Synthesis of Triglycerides from 1,3-Dibromopropan-2-ol †

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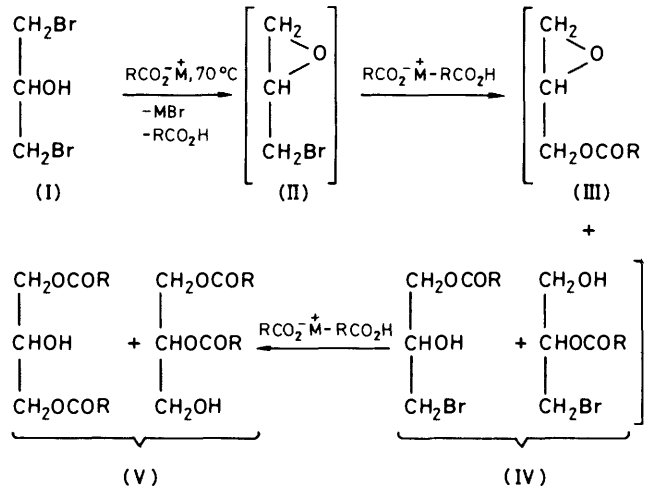
1,3-Dibromopropan-2-ol (I) was converted into an acyl derivative (VI) by reaction with an appropriate acyl chloride in the presence of pyridine. The acyl derivative (VI) was subjected to nucleophilic substitution with 3 mol. equiv. tris(decyl)methylammonium carboxylate in refluxing hexane. This led to symmetrical diacid triglycerides in 90—94% yield. Substitution with an equimolar amount of the carboxylate afforded, predominantly, the 1,2-bisacyloxy-3-bromopropane (VII) which could be easily isolated and further substituted to give unsymmetrical diacid– and triacid–triglycerides in *ca.* 96% yield. Lipolysis showed the synthetic triglycerides to be *ca.* 99% pure.

A variety of starting materials have been used to prepare triglycerides. Among these are simple derivatives of glycerol, or substances closely related to it.[1] One such compound is 1,3-dibromopropan-2-ol (I), prepared [2] from glycerol by reaction with bromine in the presence of red phosphorus. Grün,[3] Whitley,[4] Thomson,[5] and Fairbourne [6] used (I) and its dichloro-analogue to prepare triglycerides. However, the yield and structural purity of their products are not good. In view of (I) being readily available and relatively inexpensive we undertook a detailed study to investigate the causes of the drawbacks of the syntheses of the previous workers,[3-5] and also to find the best experimental conditions for converting (I) into symmetrical diacid triglycerides and mixed triacid triglycerides.

Results and Discussion

When 1,3-dibromopropan-2-ol (I) was reacted with either an alkali-metal (Na, K) or silver stearate the composition of the reaction mixture was found by g.c.–m.s. analysis to be the same (see Scheme 1 and Table 1).

The presence of 2,3-epoxypropyl stearate (III) would suggest that the major reaction is dehydrobromination to give initially 3-bromo-1,2-epoxypropane (II) which may be attacked by the metal stearate and stearic acid (produced *in situ* from $RCO_2^-\overset{+}{M}$ and HBr) at each of the three carbons yielding (III), (IV), and (V). The cause of these complications seems to be largely due to the neighbouring group participation of the hydroxy-function at C-2 in (I). This would lead to elimination of HBr prior to nucleophilic attack by the carboxylate anion at either the 1- or 3-position in (I). Attempts to prevent or minimise this undesired side-reaction by carrying out the reaction in dipolar aprotic solvents such as dimethylformamide (DMF) or hexamethylphosphoramide (HMPA) proved unsuccessful. As shown in Figure 1, in HMPA the rise in concentration of stearic acid is almost paralleled by the rise in concentration of the monoacyl bromo-compounds (IV) over the first 30 min after which the concentration of the former drops but that of the latter continues to rise steadily. This suggests concomitant consumption of stearic acid by 3-bromo-1,2-epoxypropane (II) to produce more of (IV). There is also a rise in concentration of the epoxy-compound (III) during the first 30 min, followed by a gradual drop. Also there is a steady rise in the concentration



Scheme 1. M = Na, K, Ag, R = $CH_3(CH_2)_{16}$

Table 1. Molar composition of the product from the reaction of 1,3-dibromopropan-2-ol (6.43 mmol) with sodium, potassium, or silver stearate (6.43 mmol)

Compound	Molar concentration (mM)
Stearic acid	1.24
2,3-Epoxypropyl stearate (III)	0.46
3-Bromo-2-hydroxypropyl stearate and 1-bromomethyl-2-hydroxyethyl stearate (IV)	0.53
Glycerol 1,3-distearate and glycerol 1,2-distearate (V)	1.04

of the diglycerides (V). These two observations also accord with the suggested course of reactions (Scheme 1). These results and considerations showed that 1,3-dibromopropan-2-ol (I) as such was not a suitable precursor for triglycerides, if any regioselectivity was to be achieved.

It appeared to us that the best way to suppress, and even completely avoid, neighbouring group participation of the hydroxy-function of (I) would be to block it by substituting its hydrogen atom with an electron-withdrawing group. Its acylation seemed to be an ideal solution, as this would serve

† Preliminary results of this investigation were presented at the symposium organised by the Lipid Group of the Royal Society of Chemistry, Cambridge, 1982.

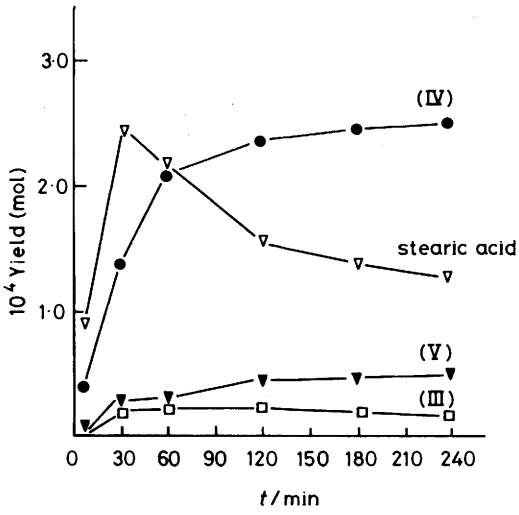
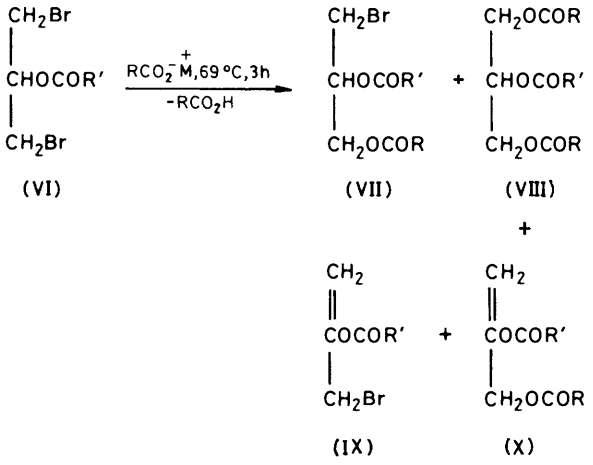


Figure 1. Reaction of 1,3-dibromopropan-2-ol with an equimolar amount of potassium stearate in HMPA at 70 °C. Similar results were obtained when DMF was used instead of HMPA



Scheme 2. M = Na, K, Ag, $(C_2H_5)_4N$, $(C_{10}H_{21})_3(CH_3)N$, 18-crown-6–K; R = $CH_3(CH_2)_{16}$; R' = $CH_3(CH_2)_{14}$

the desired purpose of putting the necessary protecting group where it would also form part of the final diacid or triacid triglyceride. However, use of such an ester (VI) may entail unwelcome side-reactions, such as acyloxy migration and dehydrobromination. Bearing these possibilities in mind, we decided to investigate the ester (VI) as a precursor for triglycerides. The palmitoyl ester of (I), prepared by reaction with palmitoyl chloride in the presence of pyridine, was subjected to nucleophilic substitution with stearate anion [from sodium, potassium, and silver stearate, tetraethylammonium and tris(decyl)methylammonium stearate, and the complex of 18-crown-6 with potassium stearate] in the presence of different solvents [*viz.* hexane, toluene, tetrahydrofuran (THF), acetone, DMF, and HMPA] whose dielectric constants ranged from 1.89 to 36.7. The reaction mixture contained both substitution and elimination products* as well as stearic acid (see Scheme 2) in varying proportions (see Tables 2—7).

In the reaction in Scheme 2 the proportions of the ester (VI) and the reagent (RCO_2 M) used were 1 : 3.2. In hexane, toluene, THF, and acetone there was hardly any reaction (<1%) with sodium, potassium, or silver stearate. The results of reaction in other solvents and with other reagents are summarized in Tables 2—7, where the concentrations of elimination products, (IX) and (X), are indicated collectively.

Most of the above results can be explained by considerations of the nature of the solvent and the type of the counterion (M^+) used. These considerations provide information about

* The extent of the reaction was measured by estimating the amounts of substrate (VI) consumed and products formed.

Table 2. Reaction of substrate (VI) with RCO_2 M in hexane (ε 1.89) at 69 °C for 3 h

	Substrate consumed	Products (mol %)	
		Elimination	Substitution
M^+	(mol %)	(IX) + (X)	(VII) (VIII)
$(C_2H_5)_4N$	33	2	29 2
$(C_{10}H_{21})_3(CH_3)N$	100	9	25 66
18-Crown-6–K	60	5	51 4

Table 3. Reaction of substrate (VI) with RCO_2 M in toluene (ε 2.4) at 69 °C for 3 h

	Substrate consumed	Products (mol %)	
		Elimination	Substitution
M^+	(mol %)	(IX) + (X)	(VII) (VIII)
$(C_2H_5)_4N$	27	1	24 2
$(C_{10}H_{21})_3(CH_3)N$	100	11	29 60
18-Crown-6–K	52	3	45 4

Table 4. Reaction of substrate (VI) with RCO_2 M in THF (ε 7.6) at 69 °C for 3 h

	Substrate consumed	Products (mol %)	
		Elimination	Substitution
M^+	(mol %)	(IX) + (X)	(VII) (VIII)
$(C_2H_5)_4N$	37	4	31 2
$(C_{10}H_{21})_3(CH_3)N$	100	15	15 70
18-Crown-6–K	100	23	44 33

Table 5. Reaction of substrate (VI) with RCO_2 M in acetone (ε 21.2) at 69 °C for 3 h

	Substrate consumed	Products (mol %)	
		Elimination	Substitution
M^+	(mol %)	(IX) + (X)	(VII) (VIII)
$(C_2H_5)_4N$	28	5	22 1
$(C_{10}H_{21})_3(CH_3)N$	100	18	58 24
18-Crown-6–K	83	17	45 21

Table 6. Reaction of substrate (VI) with RCO_2 M in HMPA (ε 30.0) at 69 °C for 3 h

	Substrate consumed	Products (mol %)	
		Elimination	Substitution
M^+	(mol %)	(IX) + (X)	(VII) (VIII)
Na	100	39	3 58
K	100	44	1 55
Ag	19	3	16 0
$(C_2H_5)_4N$	100	40	0 60
$(C_{10}H_{21})_3(CH_3)N$	100	42	0 58
18-Crown-6–K	100	40	2 58

Table 7. Reaction of substrate (VI) with RCO_2 M in DMF (ε 36.7) at 69 °C for 3 h

M+	Substrate consumed (mol %)	Products (mol %) Elimination (IX) + (X)	Substitution (VII)	Substitution (VIII)
Na	24	5	16	3
K	40	13	19	8
Ag	3	1	2	0
$(C_2H_5)_4N$	100	40	42	18
$(C_{10}H_{21})_3(CH_3)N$	100	50	0	50
18-Crown-6–K	100	46	4	50

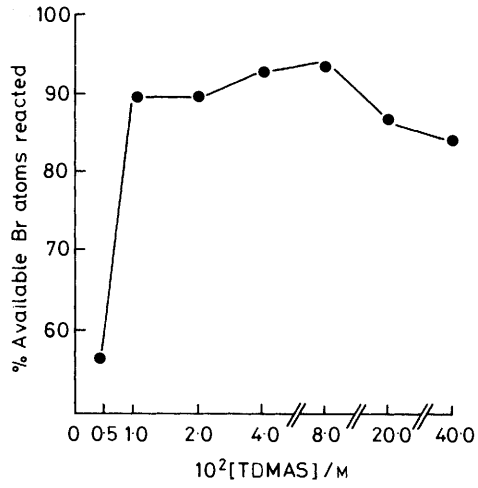


Figure 2. Extent of reaction with concentration of TDMAS in n-hexane

the strength and environment of the anion species involved in the reactions. In low polarity solvents (hexane, toluene) in which the stearate salts exist as ion-pairs, RCO_2 M, or ion aggregates, $(RCOO\ M)_n$, hardly any reaction is observed with those salts (Na K, Ag stearate) in which the counterion is tightly held. In high polarity solvents (HMPA, DMF, but not acetone) where the solvent-separated free ions (RCO_2^- and $\overset{+}{M}$) prevail considerable reaction is observed for both the tightly and loosely [$(C_2H_5)_4\overset{+}{N}$, $(C_{10}H_{21})_3(CH_3)\overset{+}{N}$, and 18-crown-6–$\overset{+}{K}$] held counterions. When the reaction does occur, it leads to both substitution and elimination products. This suggests that the solvent or more likely the exposed anion (from tetra-alkylammonium stearates and 18-crown-6-complex) removes a proton from C-2, initiating elimination of HBr. This action of the solvent–anion may be complementary to the attractive interactions between the leaving group (Br) and the counterion. Such attractive interactions have been considered previously in explaining certain $E2$ [7-9] and S_N2 [10] reactions.

As our aim was also to develop the best conditions for triglyceride synthesis, the reaction of (VI) in hexane with tris(decyl)methylammonium stearate, which gave (see Table 2) the highest yield of the desired substitution product with only 9% of the elimination products, was studied closely to find if variation in temperature, concentration (dilution), and stoicheiometry of the reactants would further improve the yield of substitution product (VIII), and at the same time minimise elimination reactions. The results show that at, and

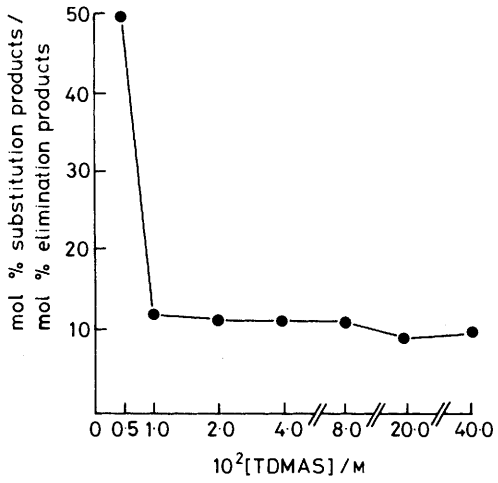


Figure 3. Variation of the substitution : elimination ratio with the concentration of TDMAS in n-hexane

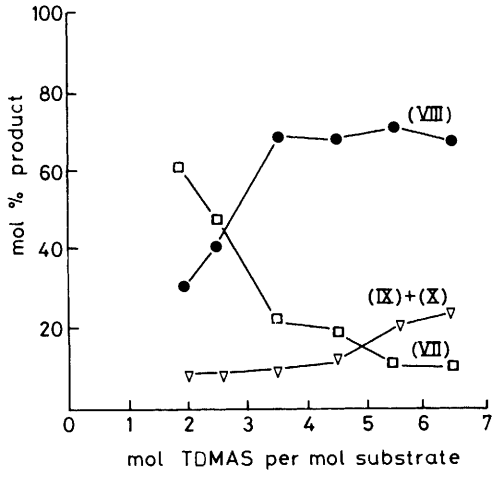


Figure 4. The distribution of reaction products as the mole ratio of TDMAS to substrate varies

up to the concentration of 1.0×10^{-2} mol l^{-1} of tris(decyl)-methylammonium stearate (TDMAS), there is an abrupt increase in the extent of the reaction, and a marked decrease in the ratio of substitution to elimination products (Figures 2 and 3); and this would appear to be the critical concentration. It can be seen (Figure 4) that, as the number of moles of TDMAS increases relative to the substrate (VI), the proportion of elimination product increases. The optimum molar ratio of TDMAS to substrate (VI) is 3 : 1 because beyond that the proportions of elimination product increase substantially. As the dielectric constants of hexane and toluene are close, the effect of temperature was investigated by performing the reaction in these solvents in the temperature range 20—110 °C. Figure 5 shows that the substitution–elimination ratio increases as the reaction temperature is raised.

We adopted the experimental conditions given in Table 2, and used TDMAS and the substrate (VI) in the ratio of 3 : 1. The reaction mixture was separated by preparative t.l.c. In this way the following symmetrical diacid triglycerides (purity by lipolysis >99%) [11] were obtained (yield, 90—94%); glycerol 1,3-distearate 2-palmitate (SPS), glycerol 1,3-distearate 2-acetate (SAS), glycerol 1,3-diacetate 2-palmitate (APA), glycerol 1,3-dipalmitate 2-oleate (POP), glycerol 1,3-

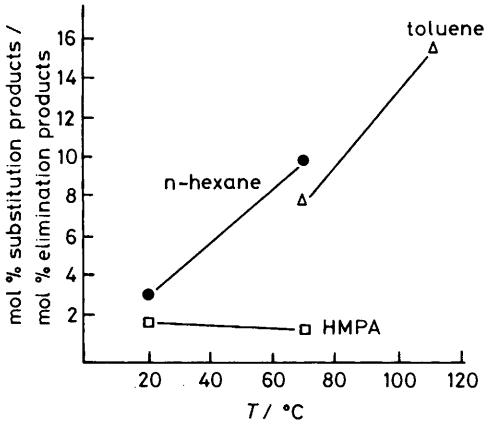


Figure 5. Effect of temperature on the substitution : elimination ratio

dioleate 2-palmitate (OPO), and glycerol 1,3-distearate 2-oleate (SOS).

We have also investigated the substrate (VI) for the synthesis of triacid triglycerides and unsymmetrical diacid triglycerides. The main problem encountered during these syntheses is the isolation of the monosubstituted compound (VII) (see Scheme 2) in high yield and structural purity. Using equimolar amounts of the substrate (VI) and TDMAS in refluxing toluene the proportion of the desired monsubstituted compound in the product could be improved (yield *ca.* 45%). Using silver stearate in place of TDMAS the yield of (VII) could be improved still further, but the product was contaminated with the rearranged isomer, namely 1-palmitoyloxy-2-stearoyloxy-3-bromopropane. Pure (VII) was isolated by t.l.c. and converted into *rac*-glycerol 1-stearate 2-palmitate 3-oleate (SPO) and *rac*-glycerol 1-stearate 2,3-dipalmitate (SPP) by reaction with TDMAS. The yield of these mixed triglycerides was *ca.* 96%, and purity >99%.

Experimental

Solvents were purified before use. Light petroleum refers to the fraction b.p. 40—60 °C. M.p.s were determined in open capillary tubes using a Gallenkamp electrically heated apparatus. Anhydrous magnesium sulphate was used for drying solutions. Solvents were removed from solution on a rotary evaporator. For preparative t.l.c., plates coated with silica gel G, and activated at 100 °C for 1 h were employed using light petroleum and diethyl ether (95 : 5, v/v) as eluant and 0.2% ethanolic 2,7-dichlorofluorescein and u.v. light for visualising the bands. ^{1}H and ^{13}C n.m.r. spectra refer to deuteriochloroform solution with tetramethylsilane as internal standard, and were determined on a Brucker WP 100 MHz instrument.

G.c. analysis was performed on a Perkin-Elmer Sigma 3 instrument fitted with a glass column (1.83 m × 2.5 mm) packed with 3% OV-17 on Supelcoport (100—120 mesh). The column for 1,3-dibromopropan-2-ol (I) was temperature-programmed from 85 to 200 °C at 6 °C min^{-1} using nitrogen as a carrier gas (flow rate, 80 cm^3 min^{-1}), the injection port and detector being kept at 250 °C and 275 °C respectively. For the analysis of di- and tri-glycerides, a glass column (0.45 m × 2.5 mm) packed with 2% OV-17 on Supelcoport (100—200 mesh) was used. It was temperature-programmed from 160 to 350 °C at 6 °C min^{-1}, and the nitrogen flow-rate was 80 cm^3 min^{-1}. The temperatures of the injection port and detector were 290 and 375 °C, respectively. G.c.–m.s. analysis was performed with a VG Micro Mass 12F, linked with the gas chromatograph *via* a jet separator. The mass spectrometer was operated in the electron impact mode at 70 eV (trap current, 200 μA; accelerating voltage, 2.6 kV). It was also operated in the chemical ionisation mode at 100 eV (trap current, 500 μA; accelerating potential, 2 kV) using isobutane as reagent gas (ion-source pressure *ca.* 8 × 10^{-5} Torr).

Preparation of 1,3-*Dibromopropan*-2-*ol* (I).—This was prepared by a known procedure [2] as mentioned before, yield 46%, b.p. 110—120 °C at 20 mmHg. G.c.–m.s. analysis showed this product to comprise the desired compound (I) (80%; retention time 4.1 min), the isomeric 2,3-dibromopropan-1-ol (8% ;retention time 4.9 min), and 1,2,3-tribromopropane (12%; retention time 6.2 min). The product was fractionally distilled, and the fraction of b.p. 58 °C at 1.5 mmHg was used without further purification. For the pure compound (I) the following data were obtained, *m/e* 220 ($M^{+\cdot}$ + 4), 218 ($M^{+\cdot}$ + 2), 216 ($M^{+\cdot}$), 138 ($M^{+\cdot}$ + 4 − H^{81}Br or $M^{+\cdot}$ + 2 − H^{79}Br), 136 ($M^{+\cdot}$ − H^{79}Br), 125 ($M^{+\cdot}$ + − 4 $CH_2{}^{81}$Br or $M^{+\cdot}$ + 2 − $CH_2{}^{79}$Br), 123 ($M^{+\cdot}$ + − 2 $CH_2{}^{81}$Br or $M^{+\cdot}$ − $CH_2{}^{79}$Br), 95 ($CH_2{}^{81}$Br), 93 ($CH_2{}^{79}$Br), and 81/79 (^{81}Br/^{79}Br); δ_H 2.66(OH), 3.58(CH_2Br), and 3.97(C*H*OH); δ_C 35—36(CH_2Br) and 70.1 p.p.m. (CHOH).

Sodium, potassium, silver, and tetra-alkylammonium stearate, 18-crown-6–potassium stearate complex, palmitoyl chloride, and oleoyl chloride were prepared by standard methods.

Preparation of Tris(decyl)methylammonium Stearate.—A mixture of 5M methanolic potassium hydroxide (12 ml) and a solution of tris(decyl)methylammonium chloride (30.4 g) was stirred for 15 min, cooled to 0 °C, and stirred for a further 15 min. The chilled mixture was filtered and the filtrate added to a warm solution of stearic acid (17.28 g) in methanol (80 ml). The mixture was stirred vigorously for 30 min, and the solvent distilled off *in vacuo*. The viscous residue, which contained water, was dissolved in hexane (200 ml), the solution dried, and hexane distilled off. The product was dried to constant weight over phosphorus pentaoxide at 35 °C at 0.1 mmHg in a vacuum desiccator (yield quantitative).

Reaction of 1,3-*Dibromopropan*-2-*ol* (I) *with Sodium, Potassium, or Silver Stearate.*—A mixture of compound (I) (1.4 g, 6.43 mmol) and stearate salt (6.43 mmol) was heated at 70 °C under anhydrous conditions with stirring for 12 h, the reaction using silver stearate being conducted in the dark. The cooled reaction mixture was treated with chloroform (15 ml), filtered, and the inorganic salts washed with chloroform (2 × 10 ml). The filtrate and washings were transferred to a volumetric flask containing pure tripalmitin (0.569 g) as internal standard; the contents were thoroughly shaken and the solution was made up to 50 ml with chloroform. A portion (0.5 ml) of this solution was silylated with bistrimethylsilylacetamide reagent (1.5 ml) by allowing the mixture to stand at 45 °C for 10 min. The product was analysed and quantified by g.c. and g.c.–m.s. The first fraction [retention time 3.20 min; EI-MS *m/e* 356 ($M^{+\cdot}$)] was found, by comparison of its data with those of an authentic trimethylsilyl derivative, to be stearic acid. The second fraction [retention time 10.1 min; CI-MS *m/e* 342 (M^+ + H) and 267(CH_3-$(CH_2)_{16}$CO)] was found to be 2,3-epoxypropyl stearate (III). The third fraction [retention time 11.1 min; CI-MS *m/e* 495 ($M^{+\cdot}$ + 2 + H) and 493 ($M^{+\cdot}$ + H); EI-MS *m/e* 479 ($M^{+\cdot}$ + 2 − CH_3), 477 (M^+ − CH_3), and 267 (CH_3-$(CH_2)_{16}$CO)] proved to be the trimethylsilyl derivatives of the isomeric compound (IV). The fourth fraction (retention time

25.4 min) was found by comparison with g.c. and m.s. data with those of authentic silylated distearin to be the trimethylsilyl derivative of (V).

Reaction of (I) *with an Equimolar Amount of Potassium Stearate in HMPA or DMF.*—A mixture of (I) (0.155 g), potassium stearate (0.227 g), and tripalmitin (0.219 g; used as internal standard) in HMPA or DMF (25 ml) was heated at 70 °C under anhydrous conditions. Portions (1.5—2.0 ml) were removed at regular intervals (5, 30, 60, 120, 180, and 240 min) and added to water (2 ml) and the mixture saturated with sodium chloride. The insoluble products were filtered off, washed with ice-cold water (2 × 1 ml), and finally dried in air. The organic compounds from this mixture were extracted with chloroform (2 ml), and the extract concentrated to *ca.* 0.5 ml by blowing nitrogen, and then treated with silylating reagent. The reaction product was analysed and quantified as in the previous experiment.

Preparation of 2-*Bromo*-1-(*bromomethyl*)*ethyl Palmitate* (VI).—To a vigorously stirred mixture of compound (I) (45.9 g), pyridine (18.4 g), and dry hexane (150 ml) was added, under anhydrous conditions during 30 min, a solution of freshly prepared palmitoyl chloride (51.2 g) in dry hexane (100 ml), such that the temperature of the reaction mixture did not rise above 30 °C. The reaction was allowed to proceed for 4.5 h when all the acid chloride was used up as evidenced by the disappearance of the i.r. absorption at 1 809 cm^{-1}. The reaction mixture was washed successively with water (2 × 30 ml), 6M-hydrochloric acid (2 × 30 ml), and water (until neutral). The hexane solution was dried, and the solvent removed by distillation to give a crude product which was dissolved in hot methanol, and the saturated solution allowed to deposit crystals at 0 °C. The crystalline compound (VI) (78 g, yield 92%) was dried at 25 °C at 0.1 mmHg; m.p. 35.5 °C; $\nu_{max.}$ (film), 1 743 cm^{-1}; EI-MS *m/e* 458 ($M^{+\cdot}$ + 4), 456 ($M^{+\cdot}$ + 2), 454 ($M^{+\cdot}$), and 239 [$CH_3(CH_2)_{14}CO$]; δ_C 31.4 (CH_2Br) 70.8 (CH–O–), 13.95 (CH_3), and 70.8 p.p.m. (–O–CO–).

Reaction of (VI) *with Stearate salts in Different Solvents.*—A mixture of compound (VI) (1.03 g, 2.26 mmol), the stearate salt (7.23 mmol), and the solvent (40 ml) was heated at 70 °C for 3 h with vigorous stirring and exclusion of moisture. In all cases the apparatus included facilities to heat under reflux. To isolate products from hexane, toluene, THF, or acetone, the reaction mixture was cooled to room temperature, and the solvent distilled off. Chloroform (30 ml) was added to the residue, the insoluble salts were filtered off, and washed further with chloroform (2 × 10 ml). The combined chloroform extracts were analysed by g.c. To isolate the reaction products from DMF or HMPA the reaction mixture was cooled to room temperature and poured into water (60 ml). Sodium chloride was added to effect complete precipitation of the solid organic products which were extracted with hot hexane (3 × 40 ml). The extract was dried and then mixed with chloroform (20 ml) to ensure that the products remained in solution. When tris(decyl)methylammonium stearate was used, this isolation procedure was modified. For non-polar solvents, the solvent was removed and the products were precipitated from the residue by adding 84% (w/w) aqueous methanol (30 ml) and cooling the mixture at 0 °C for 15 min. The products were filtered off, washed with ice-cold water (2 × 10 ml), and dissolved in chloroform (30 ml). The solution was dried and then analysed by g.c. For DMF and HMPA the products were partitioned into hexane and isolated as described above for other stearates.

T.l.c. of these products gave bands which were identified as stearic acid (R_F 0.15; g.c. retention time 2.4 min), glycerol 1,3-distearate 2-palmitate {R_F 0.24; retention time 33.8 min, m.p. 61—61.5 °C; EI-MS *m/e*, 607 [$M^{+\cdot}$ – $CH_3(CH_2)_{14}CO_2$], 579 [$M^{+\cdot}$ – $CH_3(CH_2)_{16}CO_2$], 267 [$CH_3(CH_2)_{16}CO$], and 239 [$CH_3(CH_2)_{14}CO$]}, 1-stearoyloxy-2-palmitoyloxy-3-bromopropane {R_F 0.46, retention time 23.4 min, m.p. 57—58 °C; CI-MS *m/e*, 661 (M^+ + 2 + H), 659 ($M^{+\cdot}$ + H), 579 ($M^{+\cdot}$ – ^{79}Br), 405 [$M^{+\cdot}$ + 2 – $CH_3(CH_2)_{14}CO_2$], and 403 [$M^{+\cdot}$ – $CH_3(CH_2)_{16}CO_2$]}, 1-(bromomethyl)vinyl palmitate (IX) [R_F 0.51; retention time 4.6 min; CI-MS *m/e* 377 ($M^{+\cdot}$ + 2 + H) and 375 ($M^{+\cdot}$ + H)] and 2-palmitoyloxy-1-stearoyloxyprop-2-ene (X) {R_F 0.51; retention time 22.0 min; CI-MS *m/e* 568 ($M^{+\cdot}$), 295 [CH_2=C(CH_2)OCO(CH_2)$_{15}CH_3$], 267 [$CH_3(CH_2)_{16}CO$], and 239 [$CH_3(CH_2)_{14}CO$]; δ_C 105.07 (CH_2=C), 62.64 (CH –O–), and 34 p.p.m. (CH_2CO); δ_H 5.08, 5.01 (CH_2=C–), and 4.64(CH_2O).

Preparation of Glycerol 1,3-*Distearate* 2-*Palmitate* (VIII).—A mixture of 2-bromo-1-(bromomethyl)ethyl palmitate (VI) (1.37 g, 3 mmol), tris(decyl)methylammonium stearate (7.25 g), and toluene (50 ml) was heated under reflux for 4 h. The solvent was distilled off *in vacuo* and the crude product, isolated as above, was found by g.c. to comprise 94% of the triglyceride. A small amount (50 mg) was purified by t.l.c. It possessed the data mentioned above. Its purity by lipolysis [11] was 99%.

Other diacid triglycerides were prepared and isolated in the same way as (VIII). The yields, m.p.s, g.c. retention times (R_t), and purities of all the triglycerides synthesized are given in Table 8. The mass spectra obtained accord with their structures.

Table 8. Data on triglycerides synthesized

Name	Yield (%)	M.p. (°C)	R_t (min)	Purity by lipolysis (%)
SPS	94	[61—61.5]	33.8	99
SAS	93	[56.5]	25.2	99
APA	90			99
POP	94	[34]	32.0	99
OPO	90		34.2	99
SOS	93	[35.5—36.5]	36.6	99
PPS	96		32.8	99
POS	96	[50—51]	34.2	99

Preparation of 1-*Stearoyloxy*-2-*palmitoyloxy*-3-*bromopropane* (VII) *using Equimolar Amounts of* (VI) *and Silver Stearate.*—A mixture of 2-bromo-1-(bromomethyl)ethyl palmitate (3.0 g) and silver stearate (2.57 g) was stirred vigorously for 15 h in a tightly stoppered flask which was wrapped with aluminium foil and immersed in an oil-bath at 70 °C. Chloroform (20 ml) was added to the cooled reaction mixture, and the insoluble silver salts filtered off and washed with chloroform (50 ml). The combined filtrate and washings were found by g.c. to contain 1-stearoyloxy-2-palmitoyloxy-3-bromopropane (74 mol %), glycerol 1,3-distearate 2-palmitate (VIII) (13 mol %), and unchanged (VI) (13%). Chloroform was distilled off *in vacuo*, and the residue dissolved in warm acetone (70 ml). The solution was allowed to cool to room temperature, and water was added dropwise with continuous stirring until it became turbid. The mixture was allowed to stand until the precipitated triglyceride was filtered off. To the clear filtrate more water was added dropwise, with continuous stirring, until the diacyl compound (VII) started to precipitate.

Stirring was continued and the product was allowed to settle for 15 min, then filtered off and dried in air. The yield was 65%, m.p. 57—58 °C (after purification by t.l.c., light petroleum–diethyl ether 95 : 5 v/v, R_F, 0.46, g.c. retention time 23.4 min). G.c. showed that the crude product comprised 98% of the expected diacyl compound (VII).

Preparation of Glycerol 1,2-*Dipalmitate* 3-*Stearate and Glycerol* 1-*Oleate* 2-*Palmitate* 3-*Stearate*.—These were prepared using the diacyl compound (VII) and the experimental conditions used for the preparation of (VIII). The yields and other data for these triglycerides are recorded in Table 8.

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