prime PSP is not correct but that his value for "beta" is the true beta prime long spacing value. Malkin's beta prime value for a pure SPS is tentatively questioned on the basis of the present authors' failure to obtain such a form.

Acknowledgment.—The authors wish to express their appreciation for permission from the Procter & Gamble Co. to publish the portions of this investigation which are of general interest, and to the members of this laboratory who have assisted in the experimental work and have given advice in the preparation of the manuscript.

Summary

As compared with the great similarity in polymorphic behavior of the single fatty acid saturated triglycerides, the mixed palmitic–stearic triglycerides show a remarkable individuality. Many of the conclusions here reached with regard to their behavior are at variance with those of Malkin and co-workers.

The symmetrical isomers show a high degree of crystallinity; the unsymmetrical compounds are microcrystalline. All four compounds exhibit a lowest melting alpha form—unusually stable in the case of 2-palmityldistearin and unusually labile in the case of 2-stearyldipalmitin.

Occurrence of forms other than alpha can be briefly tabulated:

Glyceride	Forms beside *alpha*
2-Palmityldistearin	Only beta
2-Stearyldipalmitin	Only beta prime
1-Palmityldistearin	Only beta prime from melt, beta from solvent (beta prime and beta equally stable)
1-Stearyldipalmitin	Beta prime and beta (beta stable)

A given form of a given glyceride may vary several degrees in melting point depending on its degree of stabilization. This variation may account for the fact that previous workers have reported more characteristic thermal points for a given glyceride than can be substantiated by X-ray diffraction patterns.

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[CONTRIBUTION FROM THE PROCTER & GAMBLE CO.]

The Polymorphism of 1-Monostearin and 1-Monopalmitin

BY E. S. LUTTON AND F. L. JACKSON

Introduction

The polymorphism of the compounds 1-monocaprylin through 1-monostearin has been studied by Rewadikar and Watson[1] by means of capillary melting point methods but without the help of X-ray diffraction data. Malkin and coworkers,[2,3,4] using X-ray diffraction and thermal techniques, have studied the polymorphism of saturated 1-mono-, 1,3-di- and triglycerides. However, further work has led to corrections and new interpretations in the field of triglycerides.[5,6,7] Similarly, re-examination of the 1-monoglycerides, specifically 1-monostearin and 1-monopalmitin, as reported in the present paper has shed new light on the polymorphic behavior of this class of compounds.

As in the case of the triglycerides[6] every effort has been made to maintain the nomenclature introduced by Malkin.[3] However, the discovery of four polymorphic forms (here called subalpha, alpha, beta prime and beta) instead of three for the 1-monoglycerides and the fact that subalpha and beta prime have very similar X-ray patterns required some revision and refinement of Malkin's basis for nomenclature. A particular complication is the subalpha form, a distinct form accounting for the reversible thermal effects reported by Malkin on cooling alpha and subsequent reheating.

The basis for monoglyceride nomenclature may be summarized as follows.

Subalpha has a single strong short spacing line at 4.15 Å., other medium lines at 3.9, 3.75 and 3.55 Å. This form undergoes a reversible transformation to alpha and therefore has no m. p.

Alpha has a single strong short spacing line at 4.15 Å. with other weak short spacing lines. This form has the lowest complete m. p. Triglyceride alpha similarly has a single strong short spacing line at 4.15 Å. and is the lowest melting form.

Beta prime has a strong short spacing line at 4.15 Å., and a 3.65 Å. medium line which is the strongest one between 4.2 and 2.6 Å. This form has an intermediate complete m. p. Triglyceride beta prime has strong spacings at 4.2 and 3.8 Å., and is normally the intermediate melting form.

Beta has a strong short spacing line at 4.55 Å. and is the highest melting form. Triglyceride beta has a strong line at 4.6 Å. and is generally the highest melting form.

It is apparent from the preceding paragraphs that the bases for nomenclature are similar for the mono- and triglycerides.

Experimental

The monoglycerides were prepared according to the

(1) Rewadikar and Watson, *J. Indian Inst. Sci.*, **13**, A, 128 (1930).
(2) Clarkson and Malkin, *J. Chem. Soc.*, 666 (1934).
(3) Malkin and Shurbagy, *ibid.*, 1628 (1936).
(4) Malkin, Shurbagy and Meara, *ibid.*, 1409 (1937).
(5) Bailey, *et al.*, *Oil & Soap*, **22**, 10 (1945).
(6) Lutton, THIS JOURNAL, **67**, 524 (1945).
(7) Filer, *et al.*, *ibid.*, **68**, 168 (1946).

directed rearrangement method of Eckey.[8] Monostearin was prepared from a mix of 35% completely hydrogenated linseed oil and 65% linseed oil, to which was added 15–20% of dry glycerol and 0.5% NaOMe (a catalyst suspended in xylene). The mixture was agitated for forty-eight hours each at 60, 49 and 38°, during which time the crude monostearin precipitated in increasing amounts. An excess of glacial acetic acid was added to kill the catalyst, the mix was water-washed to remove sodium acetate, and the final purification accomplished by six crystallizations from Skelly B-ethyl alcohol mixtures.

Monopalmitin was prepared similarly from cottonseed oil stearine plus 15–20% of glycerol and 0.5% NaOMe catalyst. (The stearine was the precipitate from a partially crystallized oil and contained 30–35% combined palmitic acid.) The temperature cycle used here was 38, 32 and 27°.

The degree of purity of the monoglycerides is indicated by the analyses in Table I.

TABLE I

ANALYSES OF MONOGLYCERIDES

I. V. = iodine value, S. V. = saponification value, % monoglyceride by the periodic acid method.[9]

	Experimental				Theory			Lit.[3]
Glyceride	I. V.	S. V.	% Monoglyceride	C. m. p., °C.	I. V.	S. V.	% Monoglyceride	C. m. p. °C.
1-Monostearin	0.0	156.2	104.5	81.5	0.0	156.4	100.0	81.5
1-Monopalmitin	.0	169.0	101.9	77.0	.0	169.6	100.0	77.0

The samples were examined by X-ray diffraction, thermal methods and by dilatometry. The techniques of X-ray diffraction and thermal examination have been described elsewhere.[6,10]

The X-ray specimens were prepared in three ways: (1) melted samples were drawn into Pyrex glass capillaries and tempered in various ways depending on the polymorphic form desired, (2) powdered crystalline samples were made into 0.5 mm. thick disk-shaped pellets which were X-rayed perpendicularly to the flat side of the disk, and in addition (3) powdered samples were made into 1-cm. rods of 0.5 mm. diameter after the manner of Piper.[3] The rods were mounted vertically in the path of the X-ray beam. They gave excellent long and short spacing X-ray lines on the same film, while the disk-shaped pellets yielded very poor long spacings presumably due to orientation of the hydrocarbon chains perpendicularly to the face of the disk.

Thermal examination was accomplished with samples in capillary tubes. Beta prime and beta melting points were obtained by ordinary complete melting point determination with a rise in bath temperature of 0.5° per minute. Alpha melting points were obtained by thrusting capillaries into a bath of definite temperature. The alpha m. p. was the point halfway between the maximum temperature for remaining solid (indicated by any cloudiness, however faint) and the minimum temperature for complete clarity. These two temperatures were usually less than 0.2° apart.

The dilatometer procedure was without special features. A one-gram sample was placed in a glass bulb and the bulb joined to the dilatometer capillary by an interchangeable joint. The sample was melted, the dilatometer evacuated and the sample then frozen. At this point the dilatometer was completely filled by running mercury into the evacuated space and onto the sample.[11] The mercury content was adjusted by setting the sample at a temperature about 10° above the melting temperature. After the desired sample treatment, dilatometer readings (distance of the mercury meniscus from the top of the dilatometer) were taken at successive temperatures. The dilatometer was particularly helpful in studying the alpha–subalpha relationships.

The alpha form was obtained by rapid cooling of the melt. As in the case of triglycerides, its melting point represents the approximate supercooling limit. Alpha has a low temperature limit of existence at which it transforms reversibly to subalpha, so that at room temperature both monostearin and monopalmitin exist in the subalpha rather than the alpha form.

The beta prime form was obtained by fairly rapid crystallization from dilute (1:300) ether or Skellysolve B solutions. It was not obtained from a melt nor by tempering alpha. By a similar procedure Chen and Daubert[12] obtained metastable forms of triacid triglycerides.

Relatively slow crystallizations from solvents (50–50 mixtures of alcohol and Skellysolve B) gave beta. This form was not obtained by direct crystallization from the melt without seeding, but was obtained by transformation of alpha or beta prime.

Results

The thermal points are recorded in Table II in comparison with the data of Malkin. The two sets of values are in reasonable agreement except that no second transition point was observed below the alpha m. p. as reported by Malkin for monostearin.

TABLE II

THERMAL POINTS, °C.

(LJ), Data of Lutton and Jackson; (MS), data of Malkin and Shurbagy

	(LJ)				(MS)			
	Subalpha Transformation Pt.[a]	Alpha M. p.	Beta prime M. p.	Beta M. p.	Subalpha Transformation Pt.	Alpha M. p.	Beta prime M. p.	Beta M. p.
1-Monostearin	49	74	78	81.5	42 and 47.5	74	79	81.5
1-Monopalmitin	39	66.9	74.6	77.0	34	66.5	74	77.0

[a] Determined by microscope (and approximately by dilatometer).

Detailed X-ray data are shown in Table III with average long spacing values which are compared with those of Malkin[3] and Filer.[7] Long spacing agreement is reasonably good except in the case of the alpha form for monostearin. The present value is 8 Å. short of that reported by Malkin. Characteristic short spacing data are shown in Table IV in comparison with those of Malkin and Filer. For the beta form, agreement is better in certain respects with Filer's data, but some of Filer's strong lines were not confirmed. It is uncertain whether Malkin's so-called beta prime data should properly be regarded as pertaining to beta prime or subalpha. From the reported spacings and description of procedure no decision can be made.

Dilatometer results for the alpha $\rightleftarrows$ subalpha reversible change are shown in Fig. 1.

Discussion

While in most features of behavior the monoglycerides were found to correspond to the beha-

(8) Eckey, U. S. Patent 2,442,534 (June 1, 1948).

(9) Pohle, Mehlenbacher and Cook, *Oil & Soap*, **22**, 115 (1945).

(10) Nordsieck, Rosevear and Ferguson, *J. Chem. Phys.*, **16**, 175 (1948).

(11) McBain and Field, *J. Phys. Chem.*, **37**, 675 (1933).

(12) Chen and Daubert, THIS JOURNAL, **67**, 1256 (1945).

TABLE III

X-RAY SPACINGS, IN Å. OBTAINED WITH Cu RADIATION, $\gamma_{K\alpha} = 1.54$ Å.

(*hkl*)	1-Monostearin				1-Monopalmitin			
	Subalpha	Alpha	Beta prime	Beta	Subalpha	Alpha	Beta prime	Beta
				Long Spacings (LJ)				
001	49.7 VS	50.7 VS	49.7 VS	50.0 VS	45.0 VS	45.1 VS	45.0 VS	45.5 VS
002	25.5 W	25.0 M	25.2 W	25.0 W	22.8 M	22.8 W		23.0 VW
003	16.9 W	16.7 S	16.8 W	16.6 M	15.3 M	15.15 M	15.1 W	15.25 S
004	12.7 W	12.5 M	12.6 W	12.5 M	11.4 M	11.4 M	11.3 VW	11.4 S
005								
006	8.42 VW	8.38 M	8.40 VW	8.34 M	7.53 M	7.60 W		7.60 M
007	7.17 VW	7.18 M			6.55 W			6.47 W
008				6.27 VW				
009				5.63 W		5.10 W		5.06 M
Av. d	50.3	50.2	50.1	50.1	45.5	45.6	45.25	45.6
(MS) d	50.0?	58.3	50.0?	50.0	45.8?		45.8?	45.8
(FSDL) d				49.9				45.7
				Short Spacings (LJ)				
(LJ)				4.88 W			5.00 VW	4.87 VW
	4.13 VS	4.64 W	4.15 VS	4.54 VS	4.14 VS	4.65 W	4.15 VS	4.55 S
	3.92 M	4.18 VS	3.89 VW	4.36 VS	3.92 M+	4.18 VS	3.85 VW−	4.37 S
	3.75 M	3.82 W	3.61 M	4.13 W	3.74 M+	3.99 VW	3.69 W	4.13 W
	3.58 M	2.47 VW	3.30 VW	3.85 VS	3.54 M+	3.80 W	3.29 W+	3.86 S
	3.28 W		2.91 VW	3.74 W	3.29 W	2.46 VW−	2.78 VW	3.74 W
	3.10 VW		2.79 VW	3.64 VW	2.92 VW		2.52 M	3.50 M
	2.94 VW		2.52 M	3.54 W+	2.78 VW		2.25 VW	3.29 M
	2.81 VW		2.25 VW	3.43 VW	2.54 W			3.08 M
	2.52 M		2.22 W	3.30 VW	2.50 W			2.67 VW
	2.42 VW			3.12 M	2.41 VW			2.54 VW
	2.32 W			2.97 VW	2.33 W			2.47 M
	2.23 W				2.21 W			2.23 VW
	2.09 W			2.45 M	2.08 W			2.14 VW
								2.06 VW−

(FSDL), Data of Filer and co-workers

TABLE IV

CHARACTERISTIC SHORT SPACINGS IN Å. FOR MONOGLYCERIDES (COMPARISON WITH PREVIOUS DATA)

	Subalpha	Alpha	Beta prime	Beta
(LJ)	4.14 VS	4.64 W	4.15 VS	4.55 S+
	3.92 M	4.18 VS	3.87 VW	4.37 S+
	3.75 M	3.99 VW	3.65 W+	3.86 S+
	3.56 M	3.81 W	3.30 W−	3.74 W
(MS)	4.24 VS?	4.2 VS	4.24 VS?	4.65 VS
	3.86 M?		3.86 M?	3.94 S

	1-Monostearin Beta	1-Monopalmitin Beta
(FSDL)	4.74 W	4.73 VS
	4.55 VS	4.55 VS
	4.37 S	4.37 VS
		4.27 VS
		3.94 VS
	3.84 VS	3.84 VS
	3.74 W	3.74 S
	3.52 S	

vior described by Malkin, there were departures of considerable significance particularly in the case of alpha and subalpha forms.

Alpha and Subalpha.—Alpha, in the correspondence of its melting point to the supercooling limit and by the value of its one strong short spacing (4.18 Å.), resembles the alpha form

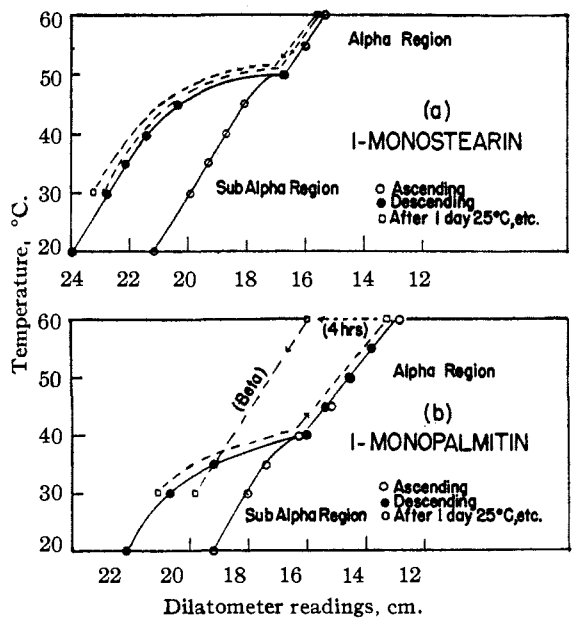

Fig. 1.—Dilatometer curves of reversible alpha to subalpha transformation.

of triglycerides. There are important differences, however. Weak short spacings on both sides of 4.18 Å. evidence certain unidentified complexities of structure not found for triglycerides. Of greater interest are the long spacing values. Double chain length structures are indicated, but the values are 8 Å. short of that to be expected for completely extended untilted molecules, 58 Å. for monostearin. (A value of this magnitude, reported by Malkin, was not confirmed.) Alpha, beta prime and beta values are very nearly equal and the simplest conclusion is that they each indicate titled molecules. A tilted alpha, supposedly of hexagonal cross-sectional type, would be contrary to previous experience and preconceptions.

The alpha form goes reversibly to a form, here called subalpha, at a temperature about 25° below the alpha melting point. The reversibility was completely established, in the present study by successive X-ray exposures above, below and above the transition point to give respectively alpha, subalpha and alpha patterns. This transition point was actually located by Malkin, with the help of thermal curves, but he did not describe a clearcut association of change in diffraction pattern with thermal effect. He said that alpha "is stable only very near its melting point," but it is actually reasonably stable clear down to the transition point. He speaks of the form below the transition point as an "intermediate form" somewhat akin to a "glass" and without "a regular crystalline lattice," but *subalpha* is actually a highly ordered structure, apparently considerably more ordered than *alpha* which is itself of a fair degree of crystallinity.

The alpha $\rightleftarrows$ subalpha change is readily followed also by the dilatometer and microscope.[13]

If a dilatometer sample is melted and chilled quickly to 20°, then heated in steps to 60° and cooled stepwise to 20°, curves such as those shown in Fig. 1 are obtained. The solid ascending curves show a small break at about 49° for 1-monostearin and 39° for 1-monopalmitin. The solid descending curves show greatly accentuated contractions in the same temperature regions indicating that the subalpha form is decidedly more dense than it was initially. The order of contraction in the alpha $\rightarrow$ subalpha change is about 0.04 specific volume units.

After the ascending and descending curves were run the dilatometers stood overnight at room temperature and then were read at 30°, heated directly to 60°, allowed to attain a constant reading, and cooled to 30°. The points obtained are joined by broken lines on Fig. 1 and the time sequence is indicated by arrows. The data show that the descending alpha to subalpha path is essentially duplicated for 1-monostearin. However, 1-monopalmitin transformed to beta in four hours at 60°. Cooling 1-monopalmitin beta to 30° revealed a lower density for this form than for subalpha—a fact which was substantiated for other samples of 1-monopalmitin as well as for 1-monostearin after long stabilization. Preliminary specific volume data for 1-monopalmitin at 30.0 are 0.937 for subalpha, 0.983 for alpha (extrapolated from 0.996 at 60.0°) and 0.949 for beta. Final data will be reported later.

The large density difference between slowly and rapidly chilled subalpha is puzzling, especially in view of the great similarity in X-ray patterns for the two states. The difference may be due to vacuoles or perhaps to a less complete stabilization and less perfect alinement of chains or crystallites in the chilled sample. (Comparable variations in density have been observed, but not yet reported, for triglycerides and in those cases have been found to be associated with observable variations in melting point.)

With the microscope the transformation of alpha to subalpha is revealed quite sharply by the appearance of many little shrinkage cracks as the temperature is lowered to a level just below the point of transformation. These cracks are almost completely "healed" by raising the temperature and holding it just above the transformation point.

It is believed that Malkin was concerned, at least part of the time, with subalpha when he used the term beta prime. Especially in the case of his recent publication[14] containing data on monoelaidin it is apparent that the so-called beta prime form conforms much more closely, in X-ray spacing, to the subalpha values than to the beta prime values here reported for monopalmitin and monostearin. Malkin's beta prime m. ps. are not accounted for by this line of thought, however.

No evidence was obtained by the various techniques employed in this study for the lower of the monostearin transformation points reported by Malkin. It is the higher value that was confirmed and that corresponds to the alpha $\rightarrow$ subalpha change.

Some indication of the stability of the alpha (and subalpha) forms is given by the observation that monopalmitin subalpha persists about thirty days at room temperature as compared with more than one hundred twenty days for monostearin. This is comparable to the room temperature stabilities of the alpha forms of the corresponding triglycerides. A difference in high temperature alpha stability between mono- and triglycerides appears on running complete melting points on alpha (subalpha) forms at a heating rate of 0.5 per minute. Monopalmitin and monostearin give approximately their respective alpha m. p.s but the triglycerides transform during heating to give approximately their beta m. p.s.

Beta Prime.—Despite considerable effort to obtain the beta prime form from the melt or from alpha, it was actually obtained only by rapid crystallization of dilute ether or Skellysolve B so-

(13) Microscopic observations by Dr. Don G. Kolp of this laboratory.

(14) Malkin and Carter, *J. Chem. Soc.*, 554 (1947).

lutions. Crystals, while well defined, were small. As has been indicated, the beta prime X-ray pattern is somewhat similar to that of subalpha. The distinguishing features are indicated in Table IV, a summary table of characteristic values. In brief, the chief difference is that beta prime lacks the two medium strength lines shown by subalpha for the region between 4.15 Å. and 3.65 Å.

Beta.—The beta form is obtained by slow crystallization from solvent or by transformation of alpha and beta prime forms. It was not obtained directly from the melt. The crystals from solvent are relatively large platelets with a beautiful gloss. Beta is the only truly stable crystalline form.

Acknowledgment.—The authors are grateful to the members of this Laboratory who have given valued advice and experimental assistance.

Summary

While largely confirming the work of Malkin, a reëxamination of the polymorphic behavior of 1-monostearin and 1-monopalmitin has resulted in new information which differs in important aspects from earlier findings.

These monoglycerides have four forms—subalpha, alpha, beta prime and beta. The last three have melting points increasing in the order named. Beta alone is thermodynamically stable. Beta prime has been obtained only from solvent. There is a reversible alpha–subalpha transformation about 25° below the alpha m. p. but above room temperature. All forms for a given monoglyceride have very nearly the same long spacing and appear to be tilted double-chain-length structures. The forms are readily distinguished by means of short spacings except for subalpha and beta prime, which, in spite of notable differences in thermal behavior, show only minor differences in diffraction pattern.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Kinetics of the Reaction between Ethylene Chlorohydrin and Hydroxyl or Alkoxyl Ions in Mixed Solvents[1,2]

BY JOHN ED STEVENS,[3] C. LAW MCCABE AND J. C. WARNER

Previous investigations of the reaction between ethylene chlorohydrin and hydroxyl ion have established the following facts concerning the reaction. It is clearly second order,[4,5,6] the rate being proportional to the concentration of chlorohydrin and to the concentration of hydroxyl ion, and the side reaction with water at temperatures in the vicinity of 30° is so slow[7] that it may be neglected. There is no significant back reaction in alkaline solution[8] and the product with water as the solvent is ethylene oxide and not ethylene glycol.[9] There is a very small negative kinetic salt effect in water and in water–ethanol mixtures.[6] More recently, Porret,[10] who apparently was unaware of the work of Winstrom and Warner,[6] has reported the results of an investigation which duplicates their kinetic studies in water as solvent. His velocity constants, activation energy and kinetic salt effects are in excellent agreement with those reported by Winstrom and Warner. Porret[11] has also determined equilibrium constants for the reaction in the temperature range 0 to 50°. These results confirm the view that no correction for the back reaction needs to be made in alkaline solutions.

It was the purpose of the present investigation to study the kinetics of this reaction in a number of water–non-aqueous solvent mixtures down to low dielectric constants for the mixtures, *i. e.*, to high concentrations of the non-aqueous solvents.

Experimental

Materials and Procedure.—Previously described[6] methods for the purification of materials and the preparation of reagents were used with only minor modifications. Temperature variations in thermostats were followed by means of Beckman thermometers and absolute temperatures were established within 0.01° by use of a N.B.S. platinum resistance thermometer. The thermostat operated at 30 ± 0.005° was of the conventional type, and the one operated at 15 ± 0.01° was also of the conventional type, but was placed inside a large insulated container through which air, cooled by ice, was circulated to maintain the environment at 10 to 12°. Experiments at 0 ± 0.005° were carried out in large Dewar flasks filled with washed cracked ice and distilled water.

Standard solutions of sodium ethoxide and sodium methoxide were prepared by treating metallic sodium with the corresponding anhydrous alcohol, determining the concentration by titration and then diluting to the desired strength with the anhydrous alcohol.

Since the reaction proceeds with a decrease in hydroxyl or alkoxyl ion concentration and a corresponding increase in

(1) Abstracted from a dissertation submitted by John Ed Stevens to the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Science.

(2) Presented before the Physical and Inorganic Division at the Detroit meeting of the American Chemical Society, April, 1943.

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(4) Evans, *Z. physik. Chem.*, **7**, 335 (1891).

(5) Smith, *ibid.*, **81**, 339 (1912); **A152**, 153 (1931).

(6) Winstrom and Warner, THIS JOURNAL, **61**, 1205 (1939).

(7) Radulescu and Muresanu, *Bull. Soc. Sci. Cluj. Roumanie*, **7**, 128 (1932).

(8) Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

(9) British Patents 286,850 (Feb. 8, 1927); 292,066 (Jan. 11, 1927). Ushakov and Mikhailov, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 249 (1937).

(10) Porret, *Helv. Chim. Acta*, **24**, 80E (1941).

(11) Porret, *Helv. Chim. Acta*, **27**, 1321 (1944).