[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTOR & GAMBLE CO.]

Microscopic Appearance of Polymorphic Forms of One-Acid Triglycerides[1]

BY OSCAR T. QUIMBY

The multiple melting of one-acid triglycerides such as tristearin has been well established by a combination of thermal and X-ray studies.[2,3,4,5,6] However, some investigators[3,4,5] report three polymorphic forms, each having its own characteristic melting point, while others[2,6] report *four* forms, the extra form (termed "vitreous") being required by the supposed observation of four types of X-ray diffraction pattern. There is also some disagreement on which X-ray pattern is to be associated with a given melting point. The careful microscopic study of Weygand and Grüntzig[7,8] was interpreted as revealing the remarkable total of *seven* crystal forms.

In the present study, it was found that the polarizing microscope can give valuable supplementary aid to X-ray and thermal methods. By a combination of all three techniques, it is shown that fats of the tristearin type crystallize in but *three* polymorphic forms, each having its characteristic microscopic appearance, as well as melting point and X-ray diffraction pattern. The supplemental microscopic evidence fully supports the simpler interpretation,[3,4,5] and gives no evidence of a "vitreous" modification. It shows further the significance of the "seven forms" of Weygand and Grüntzig and of the supposed "glassy" form observed optically by Ravich.[9]

Four Basic Appearances.—For a substance crystallizing in three polymorphic forms, only three basic appearances might be expected. However, in the case of these one-acid triglycerides, the intermediate melting form, beta prime, gives a wide range of appearances from dull to bright (between crossed nicols), so that one must be familar with the two extremes.[10] This leads to the *four* basic appearances which are shown in the photomicrographs of Plate I. Methods of producing these appearances are summarized in Table I.

TABLE I

METHOD OF OBTAINING FOUR BASIC APPEARANCES

Appearance	Conditions of crystallization[a]	Order of crystn. time
Alpha	Chill melt to temps. below cld. p.	Seconds
Dull beta prime	Chill melt to, and hold at, 0.5 to 2° above cld. p.	Minutes
Bright beta prime	Chill melt to, and hold at, 4 to 7° above cld. p.	Minutes
Beta	Chill melt to, and hold at or slightly above beta prime m. p.	Hours to weeks

[a] Cld. p. = alpha cloud point. Melts always "superheated" by 15° or more (*i. e.*, 15° or more above beta m. p.) to destroy invisible nuclei.

While these appearances can be obtained for all four fats of Table V, crystallization is faster for the lower homologs. Also nucleation and transformation rates are faster for the lower homologs under certain conditions. Thus complete crystallization as beta from "superheated" (see footnote, Table I) melt cooled to and held at a temperature 1° above the beta prime melting point occurs much faster for trilaurin than for tristearin, partially due to faster nucleation, partially due to faster crystallization. At the same time, the lower members give larger and more perfect beta crystals, as shown by uniformity of extinctions between crossed nicols. Another such difference is observed in the growth of bright beta prime: thus, while trilaurin nucleates and crystallizes rapidly at 5–6° above its alpha cloud point, beta nuclei form more readily than for tristearin under corresponding conditions, so that it is nearly impossible to obtain a sample of trilaurin fully crystallized in bright beta prime form.[11] Growth of beta prime of the dull appearance (say at 1° above the cloud point) is less likely to give beta contamination for any of the fats tested.

Optical Identification of Initial Crystal Forms.—With these one-acid triglycerides individual crystals, either isolated or projecting from spherulites, are observed (1) often for the beta polymorphic form, (2) occasionally for the beta prime, but (3) never for alpha. Thus the optical identification of alpha depends entirely on its bright spherulitic pattern (Plate I-A) and the sign of elongation of its radial striae; obviously a relatively thin preparation is required or the texture will be obscured. With the other two

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(1) Presented before the Symposium on Electron and Light Microscopy in Chicago, June, 1948.

(2) Clarkson and Malkin, *J. Chem. Soc.*, 6666 (1934).

(3) Bailey, Jefferson, Kreeger and Bauer, *Oil & Soap*, **22**, 10 (1945).

(4) Lutton, THIS JOURNAL, **67**, 524–527 (1945).

(5) Filer, Sidhu, Daubert and Longenecker, *ibid.*, **68**, 167 (1946).

(6) Clarkson and Malkin, *J. Chem. Soc.*, 985 (1948).

(7) Weygand and Grüntzig, *Z. anorg. allgem. Chem.*, **206**, 304 (1932).

(8) Grüntzig, *ibid.*, **240**, 313 (1939).

(9) Ravich, Zurinov, Volnova and Petrov, *Acta Physicochimica*, **21**, 101–108 (1946).

(10) That both the dull and the bright spherulites are beta prime was proved repeatedly by X-ray patterns and by m. p. The bright beta prime tends to melt at a slightly higher temperature than the dull, but always in the neighborhood of 65° for tristearin unless partially converted to beta form. The beta prime texture of plate 1-C shows a tendency toward dull (irregular spots) in addition to well-defined bright character. This is due to the thermal cycle of the thermostat in which the crystals were grown from a thin layer of melt between slide and coverglass. The irregular spots correspond to the low part of the thermal cycle.

(11) Whether beta nuclei form spontaneously from the uncrystallized portion of the sample, or come from transformation of beta prime crystals, has not been determined.

polymorphs, additional help is obtained from single crystals as indicated by Table II, which summarizes the properties found most useful. The most difficult distinction to make is that between alpha and bright beta prime. Sometimes all striae of a bright beta prime spherulite show only negative elongation, making it look very much like alpha. But this confusion can frequently be resolved by finding single crystals projecting from the spherulite. Either such single crystals showing parallel extinction, or neighboring spherulites showing both positive and negative elongation, make it highly probable that the specimen crystallized from melt as bright beta prime.[12] Dull beta prime is easily identified by its low interference color and irregular pattern; its spherulities often show a vague positive elongation (assuming radial striae). Beta crystals are best identified by noting the oblique extinction and chisel-shaped ends of crystals projecting from spherulites.[13] Though not specifically so tested these methods should be applicable to thin sections of fats crystallized from thick layers of melts.

TABLE II

DISTINGUISHING CHARACTERISTICS OF THE THREE POLYMORPHS

Polymorph	Growth pattern	Extinction	Elongation
Alpha	Always spherulitic	?	Always neg.[a]
Beta prime	Usually spherulitic	Parallel	Pos. and/or neg.[a]
Beta[b]	Often spherulitic	Always oblique	....

[a] In case of spherulites, refers to striae (assumed radial). [b] Often opaque relative to alpha and beta prime which are translucent.

Appearance of Transformed Crystals.—In accord with experience in other cases of polymorphism, crystals transformed to another crystalline phase (detected by X-rays) without melting look essentially the same as the phase first crystallized (Plate II, A and D). Thus in Plate II-A, beta is pseudomorphic after alpha (see thermal history A in Plate II). When partial or complete melting accompanies the transformation, the general pattern of the initial crystal phase is usually wiped out as in Plate II-B, but may persist if little flow or convection occurs (Plate II-C). Hence by a combination of microscopic and X-ray observations it is sometimes possible to infer the thermal history to which fat crystals have been subjected.

Seven Forms of Weygand and Grüntzig.—In comparing these observations with those of Weygand and Grüntzig,[7,8] it is convenient to use the shorthand notation of Table III. The first Greek letter of a symbol combination indicates the phase first crystallized and a following Greek letter indicates a phase formed from the first phase, the transformation occurring without melting unless an *m* intervenes.

TABLE III

SYMBOLS TO EXPRESS THERMAL HISTORY AND PROBABLE APPEARANCE

Initial cryst. phase	Final crystalline phase Alpha	Beta prime	Beta
			$\alpha\beta$
			$\alpha m\beta$
Alpha	α	$\alpha\beta'$	$\alpha\beta\beta'$
			$\alpha\beta' m\beta$
		$\alpha m\beta'$	$\alpha m\beta'\beta$
			$\alpha m\beta' m\beta$
Beta prime		β'	$\beta'\beta$
			$\beta' m\beta$
Beta			β

From careful and complete description given by Weygand and Grüntzig, it is easy to deduce the relation between their "seven forms" and the three polymorphs established by X-ray diffraction as shown in Table IV; the thermal history is concisely indicated by the symbols of Table III.

TABLE IV

"SEVEN FORMS" OF WEYGAND AND GRÜNTZIG

W. & G. symbol	O. T. Q. symbol	Microscopic appearance	Probable X-ray pattern	M. p. for W. & G.'s tristearin
III-C	α	Alpha mosaic	α	55°C.
II-C	β'	Dull β'	β'	65
II-B	β'	Dull to bright β'	β'	65
II-A	β'	Bright β'	β'	65.5
I-C	$\alpha\beta'\beta$ or $\alpha m\beta'\beta$[a]	Often alpha mosaic, but may be imperfect or hazy	β	69.5
I-B	Essentially β	β spherulites grown from seed formed thus: $\alpha m\beta$, $\alpha m\beta'\beta$, $\beta'\beta$, or $\beta' m\beta$	β	70.5
I-A	β	Beta rhombs	β	71

[a] Possibly also $\alpha\beta$ or $\alpha m\beta$.

Their multiplication of forms is understandable since X-rays were not used to reveal the submicroscopic order of the crystal phases. Upon examining the manuscript of Grüntzig's paper,[8] Malkin wrote that the one-acid triglycerides of the odd acids (*e.g.*, *n*-pentadecanoic) crystallized in four polymorphic forms, namely gamma (vitreous), alpha, beta prime and beta.[14] Since this represented an increase of one crystal form over the three reported earlier by Malkin[2] for the even acid homologs, Grüntzig expressed the hope that further X-ray studies might reveal still more crystal forms for both the odd and even acid homologs. He reiterated his belief in seven forms of one-acid triglycerides of even acids, but

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(12) A mixture of alpha and bright beta prime could result from partial crystallization at 5° above the alpha cloud point followed by sudden chilling below the cloud point. An X-ray diffraction pattern would reveal whether two phases were present.

(13) Neither quantitative extinction angles, nor silhouette angles are very useful because of the wide range of values encountered as a result of variation in crystal orientation.

(14) Footnote, p. 315 in ref. 8. More recently Malkin[6] has reported the same four forms for even-acid triglycerides like tristearin.

offered evidence based only on microscopic appearance and melting points.

Melting Point Variation with Stabilization.—The multiplication of melting points observed by Weygand and Grüntzig is real and arises from varying degrees of stabilization or perfection of the crystals. This has been known to lead to variations of several degrees for the melting point of a single polymorphic form of a triglyceride.[15] With tristearin type fats the variations are not so large,[4] but nevertheless real as can be shown by some data on the beta melting point of the sample of tristearin used in the present study. As crystallized from isopropyl alcohol at 58°, it melted at 73.0°, the highest melting point obtained for this sample. Once melted, however, this high melting point was not obtained again until the sample was carefully stabilized. Thus, the product of transforming alpha to beta at 52°, *i.e.*, $\alpha\beta'\beta$ and/or $\alpha\beta$, melted at 71.5 to 72.5° depending on how long it was stored at 52°. Another preparation, $\alpha m\beta$, made by storing alpha tristearin at 58° for one to three days, melted at 72.7–72.8°. Beta crystals made in any way, and held for about an hour at 70°, melted at 73.0°. Thus, the highest three melting points given by Weygand and Grüntzig for tristearin (Table IV) are due to beta crystals at different degrees of stabilization; similarly the next three are probably due to beta prime crystals at different stages of stabilization.

Such variation of melting point with degree of stabilization also makes understandable the extra melting point recently reported by Malkin[6] for tristearin type fats. This melting point (70° for Malkin's tristearin) is not due to beta prime, but to poorly stabilized beta.

Microscopic Evidence that Tristearin Melting at 65° is Beta Prime.—Recently Malkin[6] has again stated that the 65° melting point is to be associated with the alpha X-ray pattern, whereas other investigators[3,4,5] have associated it with the beta prime X-ray pattern. In the course of the present study, two types of evidence were obtained which favor the latter association.

As already indicated,[10] crystals of tristearin, grown in a flat capillary from a melt superheated and held 1–5° above the alpha cloud point, always melt at about 65°, if the X-ray has shown them to be beta prime. This is easily proven for the case of dull beta prime crystals grown at 0.5–2° above the alpha cloud point, for with tristearin it is fairly easy to obtain *complete crystallization in beta prime form* without contamination by the other polymorphs.[16] In the case of bright beta prime crystals grown at 4–6° above the alpha cloud point, contamination by beta is more likely, and in trying to avoid this, the melt may be chilled too soon and produce considerable alpha form. However, by using very thin ribbons of fat, and making many trials, it has been found possible to obtain considerable areas (*e.g.*, 1 mm. diameter) of bright beta prime free of detectable contamination by alpha and beta. These areas, tested by the "thrust-in" procedure described below for the beta prime melting point, show extensive melting in the neighborhood of 65°. Such evidence makes it clear that the 65° melting point of tristearin is that of the beta prime polymorph, not that of the alpha as indicated by Malkin.[6]

The beta prime character of crystals of tristearin grown from a superheated melt cooled to and held at 58–59° can also be demonstrated by means of optical properties. By choosing a fat whose beta prime form is more stable, one can grow beta prime crystals from melt or solvent that can be carefully characterized optically. Thus, 2-stearyldipalmitin (PSP) whose stable form is beta prime,[15] gives lath-like crystals (Plate III-A), showing parallel extinction and either positive or negative elongation depending on orientation about their long axis, and giving the beta prime X-ray pattern. Occasionally, a tristearin melt crystallizing at 58–59° gave crystals sufficiently isolated[16a] to show clearly their parallel extinction, some oriented to show positive, others to show negative, elongation. These beta prime crystals are easily differentiated from any isolated beta crystals, which may be present simultaneously, for the latter are similar to, although less perfect than, the beta crystals of 2-palmityldistearin (SPS) shown in Plate III-B, and always show oblique extinction. These observations support the X-ray and melting-point data in showing that at 5° above the alpha cloud point fats of the tristearin type crystallize in the beta prime form.

Crystallinity of Alpha Fat.—Malkin[2,6] has repeatedly maintained that the lowest melting form of saturated triglycerides is "vitreous." Ravich, *et al.*,[9] have given some support to the existence of a vitreous or glassy form. However, as pointed out by Grüntzig,[8] glassy nature is inconsistent with the strong birefringence observed for the lowest melting form (see Plate I-A). It is also inconsistent with the sharp melting and with the two groups of sharp X-ray diffractions (long and short spacings) of this lowest melting form.

The bright spots of high interference color, which are obtained as first nuclei "flash-out" from isotropic melt, are observed to grow rapidly outward in spherulitic fashion until all melt is used up and a rigid product is obtained. Such a growth pattern is characteristic of crystallization

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[15] Lutton, Jackson and Quimby, THIS JOURNAL, **70**, 2441 (1948).

[16] In chilling a sample preparatory to making an exposure to X-rays or to observing the melting point, any trace of melt present is converted to alpha form. While this can sometimes be detected microscopically, it is better shown by X-ray diffraction, using the long spacings. Beta contamination is readily detected in beta prime by means of X-rays, using the beta short spacings (especially the strong 4.6 Å. line).

[16a] No isolated crystals were found for tristearin crystallizing at 55–56°, *i. e.*, as dull beta prime.

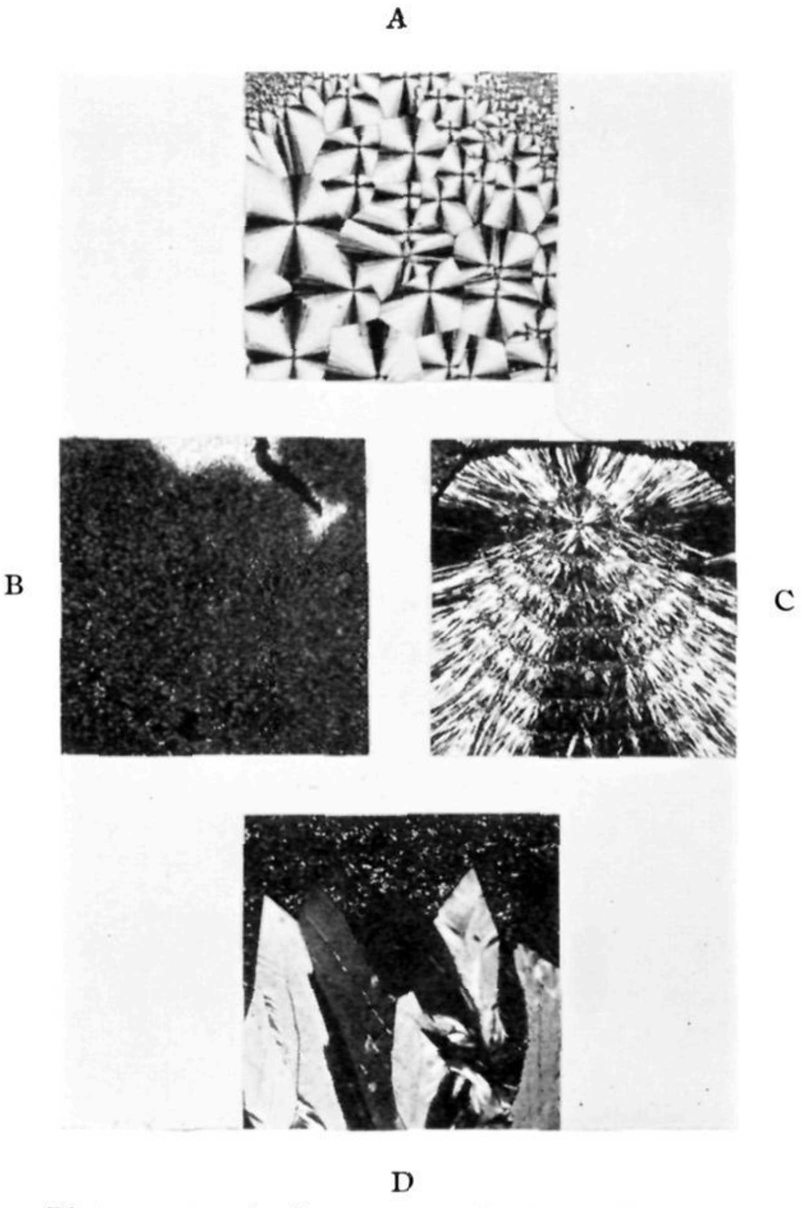

Plate I.—Four basic textures: A, alpha, MMM, 63 ×; B, dull beta prime, SSS, 63 × (trace of alpha, top center); C, bright beta prime, PPP, 33 ×; D, beta, SSS, 65 ×.

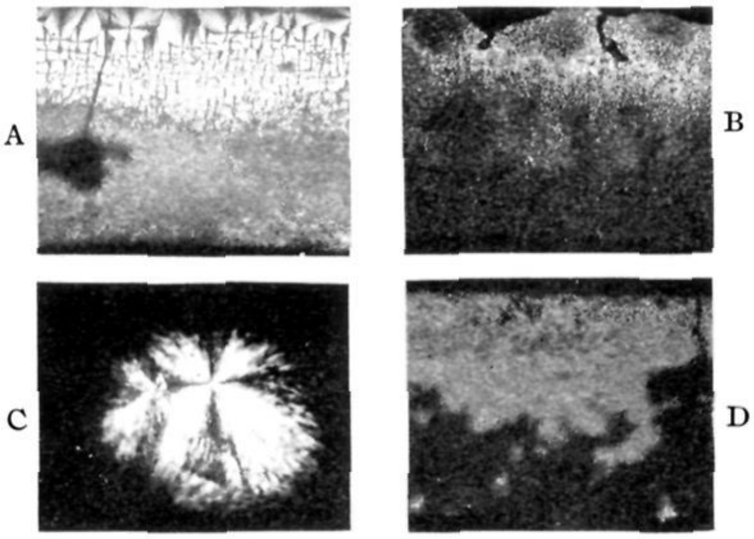

Plate II.—Appearance of transformed tristearin: A, $\alpha\beta$(or $\alpha\beta'\beta$), 65 ×, 10″ 100°, 10″ 0°, 10′ 53.8°, R. T.; B, $\alpha m\beta'$, 65 ×, 10″ 100°, 10″ 0°, 10′ 55.8°, R. T.; C, $\alpha m\beta$, 280 ×, 10″ 100°, 10″ 0°, 60′ 64.5°, R. T.; D, dull $\beta'\beta$, 65 ×, 10″ 100°, 30′ 54.8°, 30′ 63.5°, R. T.

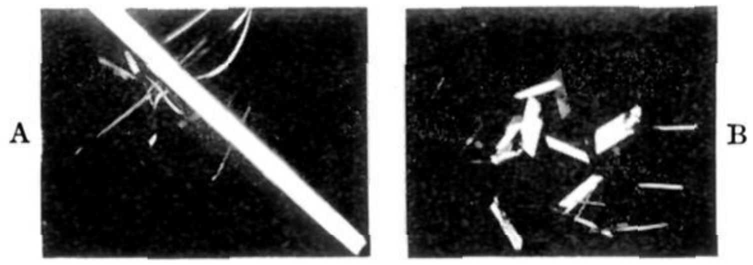

Plate III.—Individual crystals of beta prime and beta: A, beta prime, PSP, solvent crystallized; B, beta, SPS, crystallizing from melt.

rather than formation of a glass (with strained areas). Furthermore, quick heating to a temperature 0.5–1.5° above the alpha cloud point wipes out the bright pattern, giving a mobile isotropic melt which soon recrystallizes as the beta prime polymorph resembling either the dull appearance of Plate I-B or the original bright alpha spherulites.

While the data on the alpha polymorph distinguish it clearly from the vitreous state, they do not completely exclude the possibility of its being mesomorphic. Mesomorphic phases often show high birefringence and sharp melting points. However, relatively mobile mesomorphic types such as are found in neat or middle soap[17] are excluded by the rigidity and brittleness of alpha fat, which shows no deformation under moderate pressure, but fractures under high pressure. This is also supported by X-ray data, for alpha fat shows both sharp long and sharp short spacings[18] whereas neat and middle show only sharp long spacings. This means that there are at least two sets of planes in alpha fat compared to but one in neat and middle phases. Thus if alpha fat is mesomorphic, it must be one of the more ordered cases, *e. g.*, DRR, DR(RP$_0$), or DR(RD) in Hermann's notation.[19]

The X-ray patterns suggest that alpha fat is not mesomorphic. Mesomorphic phases would be expected to give diffuse spacings whose intensity distribution is unsymmetrical, *i. e.*, more sharply defined on the low angle side.[19] Visual examination of the weak diffuse spacings does not reveal such dissymmetry. While the possibility of a mesomorphic phase is not entirely excluded, it is probable that alpha fat represents a disordered crystal.

Apparatus and Method.—Most observations were made on fat sealed in a flat capillary located in a micro-oven, which could be heated electrically or cooled by an air stream through symmetrically placed channels. The temperature could be changed rapidly (50°/minute) and could be held constant within ±0.5° for a few hours at a time or to ±0.1° for a few minutes. The flat capillaries had thin walls so that X-ray patterns could be taken of the thin layer of crystallized fat to determine its polymorphic form.

Some photomicrographs were taken on the thin ribbons of fat crystals in the flat capillaries. Because of the variable thickness of these ribbons, better pictures were obtained on thin layers (between microscope slide and cover glass) that had been treated thermally in small, constant-temperature ovens in accord with the thermal history indicated by the micro-oven studies.

Characteristics of Fats.—The melting points of the four fats used are given in Table V. The first three were purified by several recrystallizations from isopropyl alcohol under conditions such that 15–25% of the fat remained in solution at each crystallization. The trilaurin (Eastman Kodak Co.) was used as received. The melting points were determined by the methods of Lutton,[4] except that the alpha cloud point was substituted for the alpha softening point; the former may be 1° lower than the latter, but is usually closer for fats of the tristearin type. The quick melting procedure for beta prime was adapted to use of the micro-oven and microscope as described below.

TABLE V

MELTING POINTS OF FATS USED

Fat	Abbreviation	Alpha Cld. P.,[a] °C.	Beta prime M. p.,[b] °C.	Beta or complete M. p., °C.
Tristearin	SSS	54.0	64.5	73.0
Tripalmitin	PPP	44.7	56.6	66.4
Trimyristin	MMM	31.5	47.0	57.2
Trilaurin	LLL	13.6	35–36	45.0

[a] Cld. P. = cloud or setting P. obtained by rapid cooling. [b] Beta prime m. p. is known to ±0.5°, others to ±0.1°.

Alpha Cloud Point.—This constant can be determined easily and with a precision as high as that for the complete melting point for the *fully-stabilized* form. This comes about because the polarizing microscope provides a favorable means of detecting the first crystal and because the alpha cloud point is the supercooling limit.[4]

The fat is first melted at a temperature 15° or more above the beta melting point to destroy invisible nuclei, then rapidly chilled to induce crystallization, note being taken of the thermocouple temperature at which the first crystal flashes out bright against the dark background (crossed nicols). In the micro-oven used here, this temperature is too low due to lag of fat temperature behind thermocouple temperature during the rapid cooling. Hence, the fat is remelted as before and cooled rapidly to, and held at, an arbitrary temperature about 0.5 to 1° higher than the initial alpha cloud point. If the first crystals to form are bright, alpha spherulites, the process is repeated at a still higher temperature; if the crystals are dull, beta prime spherulites, the next test must be made at a slightly lower temperature. The alpha cloud point is taken as the highest temperature at which the first crystals to form are clearly recognizable as alpha. It can be so closely located that at a temperature 0.1° higher no alpha will be found, the first crystals then being those of a higher melting form (*e. g.*, beta prime for tristearin type fats).

Beta Prime Melting Point.—The method of Lutton[4] for the beta prime softening point is easily adapted for observation of the beta prime melting with the micro-oven and microscope. The thin ribbon of fat is superheated to destroy nuclei, the melt cooled to, and held at, the desired temperature (see Table I) until crystallization of bright (or dull) beta prime appears complete. The fat sample is then removed from the oven and kept at a temperature 30° below the crystallization temperature, while the oven is reset to a higher temperature, which is 8–10° below the melting point of the fully-stabilized beta polymorph. If no melting is observed microscopically when the crystallized sample is quickly thrust into the micro-oven, a newly crystallized sample must be prepared as before and retested at a higher "thrust-in" temperature. Once temporary melting has been observed, the "thrust-in" temperature is varied in successive tests until the melting point is bracketed as closely as possible. The lowest temperature of this fleeting melting, taken here as the beta prime melting or softening point, cannot be bracketed more closely than ±0.5° because of the rapid recrystallization of such melts of tristearin type fats to give the beta polymorph. Because of this rapid recrystallization, complete melting of beta prime to an optically isotropic liquid cannot be observed except at temperatures 5–8° higher.[20]

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(17) F. B. Rosevear, "The Microscopy of the Liquid Crystalline Neat and Middle Phases of Soaps and Synthetic Detergents," paper in preparation.

(18) Besides the lines due to the long spacing (50.6 Å. for tristearin) and the two reported short spacings at 4.14 Å. and 2.40 Å., a long exposure of alpha 2-palmityldistearin to Cu radiation revealed three diffuse halos. Relative to the 2.40 line as strong, the halos were rather weak: *e. g.*, 2.2–1.9 Å. weak, 1.85–1.65 Å. very weak, 1.30–1.19 Å. very weak.

(19) C. Hermann, *Z. Krist.*, **79**, 186–121 (1931).

(20) This phenomenon of rapid recrystallization when beta prime crystals are placed suddenly at their melting point has been reported repeatedly, *e. g.*, by Weygand and Grüntzig.[7]

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Summary

Microscopic observations of appearance and optical properties of the polymorphs of some one-acid triglycerides have been used to supplement X-ray and melting point data. Further support has been given for the existence of but three polymorphic forms of tristearin, etc. In particular, the minimum-melting form (alpha) is *not* vitreous, but is much more highly ordered, probably a somewhat disordered crystal. It is believed that no vitreous form exists for these triglycerides.

The crystals of lowest interference color obtainable (between crossed nicols) have the intermediate melting point (65° for tristearin), rather than the minimum melting point; they give the beta prime X-ray pattern, not the alpha. By a suitable choice of crystallization temperature one can obtain better-organized, intermediate-melting crystals of high interference color; these also melt near 65° and show the beta prime X-ray pattern; in addition, single crystals show beta prime optical properties.

It is shown how the "seven" forms, described by Weygand and Grüntzig upon the basis of microscopic observations plus thermal data alone, are to be reduced to the three revealed by X-rays.

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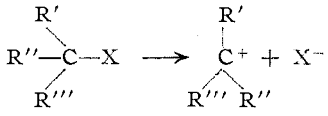
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Chemical Effects of Steric Strains. III. The Effect of the Halogen on the Rate of Hydrolysis of Tertiary Aliphatic Halides

BY HERBERT C. BROWN AND ANNETTE STERN

It has been proposed that three alkyl groups attached to a single carbon atom constitute a center of strain and that such strain may exert an important influence upon the chemistry of highly branched carbon compounds.[1] To test the value of this concept in interpreting the behavior of highly branched carbon compounds, we have undertaken quantitative studies of the effect of structure on the reactions of such compounds.

The hydrolysis of tertiary alphatic halides is believed to proceed through a rate determining ionization followed by a rapid reaction of the carbonium ion with the solvent.[2] The steric strain hypothesis proposes that the bulkier the groups, R′, R″, R‴, the greater the strain. Ionization to the presumably planar carbonium ion should diminish the strain. Therefore, other factors being maintained essentially constant, an increase in the steric requirements of the groups R should result in an increase in the rate of hydrolysis.

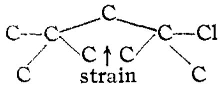


The first paper of this series[1] reported a study of the effect of structure on the rate of hydrolysis of twelve tertiary aliphatic chlorides. The results would be exceedingly difficult to interpret without the aid of the steric strain concept.

The present investigation was undertaken to determine whether the structural effects observed in the tertiary aliphatic chlorides are also present in the corresponding bromides and iodides. The recent publication of a paper reporting rate data for the hydrolysis of tertiary iodides[3] made it possible to restrict this study to the hydrolysis of tertiary bromides of the structure RMe_2CBr (with R = Me, Et, *i*-Pr, *t*-Bu and *neo*-Am).

Results and Discussion

In the alkyl chlorides the rate of hydrolysis first rises as R is changed from Me to Et, and then drops as R becomes isopropyl (Fig. 1). Because of the geometry of the ethyl and isopropyl groups which permits rotation of the groups to positions minimizing the crowding, the strain in the alkyl chloride should not be appreciably increased in this sequence of structural changes. The observed changes in rate can be attributed to the combined inductive and hyperconjugative effects of the alkyl groups.[1] However, on this basis triptyl chloride (R = *t*-Bu) should show a further drop in rate. Instead an increase is observed. This increase is attributed to steric strain. Diisobutylene hydrochloride (R = *neo*-Am) shows a large increase in rate of hydrolysis and the geometry of the molecule is such as to lead to a large increase in steric strain.



The alkyl bromides and iodides show identical changes in the rates of hydrolysis as R is suc-

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[1] Brown and Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[2] The evidence is summarized in papers by Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941), and *J. Chem. Soc.*, 968 (1946).

[3] Shorter and Hinshelwood, *J. Chem. Soc.*, 2412 (1949).