363. The Dimorphism of Certain Aliphatic Compounds. Part V. The n-Primary Alcohols and their Acetates.

By John W. C. Phillips and Stanley A. Mumford.

In Parts III and IV of this series (*Rec. trav. chim.*, 1933, **52**, 175, 181) it was shown that the series of higher aliphatic ethyl esters $C_nH_{2n+1}\cdot CO_2Et$ exhibited three distinct kinds of alternation of polymorphic type, *viz.*, (*a*) alternating monotropy (with esters up to $n = 13$), the opaque β-forms of both odd and even members being stable, and the transparent α-forms metastable and unobtainable except by admixture; (*b*) alternating monotropy and enantiotropy (with esters from $n = 13$ to about $n = 19$), the α-forms of the odd members being stable near the m. p., and those of the even members metastable but realisable; (*c*) alternating enantiotropy (with esters above about $n = 19$), the α-forms of both odd and even members being stable in the vicinity of the m. p.

Throughout the whole series the α f. p.'s were found to lie on a smooth curve, but the β m. p.'s alternated, the β m. p. curve of the even esters being higher than that of the odd. In addition, indications were obtained of the existence of third (γ-) modifications of many of the esters, having f. p.'s on a curve running approximately parallel to but lower than the β m. p. curve of the odd esters, and intersecting the α f. p. curve at or near the $n = 12$ point.

Many of our results have been confirmed by Meyer and Reid (*J. Amer. Chem. Soc.*, 1933, **55**, 1574), who examined, *inter alia*, the ethyl esters of the fatty acids from decoic to stearic;

TABLE I.

Polymorphism of the Ethyl Esters of the n-*Aliphatic Acids*, $C_nH_{2n+1}\cdot CO_2Et$.

Tr. = Temp. of transition; Tr. ↓ from cooling curve; Tr. ↑ from heating curve.

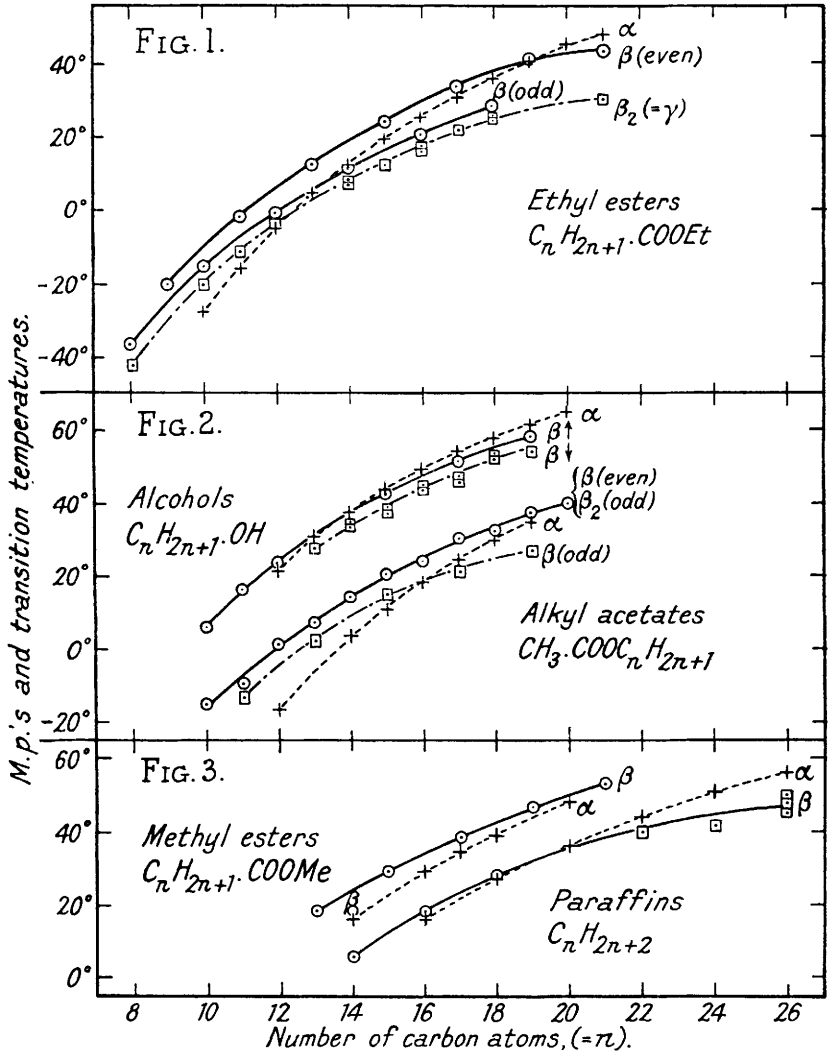
			β-Form.			
C_n.	Ester.	α-Form.	Even esters.	Odd esters.	γ (β_2)-Form.	Ref.
8	Nonoate	—	—	f. p. *ca.* −36·5°	f. p. *ca.* −42°	PM. IV.
		—	—	m. p. *ca.* −35	—	
		—	—	f. p. −36·7	—	D.
9	Decoate	—	m. p. −20·3°	—	—	PM. IV.
		—	f. p. −19·9	—	—	D.
		—	f. p. −19·96	—	—	MR.
10	Undecoate	f. p. −27·8°*	—	m. p. −15·0	f. p. −20·5	PM. IV.
		—	—	—	m. p. −19·5	
		—	—	—	f. p. −19·39	MR.
11	Laurate	f. p. −15·5*	m. p. −1·8	—	f. p. *ca.* −11 *	PM. II, IV.
		—	f. p. −1·68	—	—	MR.
12	Tridecoate	f. p. −4·8 *	—	m. p. −0·8	f. p. *ca.* −3·5	PM. IV.
		—	—	—	f. p. −3·13	MR.
13	Myristate	f. p. 4·45 *	m. p. 12·3	—	—	PM. II, IV.
		—	f. p. 11·93	—	—	MR.
		—	f. p. 11·94	—	—	RR.
14	Pentadecoate	f. p. 11·95	—	Tr.↑ *ca.* 11·5 *	Tr.↓ *ca.* 7 *	PM. III, IV.
		f. p. 12·21	—	—	Tr.— 8·34	MR.
15	Palmitate	f. p. 19·3	m. p. 24·1	—	Tr.↓ *ca.* 12 *	PM. III, IV.
		f. p. 19·4	m. p. 24·18	—	—	Sm.
		f. p. 19·72	—	—	—	MR.
16	Margarate	f. p. 25·25	—	Tr.↑ 20·6	Tr.↓ 17·2	PM. III, IV.
		f. p. 25·11	—	—	Tr.↓ 16·64	MR.
		m. p. 25·4	—	Tr.↑ 19	Tr.↓ 16	CS.
17	Stearate	f. p. 30·8	m. p. 33·5	—	Tr.— *ca.* 22 *	PM. III, IV.
		f. p. 30·9	m. p. 33·4	—	—	Sm.
		f. p. 30·56	—	—	—	MR.
18	Nonadecoate	f. p. 35·7	—	Tr.↑ 28·9	Tr.↓ 25·6	PM. III, IV.
		f. p. 35·5	—	—	Tr.↓ 24·5	Malk (1).
		m. p. 36·2	—	—	—	Sh.
19	Eicosoate	f. p. 40·5	m. p. 41·0	—	—	Malk (1).
		—	m. p. 42 †	—	—	AD., LT.
20	Heneicosoate	m. p. 45 †	—	—	—	LT.
21	Behenate	f. p. 47·8	Tr.↓ 43	—	Tr.↓ 30	Buck.
		α_2 45				
		m. p. 49 †	—	—	—	LT.

References.

AD = Adam and Dyer (J., 1925, **127**, 70).
Buck = Buckingham (*loc. cit.*).
CS = Carey and Smith (J., 1933, 635).
D = Deffett (*Bull. Soc. chim. Belg.*, 1931, **40**, 385).
LT = Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 905).
Malk (1) = Malkin (J., 1931, 2796).
MR = Meyer and Reid (*loc. cit.*).
PM = Phillips and Mumford; the Roman numerals refer to parts of the present series.
RR = Ruhoff and Reid (*J. Amer. Chem. Soc.*, 1933, **55**, 3825).
Sh = Shüna (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 569B).
Sm = Smith (J., 1931, 802).

* Indicates extrapolated value. † Indicates m. p. taken in a capillary tube.

and the series has recently been extended by an examination of the density changes of solid ethyl behenate (Buckingham, *Trans. Faraday Soc.*, 1934, **30**, 377), which, as expected, is found to exhibit double enantiotropy, the transparent α-form (f. p. 47·8°) changing into an opaque β-form at 43°, and the latter into a β_2- (γ-) form at 30°. (The α-form itself was also found to be complex, changing monotropically into an α_2-form at 45°.) These additional data, together with the results previously reported, are incorporated in Table I and Fig. 1, in which the intersection of the α f. p. and β m. p. curves in the ester series is clearly seen.



Polymorphism in Aliphatic Series.

It was suggested in previous papers that a similar intersection of these curves appeared probable in other aliphatic series, and it is the purpose of the present communication to show that such an intersection does, in fact, occur with the primary aliphatic alcohols and also with their acetates. The results of an examination of the f. p.'s and polymorphism of the alcohols and acetates from dodecyl to nonadecyl (excluding tridecyl) are summarised in Table II and given graphically in Fig. 2, together with such other data on the two series as are available in the literature, in particular the results of Smith and co-workers (J., 1931, 802; 1933, 635, 1348) on the C_{16}, C_{17}, and C_{18} compounds, and those of Meyer and Reid (*loc. cit.*) on the alcohols and acetates from C_{10} to C_{18}.*

From Fig. 2 it will be seen that in the case of the alcohols $C_nH_{2n+1}\cdot OH$ the α f. p. curve intersects the β m. p. curve at or about the C_{13} point. Dodecyl alcohol on cooling solidifies in the transparent α-form at 21·6°, which on standing or rubbing is converted monotropically into the opaque β-modification, f. p. 23·6°, m. p. 23·8°. Tetradecyl alcohol, on the other hand, like higher members of the series, solidifies in the α-form, but changes enantiotropically into a β-form on cooling. The transition temperatures of the higher alcohols estimated from their cooling curves exhibit alternation, those of the even members being on a higher curve than those of the odd. Transition arrests in the heating curves could only be obtained in the case of the odd alcohols, and these appeared to fall on a continuation of the β m. p. curve of the lower alcohols. All the alcohols from tetradecyl to nonadecyl were, however, found to be in the α-form at their m. p.'s, which in every case coincided with the α f. p.

The existence of this intersection of α f. p. and β m. p. curves explains the observation of Verkade and Coops (*Rec. trav. chim.*, 1933, **52**, 765) that, although " the alcohols up to and

TABLE II.

Polymorphism of the n-*primary alcohols and their acetates.*

	n-Primary alcohols, $C_nH_{2n+1}\cdot OH$.			*n*-Alkyl acetates, $CH_3\cdot CO_2C_nH_{2n+1}$.			
C_n.	α-Form.	β-Form.	Ref.	α-Form.	β_1-Form.	β_2-Form.	Ref.
10	—	f. p. 5·99°	MR.	—	—	f. p. −15·05°	MR.
	—	m. p. 6·4	VC.	—	—	—	—
11	—	f. p. 15·85	MR.	—	f. p −12·59°	f. p. −9·27	MR.
	—	m. p. 16·3	VC.	—	—	—	—
12	f. p. 21·6°	f. p. 23·6	PM. V.	f. p. −16·7° *	—	m. p. +1·3	PM. V.
		m. p. 23·8					
	—	f. p. 23·87	MR.	—	—	f. p. +1·13	MR.
	—	m. p. 23·8	VC.	—	—	—	—
13	f. p. 30·63	Tr. 28·35±0·4	MR.	—	f. p. +2·44	f. p. 7·03	MR.
14	f. p. 37·7	Tr. ↓ 35·0±0·2	PM. V.	f. p. 3·3 *	—	m. p. 14·0	PM. V.
	f. p. 37·62	Tr. 34·95±0·4	MR.	—	—	f. p. 14·01	MR.
	f. p. 37·7	Tr. 34	GR.	—	—	f. p. 14·0	RR.
15	f. p. 43·9	Tr. ↓ 38·9±0·1	PM. V.	f. p. 11·4	f. p. 14·7	f. p. 18·5	PM. V.
	m. p. 44·0	Tr. ↑ *ca.* 42·5		—	m. p. 15·2	m. p. 20·35	
	f. p. 43·84	Tr. 37·3	MR.	—	f. p. 14·75	f. p. 18·77	MR.
16	f. p. 49·25	Tr. ↓ 45·0±0·2	PM. V.	f. p. 18·5	—	m. p. 24·2	PM. V.
	f. p. 49·27	Tr. 43·8±0·1	MR.	f. p. 18·49	—	f. p. 24·12	MR.
	f. p. 49·27	Tr. ↓ 40	Sm.	—	—	—	—
17	f. p. 53·9	Tr. ↓ 47·3±0·1	PM. V.	f. p. 24·6	Tr. ↓ *ca.* 10·5	—	PM. V.
	m. p. 54·0	Tr. ↑ 51·2		—	Tr. ↑ 21·5	m. p. 30·25	
	f. p. 53·3	Tr. 45·7±0·15	MR.	f. p. 24·39	—	—	MR.
	f. p. 53·8	Tr. ↓ 43·5	CS.	f. p. 24·6	Tr. ↓ 10	m. p. 30·2	CS.
18	f. p. 57·95	Tr. ↓ 53·6±0·2	PM. V.	f. p. 30·25	—	m. p. 32·85	PM. V.
	f. p. 57·85	Tr. 52·4±0·5	MR.	f. p. 29·97	—	f. p. 31·95	MR.
	f. p. 57·95	—	Sm.	—	—	—	—
19	f. p. 61·65	Tr. ↓ 54·0±0·2	PM. V.	f. p. 35·35	Tr. ↓ *ca.* 14	—	PM.V.
	m. p. 61·7	Tr. ↑ 58		—	Tr. ↑ 27·2	m. p. 37·6	
	m. p. 62—63 †	—	LT, Malk (2)	—	—	—	—
20	m. p. 65—66 †	—	AD, LT.	—	—	m. p. 40±0·5 †	AD.

References (not included in Table I) :—

GR = Garner and Rushbrooke (J., 1927, 1351).
Malk (2) = Malkin (*J. Amer. Chem. Soc.*, 1930, **52**, 3739).
VC = Verkade and Coops (*Rec. trav. chim.*, 1927, **46**, 903).

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* With regard to the latter it is to be noted that these authors make an unconventional use of the symbol α in designating by it the first crystals obtained on solidification, irrespective of their nature. The present authors follow the customary usage of restricting the term " α-form " to the soft transparent varieties which appear invariably to crystallise without appreciable supercooling, and " β-form " to the harder, more compact and opaque modifications into which the α-forms change spontaneously or on cooling.

including term-number 11 show a definite m. p. alternation . . . data available in the literature concerning the m. p.'s of the higher terms of the series strongly suggest the absence of an alternation in this constant."

Similarly, Meyer and Reid (*loc. cit.*) found that, whereas the alcohols from C_{13} upwards solidified, without supercooling (in the α-form), and showed an arrest on cooling, yet C_{10}, C_{11}, and C_{12} alcohols, especially if containing a trace of water, supercooled greatly and gave continuous cooling curves.

Malkin's observation (*J. Amer. Chem. Soc.*, 1930, **52**, 3739) that, whilst the C_{12} and C_{14} alcohols give a long spacing only, the C_{16} and C_{18} alcohols give, in addition, a shorter spacing, and the C_{22} and C_{24} alcohols only the shorter spacing, also appears to be connected with the intersection of α and β f. p. curves.

His conclusion that " the vertical form is clearly a stable form for the odd alcohols, and the tilted form for the even, but the latter change into the vertical form at some point below fusion," would, however, appear to be based on a misinterpretation, for our results, confirming in detail those of Meyer and Reid, show definitely that in the case of both odd and even alcohols above C_{14} the transparent α-(vertical) form is first obtained on cooling, and this changes reversibly into an opaque β-(tilted) form a few degrees below the f. p.

From visual observation it would appear that the α-forms of all the higher alcohols are converted into α_2-forms just below the α f. p. (cf. ethyl behenate, referred to above; also the " first transition point on cooling " found by Piper and co-workers with the higher paraffins, *Biochem. J.*, 1931, **25**, 2072). The heat effect of the change, if any, could not, however, be differentiated from that of solidification.

The acetates of the even alcohols closely resemble the isomeric even ethyl esters (cf. Part II, J., 1932, 898) in exhibiting monotropic dimorphism, the α-forms of the C_{18} and C_{16} members being metastable but realisable, those of the C_{14} and C_{12} alcohols metastable and unrealisable except by admixture (very considerable in the case of the latter). The acetates of the odd alcohols, however, differ somewhat from the isomeric odd ethyl esters. As with the latter, the transparent α-form changes first into an opaque (β-) form, monotropically in the case of the lower members and enantiotropically with the higher members, but in addition, this β-form, on cooling, changes slowly and monotropically into a further high-melting (β_2) form, the β_2 m. p.'s of the odd acetates lying on a curve slightly above the β m. p. curve of the even acetates. As will be seen from Fig. 2, the α f. p.'s of both odd and even acetates fall on a smooth curve, which is intersected by the β m. p. curve of the odd members between the C_{15} and C_{17} points, and appears to be intersected by the β_2 m. p. curve of the odd, and the almost coincident β m. p. curve of the even, acetates somewhere above the C_{20} point. Changes in direction of the cooling curves of the α-forms of the C_{15}, C_{17}, and C_{19} acetates at about 5°, 15·3°, and 24·5°, respectively, possibly indicate additional transformations, but these require further investigation. The β_2 odd acetates, it will be observed, differ considerably from the β even acetates in rate of growth. With the latter, when the cooled ester is seeded with a β-crystal, rapid crystallisation occurs and the temperature rises to a reproducible f. p. which approximates to the β m. p. With the odd acetates, particularly the higher ones, however, a period of several hours is required for complete crystallisation of β_2, and the highest temperature reached during the process is considerably lower than the subsequent m. p. This circumstance accounts for the low f. p.'s recorded by Meyer and Reid, and possibly also for their inability to obtain β_2-heptadecyl acetate.

Evidence of the intersection of α and β f. p. curves is also available in the literature (see Table III) in the case of the even paraffins $C_{14}H_{30}$ to $C_{26}H_{54}$. For instance, Smith (J., 1932, 737) has found that both hexadecane and octadecane exhibit monotropic dimorphism, whilst the work of Garner, van Bibber, and King (J., 1931, 1533) and of Piper and others (*loc. cit.*) shows that with the higher even paraffins from C_{22} upwards the transparent α-form changes enantiotropically on cooling into an opaque β-form (see Fig. 3). For the intermediate member, $C_{20}H_{42}$, Parks, Huffman, and Thomas (*J. Amer. Chem. Soc.*, 1930, **52**, 1032) observed no transition on cooling, but from *X*-ray spacing data, Müller (*Proc. Roy. Soc.*, 1930, *A*, **127**, 417) deduced the existence of two forms.

For the methyl esters of the fatty acids, Malkin (J., 1931, 2796) gives *X*-ray spacing data

TABLE III.

Polymorphism of the even n-*paraffins and the* n-*aliphatic methyl esters.*

Paraffins.

C_n.	α-Form.	β-Form.	Ref.
14	—	m. p. 5·5	Kr.
16	f. p. 16·2°	m. p. 18·13	Sm; CS.
		m. p. 18·2	Kr.
18	f. p. 27·3±0·2	m. p. 28·02	Sm; CS.
	—	m. p. 28	Kr.
20	m. p. 36·7		Kr.
	m. p. 38 ‡		M (1).
	m. p. 36·4 §		PHT.
22	f. p. 43·8	Tr. 40·2	GBK.
	m. p. 44·4	—	Kr.
	m. p. 44	—	M (2).
24	m. p. 51·1	—	Kr.
	m. p. 51·2	Tr. 40—41	M (2).
26	f. p. 56·1	Tr. 50·1	GBK.
	f. p. 56·1	Tr. 48·3	Pip.
	m. p. 58·0	Tr. 45—46	M (2).

Esters.

C_n.	Ester.	α-Form.	β-Form.	Ref.
13	Myristate	—	f. p. 18·35	GR.
14	Pentadecoate	f. p. 16·1	m. p. 18·65	PM. V.
		—	m. p. 18·5	LeS.
		f. p. 15·46	—	RR.
15	Palmitate	solidifies 22	melts 28	Watts.
		—	28—30	Ad; RD.
16	Margarate	m. p. 29	—	LeS; Rutt.
17	Stearate	f. p. 35·3	—	Malk (3).
		—	m. p. 38—39	LT; RD; Wh.
18	Nonadecoate	m. p. 39	—	LT; Sh.
19	Eicosoate	—	m. p. 46—47	AD; LT.
20	Heneicosoate	m. p. 48·5	—	LT.
21	Behenate	—	m. p. 53·5	LT.

‡ Two spacings. § No transition.

References (additional to foregoing) :

Ad = Adam (*Proc. Roy. Soc.*, 1922, **101**, *A*, 516).
GBK = Garner, van Bibber, and King (*loc. cit.*).
Kr = Krafft (*Ber.*, 1882, **15**, 1700; 1886, **19**, 2218).
LeS = Le Sueur (J., 1904, **85**, 827; 1905, **87**, 1898).
M (1) = Müller (*Proc. Roy. Soc.*, 1930, **127**, *A*, 417).
M (2) = *Idem* (*ibid.*, 1932, **138**, *A*, 514).
Malk (3) = Malkin (*Trans. Faraday Soc.*, 1933, **29**, 977).
PHT = Parks, Huffman, and Thomas (*loc. cit.*).
Pip = Piper *et al.* (*loc. cit.*).
RD = Ryan and Dillon (*Proc. Roy. Irish Acad.*, 1912, **29**, *B*, 235).
Rutt = Ruttan (8*th Intern. Cong. Appl. Chem.*, 1912, **25**, 431).
Watts = Watts's " Dictionary of Chemistry," Vol. IV, p. 385.
Wh = Whitby (J., 1926, 1458).

(but not thermal results) to show that the esters of the odd acids exhibit dimorphism, but not those of the even acids. From an examination of the literature, however, it seems probable that polymorphism in this series will resemble that in the ethyl ester series (see Table III and Fig. 3), the α f. p. curve being at present represented by a line drawn through the m. p.'s given for methyl margarate, nonadecoate, and heneicosoate and the s. p. given by Malkin (*Trans. Faraday Soc.*, 1933, **29**, 977) for methyl stearate. An examination of methyl pentadecoate shows that this ester gives a transparent α-form, f. p. 16·1° (which point falls on the above curve), changing monotropically to an opaque β-form having m. p. 18·65°, but other methyl esters are at present not available for examination. In this connexion, however, the observation of early workers (cf. Watts's " Dictionary of Chemistry," Vol. IV, p. 385) that methyl palmitate solidifies at 22° but melts at 28° is of interest. Malkin (*loc. cit.*) has also examined the propyl, butyl, and amyl esters of palmitic, margaric, and stearic acids and finds that, as would be expected from the above, the margarates exhibit enantiotropic, but the palmitates and stearates monotropic, dimorphism. Experimental details are, however, not given, and the data in the literature are too scanty for generalisation in these series.

In the case of three of the homologous aliphatic series which, according to Malkin (J., 1931, 2796), show no alternation of physical constants amongst the higher members, but according to Verkade and Coops (*Rec. trav. chim.*, 1933, **52**, 747) do exhibit such alternation phenomena in the lower terms (*viz.*, the *n*-primary alcohols, the *n*-paraffins, and the esters of the *n*-fatty acids), the observed apparent discrepancy is thus traceable to the intersection of the α f. p. and the β m. p. curves of the series. With the higher members of each of these series, absence of alternation of m. p. and of other physical properties *in the vicinity of the* *m. p.* is to be ascribed to the fact that the transparent α- (or vertical-chain) form is stable at the m. p. Alternation phenomena, however, may, and do, occur with these higher members at temperatures below the m. p. when the α ⟶ β transition has taken place, alternation being, apparently, in some way connected with the tilted chain β-structure. With the lower members of the series, however, alternation of m. p. and other properties is general, as in their case the opaque β- (or tilted-chain) form is the stable form, the metastable α-modification being in most cases unrealisable with the pure compounds. Over a small intermediate range (from about $n = 13$ to 19 in the case of the esters $C_nH_{2n+1}\cdot CO_2Et$) apparent alternation at the m. p. is due to the circumstance that it is the β-forms of the even and the α-forms of the odd esters that are being compared.

EXPERIMENTAL.

Even Alcohols and Acetates.—Details of the preparation and purification of tetradecyl and octadecyl alcohols and acetates have already been given (J., 1933, 235). Two preparations of the octadecyl compounds gave an alcohol having α f. p. 57·95°, and transition temperature (from the cooling curve) 53·6° ± 0·2°; and an acetate of α f. p. 30·25° and β m. p. 32·85°. With the tetradecyl compounds, the alcohol α f. p. 37·7°, transition temperature 35·0° ± 0·2°, was not altered by further purification, but the β m. p. of the acetate was raised slightly to 14·0°, this final purification having the effect of rendering the α-form, f. p. 3·3°, unobtainable except by admixture with a small percentage of higher homologue.

The hexadecyl compounds were obtained from crude cetyl alcohol extract from the hydrolysis products of spermaceti (cf. Part I, J., 1931, 1732). Fractionation and subsequent recrystallisation in the β-form of the acetate eventually gave an ester having α f. p. 18·55° and β m. p. 24·2°, from which, on hydrolysis, an alcohol of α f. p. 49·25° and transition temperature 44·8° was obtained. For comparison, specimens of *n*-hexadecyl acetate and alcohol were also prepared by the reduction of pure ethyl palmitate (β m. p. 24·1°); the former had α f. p. 18·5° and β m. p. 24·22°; the latter α f. p. 49·25° and transition temperature 44·9—45·0°.

Pure dodecyl alcohol, β m. p. 23·8°, was prepared by recrystallisation of the alcohol previously used (Part IV) and found to be identical with a specimen obtained by reduction of ethyl laurate. On cooling without stirring, transparent metastable α-crystals, f. p. 21·6°, separated, but these readily changed into the opaque β-modification, m. p. 23·8°. Acetylation gave an acetate, b. p. 120·4° ± 0·2/4 mm., β m. p. + 1·3°.

In order to evaluate the unrealisable α f. p.'s of the dodecyl and tetradecyl acetates, the binary acetate systems C_{12}—C_{14} and C_{14}—C_{16} were partially investigated by a procedure similar to that adopted in the case of the ethyl esters (Part IV).

Examination of mixtures of hexadecyl and octadecyl acetates showed that the even acetate systems resemble the corresponding isomeric ethyl ester systems in that the α-forms give a continuous series of solid solutions having f. p.'s intermediate between those of the two component esters, whilst the incompletely realisable β-system apparently exhibits a eutectic. Moreover, as with the ethyl ester systems, the α f. p.'s of the various mixtures were found to deviate slightly and approximately symmetrically from the line joining the α f. p.'s of their components (F_1 and F_2) to an extent determined by the empirical equation

$$F_x = F_2 - (F_2 - F_1)x + 0{\cdot}016(F_2 - F_1)^2x(1 - x)$$

where x is the mol. fraction of the lower ester (α f. p. = F_1) present in the mixture.

It is thus possible to evaluate the unrealisable α f. p. of any ester in terms of the composition and α f. p. of its mixtures with a higher homologue of known α f. p.

The freezing points of the various acetate mixtures are given in Table IV. The results show that the α-form of tetradecyl acetate has f. p. 3·3° and requires about 4 mols.% of hexadecyl acetate to stabilise it; whilst that of dodecyl acetate has f. p. −16·7° and is only stable in the presence of some 40—60 mols.% of tetradecyl acetate.

It is of interest, in connexion with our previous note on the subject (J., 1933, 235), that we have now prepared pure dodecyl, tetradecyl, and octadecyl alcohols and acetates from the products of the Deutsche Hydrierwerke A.-G. and found them to be identical with the corresponding compounds obtained by orthodox reduction methods. So, too, cetyl alcohol prepared by purification of the crude alcohol extracted from spermaceti is identical with the hexadecyl alcohol resulting from the reduction of pure ethyl palmitate (cf. Smith, J., 1931, 802).

Odd Alcohols and Acetates.—Methyl pentadecoate, b. p. 141—142°/3 mm., α f. p. 16·1°, β m. p. 18·65°, synthesised from pure tetradecyl alcohol, *via* the iodide, nitrile, and acid, was

TABLE IV.

F.p.'s of acetate systems.

Mol. fraction lower ester (x).	α F. p.	β M. p.	Mol. fraction lower ester (x).	α F. p.	β M. p.	Mol. fraction lower ester (x).	α F. p.	β M. p.
I. C_{16}—C_{18} Acetates [$F_x = 30{\cdot}25 - 11{\cdot}75x + 2{\cdot}2x(1 - x)$].								
1·000	18·5°	24·2°	0·763	21·6°	—	0·181	28·4°	30·0°
0·972	18·9	23·9	0·629	23·4	—	0·141	28·8	30·6
0·942	19·3	23·45	0·499	24·85	—	0·057	29·65	31·9
0·900	19·8	22·3	0·367	26·4	—	0·000	30·25	32·85
0·825	20·8	—	0·255	27·7	—			
II. C_{14}—C_{16} Acetates [$F_x = 18{\cdot}5 - 15{\cdot}2x + 3{\cdot}7x(1 - x)$].								
1·000	(3·3)	14·0	0·764	7·5	—	0·311	14·6	19·6
0·979	—	13·7	0·645	9·5	—	0·242	15·5	20·9
0·963	4·0	13·35	0·556	10·95	—	0·158	16·6	22·1
0·929	4·7	12·65	0·472	12·3	16·2°	0·085	17·6	23·2
0·880	5·5	11·0	0·410	13·2	17·5	0·000	18·5	24·2
0·836	6·3	9·2						
III. C_{12}—C_{14} Acetates [$F_x = 3{\cdot}3 - 20x + 6{\cdot}4x(1 - x)$].								
1·000	(−16·7)	+1·3	0·607	−7·3	+1·2	0·276	—	9·5
0·889	—	−1·5	0·519	−5·5	+3·9	0·192	—	10·9
0·825	—	−3·2	0·441	−3·9	+5·8	0·097	—	12·4
0·685	—	−1·2	0·370	—	7·6	0·000	(+3·3)	14·0

converted by reduction into pentadecyl alcohol. Acetylation of the latter and crystallisation of the product gave an acetate which on cooling yielded transparent α-crystals of f. p. 11·4°. On gentle rubbing, these changed into an opaque but metastable β-form, f. p. 14·7°, m. p. 15·2°, which in turn was readily converted, with rise of temperature to 18·5°, into an opaque, stable, β_2-form, m. p. 20·3°. Further recrystallisation gave an acetate of α f. p. 11·4°, β_2 m. p. 20·35°, but the intermediate β-form could not be isolated with this specimen. The cooling curve of the α-form showed a change of direction at about 5°, followed some 2° lower by a rapid rise of temperature due to conversion into the β_2-form.

From the pentadecyl acetate was obtained, by hydrolysis and subsequent crystallisation, an alcohol having α f. p. 43·9°, α m. p. 44·0°, and transition temperature 39·9° ± 0·1° from the cooling curve, *ca.* 42·5° from the heating curve.

For the preparation of heptadecyl acetate, cetyl acetate of β m. p. 24·1° was hydrolysed to an alcohol of f. p. 49·1°, and the latter converted into margaric acid by the usual methods. From this, by esterification, ethyl margarate having α f. p. 25·3°, " β m. p." 20·4° (cf. Part III), was obtained, which on reduction and purification of the product, gave heptadecyl alcohol having α f. p. 53·9°, α m. p. 54·0°, and transition temperature 47·3° from the cooling curve, 51·2° from the heating curve. The acetate obtained from this alcohol solidified in the α-form at 24·6°; the cooling curve of the solid showed a change of direction at 15·3° and an arrest at about 10·5°, the latter corresponding with an arrest in the heating curve at 21·5°. When maintained for some time at a low temperature, the third (β_2-) form, m. p. 20·35°, was obtained. This form could also be grown very slowly by keeping the liquid acetate at a temperature between 25° and 30° and seeding with β_2-crystals.

Nonadecyl alcohol, α f. p. 61·65°, transition temperature 54·0° ± 0·2° from the cooling curve, 58° from the heating curve, was obtained by reduction of the pure ethyl nonadecoate previously described (Part III). The cooling curve of its acetate, α f. p. 35·35°, showed a change of direction at 24·5° and an arrest at about 14°, the latter corresponding with a heating arrest at 27·2°. The β_2-form, m. p. 37·6°, like that of heptadecyl acetate, could only be obtained by slow growth.

In connexion with the preparation of alcohols by ester reduction, it should be noted that the crude alcohols so obtained generally contain products which are not readily removed by ordinary processes of purification, and may give rise to fictitious results in the purified alcohol, the melt being frequently cloudy (cf. Carey and Smith, *loc. cit.*, whose original heptadecyl alcohol of f. p. 54·2° was subsequently shown to be impure). To eliminate such impurities, the reduction products obtained above, after treatment with water, and boiling to hydrolyse unreduced ester, were precipitated with dilute calcium chloride solution and filtered. The crude alcohol, extracted from the precipitate with acetone, was then acetylated, and the acetate purified by repeated fractional distillation and/or recrystallisation. Hydrolysis of this purified acetate and subsequent crystallisation of the alcohol, in general, gave a pure product from which the pure acetate was then obtained.

As mentioned above, it appeared from visual observation that the α-forms of all the alcohols examined underwent a change into a less transparent modification within a degree or so of their f. p.'s, but the thermal effect (if any) of this transformation could not be differentiated from that of solidification.

The procedure adopted in determining f. p.'s and m. p.'s was similar to that previously described (*loc. cit.*). In the case of the enantiotropic alcohols, α f. p.'s were determined with the temperature of the bath not more than 0·5° below the f. p.'s. The bath was then maintained about 1° below the f. p. until complete solidification had taken place, after which the cooling curve was determined by allowing the temperature of the bath to fall as uniformly as possible at the rate of about 0·5°/min.

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