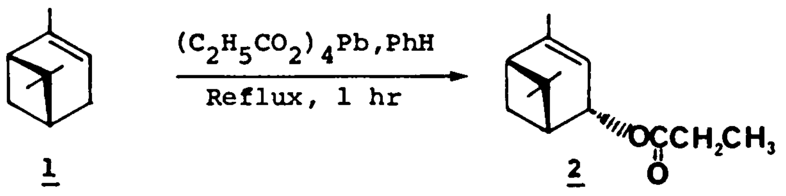
(+)-trans-Verbenyl propionate (1) is a synthetic attractant of the American cockroach (Periplaneta americana)[1]. Although the activity of this compound is less than that of periplanone B, the true sex excitant pheromone (2×10^{-2} mg and 10^{-8} mg, respectively), its preparation is much simpler.[2] Compound 1 has been previously prepared by Nishino and Takayanagi from (+)-α-pinene (2) in 20% overall yield.[1] Because of our interest in the use of 1 for cockroach control, we report an improved one-pot version of this synthesis.



1 2

The use of lead(IV)propionate[3] as acyloxylation reagents gave (+)-trans-verbenyl propionate (1) directly from (+)-α-pinene (2) in excellent yield (90%). The synthesis of lead(IV) propionate has also been modified.