Benzoylation of 3-Benzylideneaminopropanediol-1,2.—A 3.0-g. portion of the benzylidene compound was benzoylated by a similar procedure. Recrystallization from ethyl acetate–petroleum ether gave 5.0 g. of colorless crystals, m.p. 126–140°. These were recrystallized again giving 4.2 g., m.p. 120–133° (reported[8,13] 116–126°).

Anal. Calcd. for $C_{24}H_{21}NO_4$: N, 3.62; sapon. equiv. (one O-benzoyl group), 387. Found: N, 3.86; sapon. equiv., 405.

The ultraviolet spectrum (Table I) is strongly affected by the presence of an O-benzoyl group, and in fact was quite similar to that of 2-benzoylaminocyclohexyl benzoate (Fig. 1).

Ultraviolet Absorption Spectra.—Each sample was dissolved in 95% ethanol and diluted to 80–200 micro-molar concentration for examination with a Beckman model DU quartz spectrophotometer, using a 1-cm. quartz cell. The results are given in Table I and Fig. 1.

Preparation of 2-Alkylamino and 2-Tosylamimocyclohexanols. ***d,l*-*trans*-2-Ethylaminocyclohexanol.**—By the method of Brunel[14] a 62% yield of colorless crystals, b.p. 93° (8 mm.), m.p. 50.5–51°, was obtained (reported[14] m.p. 44–45°).

***d,l*-*trans*-2-Butylaminocyclohexanol.**—Cyclohexene oxide (0.98 g.) was heated with 1.10 g. of dry 1-aminobutane for 12 hours at 150–160° (sealed tube). On vacuum distillation the desired product was obtained at 115° (7 mm.), and it crystallized in the receiver, m.p. 39.0–40.5° (yield 84%). A sample was sublimed at 1 mm. for analysis, m.p. unchanged.

Anal. Calcd. for $C_{10}H_{21}NO$: C, 70.12; H, 12.36. Found: C, 70.17; H, 12.28.

(13) Bergmann[8] reported the separation of the mixture of benzoyloxazolidines from aminopropanediol into two diastereomers of m.p. 118° and 143° by a treatment with alcoholic hydrogen chloride at 0°.

(14) L. Brunel, *Ann. chim. phys.*, [8] **6**, 257 (1905).

The compound was also prepared by reductive alkylation, in slightly lower yield.

With dry ethereal hydrogen chloride, an amine hydrochloride of m.p. 232–233.5° (dec.) was obtained.

***d,l*-*cis*-2-Butylaminocyclohexanol.**—To a solution of 1.80 g. of *cis*-2-aminocyclohexanol in 50 ml. of absolute ethanol was added a 10% excess of freshly distilled butanal. The mixture was hydrogenated for four hours at 3 atm. (25°), using Raney nickel catalyst. Filtration and vacuum distillation gave a residue of 2.26 g., colorless needles, m.p. 49–54°. Sublimation at 1 mm. gave 1.90 g. of colorless silky needles, m.p. 59–60°. Resublimation for analysis caused no change in m.p.

Anal. Calcd. for $C_{10}H_{21}NO$: C, 70.12; H, 12.36. Found: C, 69.95; H, 12.22.

***d,l*-*trans*-2-*p*-Toluenesulfonylaminocyclohexanol.**—A solution of 0.231 g. of the aminocyclanol hydrochloride in water was treated with the sulfonyl chloride in acetone[15] in the presence of sodium bicarbonate. There was obtained 0.344 g. (83%) of colorless crystals, m.p. 129–130° (reported[16] m.p. 128°). A sample vacuum distilled for analysis showed no change in m.p.

Anal. Calcd. for $C_{13}H_{19}NO_3S$: C, 57.96; H, 7.11; N, 5.20. Found: C, 57.42; H, 7.12; N, 5.25.

***d,l*-*cis*-2-*p*-Toluenesulfonylaminocyclohexanol.**—By treatment of 0.210 g. of the *cis*-aminocyclanol hydrochloride in the same manner as above, there was obtained 0.359 g. (96%) of colorless crystals, m.p. 158.5–159.5 (reported[16] m.p. 152–154°).

Anal. Calcd. for $C_{13}H_{19}NO_3S$: C, 57.96; H, 7.11. Found: C, 57.83; H, 6.76.

(15) The method is similar to that used by I. S. Shupe, *J. Assn. Off. Agr. Chem.*, **24**, 755 (1941), with ethanolamine.

(16) G. Fodor and J. Kiss (THIS JOURNAL, **72**, 3495 (1950)) carried out only nitrogen analyses on their N-tosyl products. The procedures now reported give somewhat higher yields.

TORONTO, CANADA RECEIVED FEBRUARY 12, 1951

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE COMPANY]

Directed Interesterification in Glycerides. III. The Synthesis of Single-Fatty Acid 1,3-Diglycerides[1]

BY FRED J. BAUR AND WILLY LANGE

A method for the synthesis of single-fatty acid symmetrical diglycerides has been described. The process involves the use of low-temperature directed interesterification in which symmetrical diglycerides are preferentially crystallized from statistically distributed catalyzed single-fatty acid triglyceride–triacetin–glycerol mixtures. The method is useful in the preparation of symmetrical diglycerides derived from single fatty acids with melting points above 20°. A new diglyceride, 1,3-dibehenin, has been prepared.

The classical methods for the synthesis of symmetrical diglycerides involve the use of glycerol derivatives containing two free and one temporarily blocked hydroxyl group.[2] Pure diglycerides also may be obtained by direct esterification of 1-monoglycerides with either fatty acids or acid chlorides[3a] and separation from unreacted monoglyceride by solvent crystallization. A similar method, just reported,[3b] involves the direct esterification of glycidyl fatty acid esters with fatty acids.

Eckey's process of low-temperature directed interesterification of fats[4] has been modified recently by Eckey and Formo[5] to include simultaneous alcoholysis as well as ester–ester interchange. In the modified process, in the presence of catalysts, melted fats and glycerol interesterify to produce an equilibrium mixture of monoglycerides, diglycerides, triglycerides and free glycerol. Crystallization of high melting monoglycerides or diglycerides takes place when the temperature of the liquid product is lowered sufficiently. This lowering of the temperature and subsequent crystallization of a component from the liquid phase disturbs the equilibrium, re-establishment of which is promoted continuously by the rearrangement catalyst. The desired glyceride continues to crystallize out until the supply of its constituent groups is no longer suf-

(1) The papers by E. W. Eckey (ref. 4) and E. W. Eckey and M. W. Formo (ref. 5) are designated as I and II of this series, respectively.

(2) E. Fischer, M. Bergmann and H. Barwind, *Ber.*, **53**, 1589 (1920); E. Fischer, *ibid.*, **53**, 1621 (1920); D. T. Jackson and C. G. King, THIS JOURNAL, **55**, 678 (1933); B. F. Daubert and C. G. King, *ibid.*, **61**, 3328 (1939); P. E. Verkade, J. van der Lee and W. Meerburg, *Rec. trav. chim.*, **51**, 850 (1932); **54**, 716 (1935); P. E. Verkade and J. van der Lee, *ibid.*, **55**, 267 (1936); F. L. Jackson, B. F. Daubert, C. G. King and H. E. Longenecker, THIS JOURNAL, **66**, 289 (1944).

(3) (a) T. Malkin, M. R. el Shurbagy and M. L. Meara, *J. Chem. Soc.*, 1409 (1937); M. G. R. Carter and T. Malkin, *ibid.*, 554 (1947); (b) E. B. Kester (to the U. S. Dept. of Agriculture), U. S. Patent 2,523,309 (1950).

(4) E. W. Eckey (to The Procter & Gamble Company), U. S. Patent 2,442,531 (1948); E. W. Eckey, *Ind. Eng. Chem.*, **40**, 1183 (1948).

(5) E. W. Eckey and M. W. Formo, *J. Am. Oil Chem. Soc.*, **23**, 207 (1949).

TABLE I

INTERESTERIFICATION AND CRYSTALLIZATION DATA ON 1,3-DIGLYCERIDES

	Mole ratio/ triglyceride[1] triacetin	Initial directed interesterification (crystallization) temp., °C.	Final interesterification temperature, °C.	Number of solvent crystallizations	Cryst. solvents	Solvent cryst. temp., °C.	Yield, %
Dilaurin	1.7	32	16	3	Ether, EtOH	0	72
Dimyristin	1.0	32	16	3	Ether, EtOH	0	81
Dipalmitin	0.5	46	27	3	Hexane, EtOH	10	86
Dimargarin	.5	46	27	5	Hexane, EtOH, benzene, pet. ether	27	86
Distearin	.5	46	27	4	Hexane, EtOH	27	80
Dibehenin	.4	60	38	5	Hexane, EtOH, benzene	27	87
Dielaidin	.8	32	10	5	Ether, EtOH	10	70

ficient to maintain the supersaturation of the liquid phase with respect to the precipitated solid. The method was applied to natural fats and resulted in the formation of diglycerides of the constituent saturated fatty acids. The pure single-fatty acid diglycerides were isolated from the crystalline products by tedious solvent crystallization.

Pure symmetrical diglycerides may be obtained readily in good yield by an adaptation of the Eckey process. A mixture of triacetin and a pure single fatty acid triglyceride is interesterified and randomized in the presence of 0.5% sodium methoxide as a catalyst at a temperature above the complete melting point of the triglyceride. The triacetin serves, in effect, as a replacement for the unsaturated fatty acid glycerides present in natural fats. Dry glycerol is added in a slight excess over the quantity required to convert all triglycerides of the mixture into diglycerides. The random interesterification is continued in liquid phase, *i.e.*, above the temperature where crystallization of a component may occur. The temperature is decreased slowly so that the directed interesterification results in progressive crystallization of the high-molecular-weight fatty acid, 1,3-diglyceride component. Diglycerides may be obtained by this method from all saturated fatty acids as well as from unsaturated fatty acids whose melting points are above about 20°. The purity of the compounds after recrystallization is, in general, better than that of previously described preparations.

The polymorphic behavior of distearin, dimyristin and dilaurin, prepared according to the present method, has been described in a preceding paper.[6]

Experimental

Directed interesterification requires the absence of moisture and free fatty acid since both inactivate an equivalent quantity of the catalyst.

Materials.—The catalyst was a suspension of sodium methoxide in xylene.[4] Dry glycerol was prepared by the distillation of C.P. glycerol at reduced pressure. Prior distillation of a xylene–water azeotrope, as has been reported,[5] was found to be unnecessary.

Pure triacetin was obtained by distillation of a water-washed commercial product (Tennessee Eastman Co.); b.p. 171–172° (40 mm.), $n^{25}D$ 1.4289.

The single-fatty acid triglycerides were prepared by the reaction of glycerol with an excess of purified fatty acids.[7] The fatty acids had a minimum purity of 95% according to fractional distillation and setting point data. The crude triglycerides were alkali-refined, deodorized, and purified by recrystallization from solvent.

General Procedure.—A description of the synthesis of distearin will illustrate the general procedure. Four hundred forty-six grams of tristearin (0.5 mole) was melted in a 1-quart glass jar equipped with an air-tight lid. The melt was then mixed with 218 g. (1.0 mole) of acid-free triacetin. To this mixture was added, with agitation, 3.7 g. (0.5% calculated for the total mixture) of sodium methoxide as a 10% suspension in xylene. The mixture was held at 60°, or above its complete melting point, for two hours to ensure random distribution of the fatty acid radicals. After this time, 74 g. (0.8 mole) of dried glycerol was added with agitation. All air was displaced with dry nitrogen, and the mixture was held one day at 60°, wholly in the liquid phase, to complete the interesterification. The resulting mixture was agitated end-over-end for two days at each of the successive temperatures, 46°, 38°, 32°, and 27°. The catalyst was inactivated by the addition of an excess (5 ml.) of glacial acetic acid when the selective crystallization of symmetrical diglyceride was complete. The 800 g. of reaction mixture was dissolved by warming in 10 volumes of a 1:1 mixture of *n*-hexane and ethanol, and crystallized at 24–27°. Three additional crystallizations were made under the same conditions. The yield of 1,3-distearin, m.p. 89.4° (cor.), amounted to 382.5 g. (80%).

The main variables in the preparations of the symmetrical diglycerides were the interesterification temperatures and the crystallization conditions for final purification.

The initial and final interesterification temperatures, crystallization solvents, and % yields for the other synthesized diglycerides are given in Table I.

Determination of Thermal Data.—The "rapid complete melting point (cmp.)" was determined on a freshly chilled sample by the "thrust in" technique previously described.[8] This technique gives the beta-a polymorphic form.

The "regular cmp." or maximum melting point was obtained on the solvent-crystallized samples by raising the bath temperature at a maximum rate of 0.2° per minute. Solvent crystallization usually gives the beta-b form, apparently the only thermodynamically stable form.

Baur, *et al.*,[6] concluded that the beta-a and beta-b forms could have substantially identical melting points and the lower melting level obtained for beta-a by the thrust-in technique was due to crystal imperfection, as it is known that the melting level of a glyceride form can vary with the degree of stabilization. In view of the recent data of Crowe and Smyth[9] showing that the melting points of the two forms are distinguishable by dielectric constant measurement, it is felt that real melting point differences do exist between the two forms in highly purified samples. All melting point data are corrected.

Thermal and Analytical Data on the 1,3-Diglycerides.—Pertinent data on the prepared diglycerides are recorded in Tables II and III. The thermal points are compared with the data compiled by previous workers. The data indicate the high degree of purity obtainable by the low-temperature directed interesterification process. The diglycerides are of higher purity than those reported by Baur, *et al.*,[6] hence the current data constitute a revision of the previous melting point information.[6]

The analytical data obtained agree with the theoretical values, within experimental error.

(6) F. J. Baur, *et al.*, THIS JOURNAL, **71**, 3363 (1949).

(7) C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, 666 (1934); E. S. Lutton, THIS JOURNAL, **67**, 524 (1945).

(8) E. S. Lutton, F. L. Jackson and O. T. Quimby, THIS JOURNAL, **70**, 2441 (1948).

(9) R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 5281 (1950).

TABLE II

THERMAL DATA ON 1,3-DIGLYCERIDES

	Regular cmp., °C.					Rapid cmp., °C.				
	Baur and Lange	Averill, Roche and King[10]	Malkin, el Shurbagy and Meara[3]	Carter and Malkin[3]	Eckey and Formo[6]	Baur and Lange	Malkin, el Shurbagy and Meara[3]	Carter and Malkin[3]		
Dilaurin	57.8	56.6	56.5			54.5	49.5			
Dimyristin	66.8	63.8–64.4	65.5			64.4	60			
Dipalmitin	74.2	69.5	72.5		72.4	71.8	68			
Dimargarin	76.3		74.5			74.4	71.5			
Distearin	79.4	79.1	78			77.6	74			
Dibehenin	87.6					86.7				
Dielaidin	54.4			55		50.1		49		

TABLE III

ANALYTICAL DATA ON 1,3-DIGLYCERIDES

	Hydroxy value[a]		Sapn. value		Acid value		Monoglyceride,[b] %		Iodine value[c]	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Dilaurin	109	109	246.5	245.7	0.0	0.0	~0	0.0		
Dimyristin	121	123	217.8	218.5	.0	.0	~0	.0		
Dipalmitin	99	99	197.9	197,2	.0	.0	~0	.0		
Dimargarin	94	94	188.6	188.0	.0	.0	~0[d]	.0		
Distearin	89	90	180.2	179,2	.1	.0	~0[d]	.0	<0.1	0.0
Dibehenin	77	76	154.0	152.2	.0	.0	[d]	.0		
Dielaidin	90	90	181.7	180.7	.0	.0	~0	.0	80.8	81.8

[a] For accurate analysis, three times the customary sample weight was used. [b] E. Handschumacker and L. Linteris, *J. Am. Oil Chem. Soc.*, **24**, 143 (1947). [c] Wijs reagent. [d] Inaccurate due to low solubility.

Discussion

The purity of the single fatty acids used in the preparation of the triglycerides is the most important factor affecting the purity of the resulting diglycerides. Products of better than 98% purity, as determined analytically, are obtainable by one solvent crystallization when pure fatty acids are used. Contaminating fatty acids give rise to mixed symmetrical diglycerides which can be removed only by sacrificing excessive quantities of material.

Triacetin, as used in the present method, enables the original interesterification (to random distribution) and the low-temperature directed interesterification to proceed at workable temperatures. Also, it appears that the presence of acetins in the completely randomized liquid phase, containing all possible acetyl and acyl mono-, di- and triglyceride combinations as well as free glycerol, favorably influences the solubility and the rate of crystallization of the components, so that only symmetrical diglycerides precipitate. The quantity of triacetin required is not critical. Additional triacetin can be used if it is desirable to decrease further the interesterification temperatures.

A slight excess of glycerol over the theoretical amount required for the transformation of all carboxylic acids into diglycerides should be used. An excess of 10% is recommended.

Random interesterification in liquid phase is substantially complete when the reaction mixture becomes homogeneous. The rate of temperature decrease to achieve directed rearrangement should not be too rapid as the point of initial crystallization is approached. Once an adequate seed of diglyceride has been obtained, the temperature of the reaction mixture may be dropped rapidly. If the heat of crystallization of the diglyceride is removed rapidly, the time required for directed interesterification can be measured in hours rather than days. Slow cooling, however, tends to ensure maximum yields.

Either polar or non-polar solvents or their mixtures can be used for purification of the diglycerides by recrystallization from solvents. It is recommended, however, that ethanol containing a few per cent. of water be a component of the solvent mixture to expedite the removal of free glycerol and the acetyl glycerides present.

(10) H. P. Averill, J. N. Roche and C. G. King, THIS JOURNAL, **51**, 866 (1929.)

CINCINNATI 17, OHIO RECEIVED MARCH 19, 1951