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NEW SYNTHESIS OF 1-TRIACONTANOL

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Abstract: Succinic anhydride and behenic acid have been used to attach C_4 and C_{22} carbon chains on to 2 and 5 positions of thiophene through two alternate acylation sequences. Raney nickel desulphurization to the 2,5-disubstituted thiophene yielded triacontanoic acid esters which on LAH reduction gave 1-triacontanol.

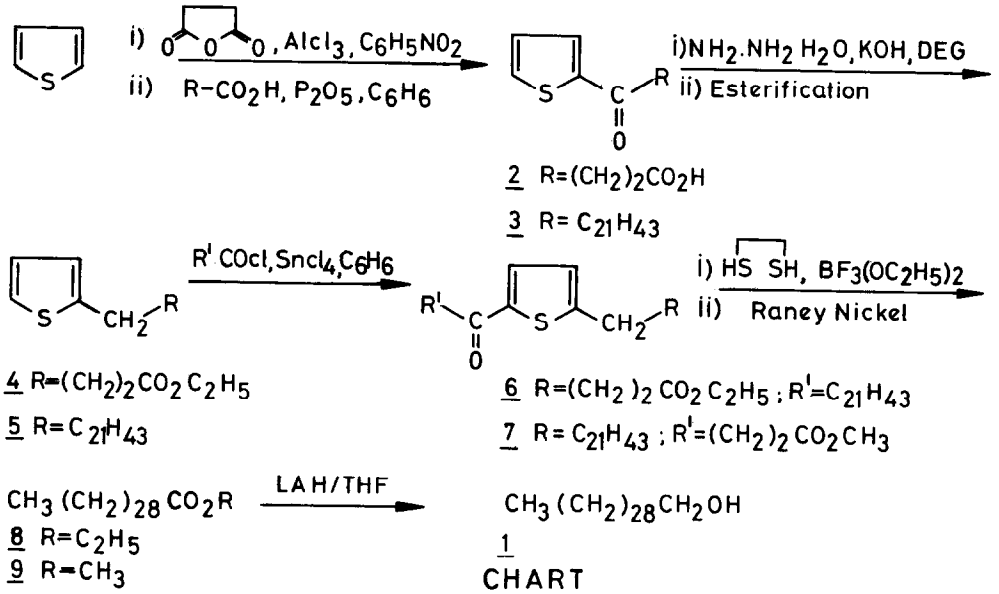
Ever since Rice et al[1] reported the plant growth stimulant activity of 1-triacontanol 1, several synthesis of the carbinol have been developed[2a-h]. We wish now to report two new synthesis of 1 which are simple, use cheap raw materials and are well suited for large scale preparations. The two synthetic routes are shown in the chart.

In the present synthesis of 1 thiophene is used as a chain extender. This approach was earlier exploited by us for the synthesis of long chain and branched chain fatty acids[3]. The high reactivity of 2 and 5 positions in thiophene permits two stepwise acylations in these positions whereby 4 and 22 carbon chains (provided by succinic anhydride and behenic acid respectively) can be introduced in these positions by two alternative sequences as shown in chart. Reductive desulphurization of the 2,5-disubstituted thiophenes finally leads to triacontanoate esters 8 and 9 in which 4 carbon unit was provided by the thiophene moiety.

The key intermediate β(α-thionyl) propionic acid 2 and 2-behenothiophene 3 were prepared by reaction of thiophene with succinic anhydride[4] and behenic acid respectively. Starting from 2, the ethylester 4 was obtained on Wolff-Kishner reduction followed by esterification, while reduction of 3 yielded 2-behenyl thiophene 5 m.p. 39°. Acylation of 4 with behenoyl chloride ($C_{21}H_{43}COCl$) and 5 with 2-carbomethoxy propionyl chloride ($CH_3OOC\,CH_2CH_2COCl$) in presence of anhydrous stannic chloride and dry benzene gave γ-(5-behenoyl-2-thienyl) butyrate 6 m.p. 58-59° and 2-ω-carbomethoxy propionyl-5-behenyl thiophene 7 m.p. 66°. Thioketalation of 6 and 7 with 1,2-ethanedithiol/boron trifluoride etherate in dry chloroform was followed by reductive desulphurization with Raney nickel (W_6) in boiling ethanol yielded ethyl tricontanoate 8 m.p. 70° (yield 70%) and methyl triacontanoate 9 m.p. 68° (yield 80%) respectively. Reduction of the triacontanoate esters 8 and 9 with lithium aluminium hydride in dry tetrahydrofuran yielded the 1-triacontanol 1 which was crystallised from hexane in colorless

flakes m.p. 87-88°, identical in all respects with authentic sample (mixture melting points undepressed). The identity of 1 was further confirmed by IR and mass spectra.

The overall yield of 1 in the sequences 2, 4, 6, 8 and 3, 5, 7, 9 are 70% and 75% respectively.



2 R=$(CH_2)_2CO_2H$

3 R= $C_{21}H_{43}$

4 R=$(CH_2)_2CO_2C_2H_5$

5 R=$C_{21}H_{43}$

6 R=$(CH_2)_2CO_2C_2H_5$; R'=$C_{21}H_{43}$

7 R= $C_{21}H_{43}$; R'=$(CH_2)_2CO_2CH_3$

$CH_3(CH_2)_{28}CO_2R$

8 R=C_2H_5

9 R=CH_3

$CH_3(CH_2)_{28}CH_2OH$

1

CHART

Thus, the above two synthetic sequences of 1 offers a facile route for the synthesis of other inaccessible long chain fatty acids and the corresponding carbinols. Work on these lines is in progress.

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