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A SIMPLE SYNTHESIS OF THE ENOL STEARATE OF 4-OXO-2-HENEICOSYNE, ENOL ESTERS XIV[1]

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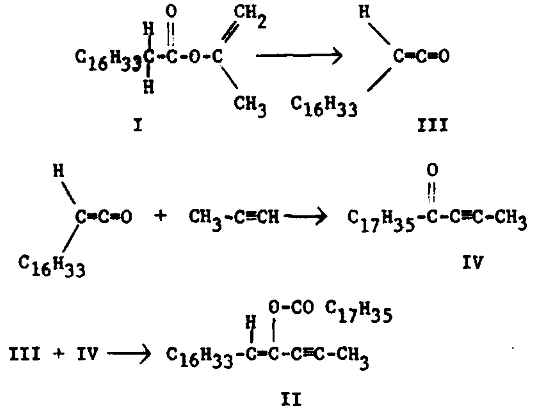
In the course of addition of stearic acid to propyne[1] we found, besides the target compound isopropenyl stearate I, an unusual by-product II absorbing in the ultraviolet at 224 nm, E = 11,000 but whose infrared spectrum nevertheless very closely resembled that of I. The by-product on mass spectrographic analysis showed a molecular weight of 572 fitting an empirical formula of $C_{39}H_{78}O_2$. The two compounds I and II were easily separated by falling-film molecular distillation due to the great difference in molecular weights. Examination of the infrared spectrum of II taken as a crystal film revealed the acetylenic group vibration at 2225 cm^{-1} (a region obscured in CS_2 solutions) as well as C=O (1758 cm^{-1}), C=C (1650 cm^{-1}), C-O (1150 cm^{-1}) and C=C-H (924 cm^{-1}). The origin of the acetylenic substance is consistent with the following reaction sequence.



(1) $$C_{16}H_{33}CH_2-C(=O)-O-C(=CH_2)CH_3 \longrightarrow C_{16}H_{33}CH=C=O$$

I III

(2) $$C_{16}H_{33}CH=C=O + CH_3-C\equiv CH \longrightarrow C_{17}H_{35}-C(=O)-C\equiv C-CH_3$$

IV

(3) $$III + IV \longrightarrow C_{16}H_{33}-CH=C(O-CO\,C_{17}H_{35})-C\equiv C-CH_3$$

II

The proof of structure of II follows from the following data: NMR triplet at 5.32 ppm (single proton on ethylenic bond) and singlet at 2.07 ppm (methyl group on acetylenic carbon). Hydrogenation over platinum gave a hydrogenolysis product, n-heneicosane (identified by mass spectrometry and m.p. comparison with an authentic sample), together with an ester hydrogenation product, m.p. 30.5°, identified as 4-heneicosyl stearate by saponification to stearic acid and 4-heneicosanol.

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[1] Previous paper in this series, E. S. Rothman & S. Serota, manuscript submitted to J.Am. Oil Chemists' Soc.

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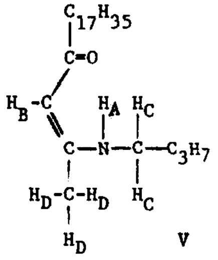
The identity of the 4-heneicosanol was further confirmed by chromic oxide-pyridine oxidation to 4-oxoheneicosane whose mass spectral fragmentation pattern was consistent only with that of a 4-oxo compound. Since our 52°C m.p. of the ketone was somewhat lower than the 56°C literature values (1,2) we further confirmed the oxygen atom placement at carbon atom 4 of the C_{21} chain by butylaminolysis of II. Besides N-butyl stearamide this process yielded 2-(4-oxoheneicos-2-en)-yl-n-butylamine (V). The NMR spectrum of V showed a broad absorption at 11.75 ppm (rel. area = 1) H_A; a singlet at 4.70 ppm (area = 1) H_B; an apparent quartet at 3.20 ppm (area = 2) H_C, collapsing to a triplet with D_2O exchange; and a singlet at 1.88 ppm (area = 3), H_D. The infrared spectrum of V resembled that of the di-oxygen analog, namely heneicosane-2, 4-dione, but showed: a, no OH bands; b, NH bands closely positioned to the large CH peaks and; c, carbonyl band shifted to the 1600 cm^{-1} region; uv max 315 nm (E = 18,000). In further confirmation, V was converted by mild acid hydrolysis to heneicosane-2, 4-dione, m.p. 57-8°C, copper chelate m.p. 124-4.5°C, both identical in every respect with authentic materials prepared by the novel method of stirring isopropenyl stearate with sodium in refluxing toluene for 1 hr. "Heneicosane-2,4-dione, double m.p. 70; 75°" reported (3) by one of us earlier is incorrectly so-designated. The structure of the latter, in spite of intensive study, has not yet been deciphered.



V

Cleavage of II was effected by acid-catalysed addition of stearic acid to form an unstable diester spontaneously decomposing to stearic anhydride and the acetylenic ketone IV. (This cleavage parallels equation II of reference 4, and is a useful technique where 1,4-additions complicate product separations.) The ketone IV showed an NMR triplet centered at 2.38 δ, J = 6 Hz (α-CH_2) and a singlet at 1.98 δ (terminal CH_3), uv max 215 (shoulder at 224) nm, E = 7300 (isooctane), ir 2220 ($C \equiv C$), 1661 ($C = O$) cm^{-1} (5), m.p. 46.0-6.5. II purified by molecular distillation at 275°/0.3 mm is formed in significant yields, 30-70%, from stearic acid, propyne, and 10 weight % zinc stearate at 160°C for 20 hours at 500 psi.

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