65. n-*Aliphatic Long-chain Alcohols.*

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An extension of our investigation of the dimorphism of certain aliphatic compounds (Part I, J., 1931, 1732; Part II, J., 1932, 898) to the monocarboxylic ethyl esters (Parts III and IV; *Rec. trav. chim.*, 1933, **52**, 175, 181) necessitated the use of pure *n*-tetradecyl and *n*-octadecyl alcohols as starting materials. Technical varieties of these and other higher alcohols have been procurable for some time (see *Chem. Trade J.*, Jan. 22nd, 1932), and the "pure" alcohols themselves are also now available from the same source. These afford a comparatively cheap and ready means of obtaining the higher normal even-chain aliphatic alcohols, which are otherwise only prepared with considerable trouble by the purification and subsequent reduction of esters of the corresponding acids.

The commercial "pure" tetradecyl alcohol, converted into acetate and systematically fractionated under reduced press. through a good column, yields about 60% of the β-form of *n*-tetradecyl acetate, m. p. 13·5°, raised to 13·85° by further fractionation. The corresponding octadecyl alcohol, by a similar procedure, followed by crystn. from EtOH (in the β-form; see Part III), gives not less than 40% of nearly pure *n*-octadecyl acetate (β-form), m. p. 32·7°, raised to 32·8° by further recrystn.

	Acetate.		Alcohol.	
	(α) F. p.	(β) M. p.	F. p.	Transition temp.*
n-Tetradecyl.				
(1) By reduction of ethyl myristate	3·25°	13·95°	37·7°	35·0°
(2) From commercial "pure" alcohol	3·2	13·85	37·7	34·8
(3) Literature values	—	12—13[1]	37·7[2]	34[2]
n-Octadecyl.				
(1) By reduction of ethyl stearate	30·25	32·85	57·95	53·8
(2) From commercial "pure" alcohol	30·3	32·8	57·95	53·5
(3) Literature values	—	31[1]	57·95[3]	—

[1] Krafft, *Ber.*, 1883, **16**, 1720. [2] Garner and Rushbrooke, J., 1927, 1351. [3] Smith, *ibid.*, 1931, 802.

* The transition temps. given in the table are the highest temps. recorded during the arrest, the bulb of the thermometer being embedded in the unstirred solid: they are, accordingly, liable to slight variation, to minimise which an approx. const. rate of cooling, *ca.* 0·6° per min., was employed throughout.

Each of the acetates exists in two monotropic modifications (see table), the transparent α-form, first obtained on cooling the liquid ester, changing spontaneously and exothermally into the white, opaque, and higher-melting β-variety (cf. cetyl acetate, Part I).

The alcohols obtained by hydrolysis of these acetates, after purification by crystn., have f. p. 37·7° and 57·95° respectively, and both exhibit the dimorphism characteristic of cetyl alcohol (see Part I), the cooling curve showing a well-defined arrest * a few degrees below the f. p., corresponding with a change in appearance from semi-transparent to white and opaque.

It will be seen from the table that the f. p.'s of the purified alcohols and their acetates agree closely with those of products obtained by the orthodox reduction method, and with the best values recorded in the literature.

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