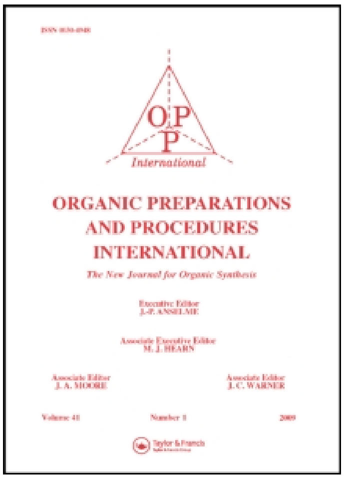

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THE SYNTHESIS OF TRIACONTANOL, SODIUM TRIACONTYL SULFATE AND DIHYDROGEN TRIACONTYL PHOSPHATE

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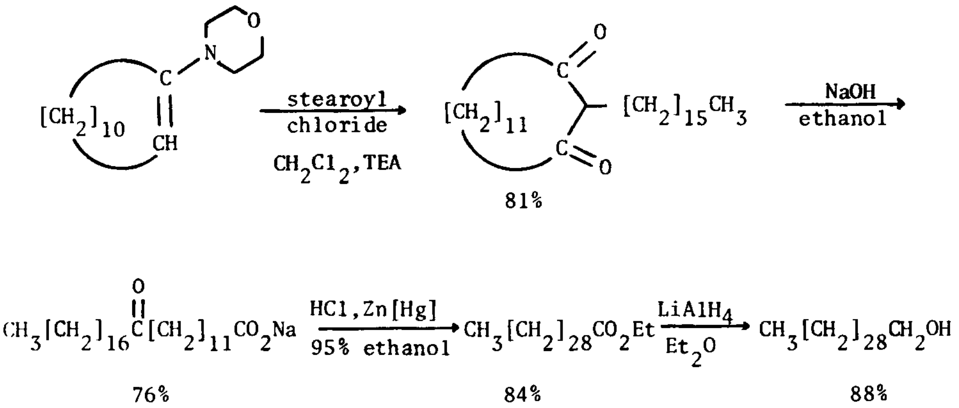
Recently there has been considerable interest in the potential use of triacontanol as a plant growth stimulant.[1,2] In order to carry out a comparative study[3] of the effect of triacontanol, sodium triacontyl sulfate and dihydrogen triacontyl phosphate on seed germination and plant growth, synthetic routes to these compounds were devised. Since these compounds have the potential for commercial use, emphasis was placed on procedures which could readily be used for large scale preparations from relatively inexpensive starting materials.

A search of the literature for a specific synthesis of triacontanol revealed only one, relatively inefficient, procedure by Robinson[4] starting from stearic and ω-bromoundecanoic acids. We anticipated that we could achieve an efficient, large scale, synthesis of triacontanol from inexpensive cyclododecanone and stearic acid by modifying literature procedures.[5-7] The success of this approach is summarized in the Equation and described in detail in the Experimental Section.

Sodium triacontyl sulfate was synthesized by reaction of the alcohol with chlorosulfonic acid followed by treatment of the product with methanolic sodium hydroxide. The dihydrogen triacontyl phosphate was prepared by treatment of triacontanol with phosphorus oxychloride and hydrolysis of the dichloro triacontyl phosphate with water.



EXPERIMENTAL

1-Morpholino-cyclododecene was prepared from cyclododecanone (Aldrich) and morpholine;[5] stearoyl chloride was obtained from stearic acid (850 g) and freshly distilled thionyl chloride (500 mL) (2 hrs. reflux) followed by removal of the thionyl chloride by distillation (1 mm). The residual acid chloride was used without further purification.

2-Hexadecyl-1,3-cyclotetradecanedione.- The procedure of Hünig[5] was modified slightly. A mixture of stearoyl chloride (583 g, 1.92 mole) and methylene chloride (425 mL) was added slowly (0.75 hr) to 1-morpholino-cyclododecene (483 g, 1.92 mole) and triethylamine (272 g, 2.7 moles) in methylene chloride (500 mL) at 0°. The mixture was warmed to room temperature and stirred for 18 hours; it was then washed successively with 1.2N HCℓ (1.5 L, twice) and saturated sodium bicarbonate (1.5 L). After drying ($MgSO_4$), evaporation *in vacuo* yielded a red oil (775 g, 90%) which crystallized on standing. Recrystallization from ethanol gave colourless crystals, mp. 62-63°, lit.[5] mp. 62-63°. IR 1700 cm^{-1}, mass spectrum m/e (relative intensity) 448 (2.0), 430 (1.1), 280 (5.2), 263 (5.4), 224 (3.8), 182 (32), 129 (100).

Sodium 13-ketotriacontanoate.- This compound was prepared by modification of the procedure reported by Hünig.[6] To a hot solution (65°) of sodium hydroxide (180 g) in 95% ethanol (1800 mL), a hot solution (65°) of 2-hexadecyl-1,3-cyclotetradecanedione (224 g, 0.5 mole) in 95% ethanol

(2 L) was added with vigorous mechanical stirring. The suspension that formed was stirred at 70° for 1 hr., then cooled and filtered to give a white powder (371 g, 76%). IR 1705, 1570 cm^{-1}.

Ethyl triacontanoate.- The ethyl ester of triacontanoic acid was prepared using a modified procedure of Jones.[7] Amalgamated zinc was prepared by adding a solution of mercuric chloride (37.5 g) and conc. hydrochloric acid (37.5 mL) in water (750 mL) to mossy zinc (750 g) and stirring for 20 minutes. The zinc was washed with water and 95% ethanol.

In a 5-litre flask was placed the amalgamated zinc (750 g), sodium 13-ketotriacontanoate (150 g) and 95% ethanol (3 L). Anhydrous HCℓ was bubbled through this solution for 2 days (approximately 1 kg of HCℓ was used). During the initial few hours, the temperature rose to reflux temperature after which it was maintained under reflux by gentle heating. The hot solution was decanted from the remaining zinc and the zinc washed with hot ethanol. The ethanol solution was cooled and filtered to yield the waxy ester (123 g, 84%), mp. 67.5-68.5°, lit.[7] mp. 68.3°. IR (nujol) 1740 cm^{-1}; mass spectrum m/e (relative intensity) 480 (1.2), 436 (0.5), 394 (0.3), 353 (0.3), 311 (18.6), 269 (14.5), 157 (100).

Triacontanol.- Lithium aluminum hydride (2.9 g) was added to ethyl triacontanoate (14 g, 0.29 mole) in anhydrous ethyl ether (365 mL) with stirring and the mixture maintained at reflux for 1 1/2 hr. To the cooled reaction mixture were added successively, aqueous sodium hydroxide (11 mL, 10% solution) and 50 g of magnesium sulfate. The salts were removed by filtration, washed with hot ether, and the combined ethereal solution was evaporated to yield a white solid (11.2 g, 88%), mp 87°, lit.[4] mp. 87°. IR 3200-3350, 1415, 1130, 1070 cm^{-1}; mass spectrum m/e (relative intensity) 438 (0.43), 437 (1.2), 420 (6.3), 392 (4.7), 239 (8.3), 167 (63), 153 (100).

Dihydrogen triacontyl phosphate.- The method of Boyd and Ladhams[8] was modified slightly. A warm solution of triacontanol (2.10 g, 0.005 mole), pyridine (4 mL) and methylene chloride (75 mL) was added to an ice-cold solution of phosphorus oxychloride (3.45 g, 0.04 mole) and pyridine (4 mL), in methylene chloride (5 mL) over 20 minutes. The mixture was allowed to become ambient (2 hrs.) and then poured onto ice (20 g). The precipitated phosphate was separated by centrifugation and washed with water and methanol to give after drying a white powder (1.75 g, 68%), mp 93-95°. This product decomposed slowly on attempted purification.

Sodium triacontyl sulfate.- A warm solution of triacontanol (1 g) in methylene chloride (100 mL) was added to an ice cold solution of chlorosulfonic acid (1 mL) in methylene chloride (50 mL). The mixture was allowed to become ambient and methanol (10 mL) was cautiously added; this was followed by the addition of methanolic sodium hydroxide (100 mL, 3%). The brown precipitate was stirred for one hr. and filtered; it was triturated with chloroform and recrystallized from ethanol to yield white crystals (1 g, 80%), mp 178-180°.

Anal. Calcd for $C_{30}H_{61}NaO_4 \cdot H_2O$: C,64.47; H, 11.36 Found: C, 64.63;H,11.30

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