hydroxide (997 mg, 17.8 mmol), the acetoxy compound (**7**) (1.27 g, 4.10 mmol), and 125 ml of water was stirred and heated on a steam bath overnight. After the reaction mixture had cooled to room temperature, it was exhaustively extracted with ether. Evaporation of the combined and dried (anhydrous magnesium sulfate) ether extracts gave residual material which was placed onto a column of alumina in benzene solution. Elution of the column with benzene gave only a trace of the starting ester. Elution with pure ether provided 820 mg (74.6% yield) of **2 ferrocenyl-2-cyclopenten-1-ol** (**6**).

Oxidation of 2-Ferrocenyl-2-cyclopenten-1-ol (6) to 2-Ferrocenyl-2-cyclopenten-1-one (5). A. Oppenauer Procedure.—A reaction mixture of 2-ferrocenyl-2-cyclopenten-1-ol (**6**) (243 mg, 0.907 mmol), aluminum isopropoxide (3.50 g, 17.2 mmol), acetone (10 ml), and toluene (50 ml) was stirred and heated under reflux for 18 hr. After the mixture had cooled to room temperature, it was washed with two portions of 50% aqueous acetic acid and then with three portions of water. The residual toluene solution was dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to a residue which was placed (benzene solution) on an alumina column for chromatographic separation. Development and elution of the column with benzene gave two bands. An odoriferous, yellow oil (130 mg), which was not identified, was obtained from the eluate of the faster moving band. The slower moving band gave 182 mg (75.5% yield) of **2-ferrocenyl-2-cyclopenten-1-one** (**5**).

B. Activated Manganese Dioxide.—A solution of the alcohol (**6**) (210 mg, 0.784 mmol) in 50 ml of methylene chloride was stirred overnight at room temperature in the presence of activated manganese dioxide[12] (1.50 g, 17.1 mmol). All of the solid material was then collected in a filter and washed with small portions of methylene chloride until a colorless wash was obtained. The washes were combined with the original filtrate, and the whole was evaporated to a residue which was chromatographed on alumina in the usual way. Elution with benzene gave the ketone (**5**) (9 mg, 7% yield), while unchanged starting alcohol (**6**) (70 mg, 30% recovery) was obtained from ether eluates.

Reduction of 2-Ferrocenyl-2-cyclopenten-1-one (5) to 2-Ferrocenyl-1-cyclopentanol (9).—A solution of 2-ferrocenyl-2-cyclopenten-1-one (**5**) (114 mg, 0.429 mmol) in 25 ml of methanol was stirred and maintained at 0° while sodium borohydride (1.00 g, 26.5 mmol) was added. After addition was complete, the mixture was stirred for an additional 10 min and then diluted with 250 ml of water. The combined ether extracts, obtained from exhaustive extraction of the diluted reaction mixture, were dried and evaporated to a residue which was chromatographed on alumina. Elution with ether gave 73 mg (63% yield) of the saturated alcohol, **2-ferrocenyl-1-cyclopentanol** (**9**).

Failure of Sodium Borohydride to Effect Reduction of 2-Ferrocenyl-2-cyclopenten-1-ol (6).—Sodium borohydride (67 mg, 1.8 mmol) was added to 25 ml of a cold (0°) methanolic solution of 2-ferrocenyl-2-cyclopenten-1-ol (165 mg, 0.557 mmol) while the latter was stirred vigorously. The stirring was continued for 10 min after the addition was complete, and then the reaction mixture diluted with 250 ml of water. The hydrolyzate was exhaustively extracted with ether, which extracts were combined, dried, and evaporated to yield only unchanged starting material—the unsaturated alcohol (**6**)—identified by means of its infrared spectrum, 150 mg (91% recovery).

Registry No.—**3**, 12260-67-2; **5**, 12260-661-; **6**, 12260-68-3; **7**, 12260-71-8; **8**, 12260-72-9; **9**, 12260-69-4.

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[12] Beacon Chemical Industries, Inc., Cambridge, Mass.

Synthesis of Macrocyclic *o*-Phthalate Esters from the Corresponding Polyesters[1]

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The esterification of phthalic anhydride with selected glycols in the presence of suitable catalysts (*e.g.*, tetrabutyl *o*-titanate) yields polyesters, from which can be distilled, at 220–260° (0–4 mm), the respective macrocyclic *o*-phthalate esters **1–11**. The *o*-phthalate polyesters of diethylene, triethylene, 1,5-pentylene, and 1,6-hexylene glycols can be converted into the respective macrocycles **1–4** in nearly quantitative yields. Macrocyclic esters **5–11** distill from the corresponding polyesters in relatively poor yields. Saponification of the macrocycles **10a** and **10b** produced the two diastereoisomers of 2-(2-hydroxypropoxy)-1-propanol which have been characterized as their bis-*p*-nitrobenzoates.

Prior to 1930, it was believed that condensations of difunctional compounds always gave rise to cyclic products. Carothers and coworkers[2] established that the condensation of difunctional compounds produces *linear polymers* unless five- or six-membered rings are possible. It was also found, however, that both "monomeric" and higher order macrocycles can often be obtained by thermolysis of these linear polymers *in vacuo*. In fact, cyclic esters of aliphatic dicarboxylic acids, with 11- to 36-membered rings, were obtained in yields of up to 65% by thermolysis of catalyzed polyesters at 270°.[2,3] Small amounts of macrocyclic esters apparently exist in equilibrium with polyester and one another and as one or more of the macrocycles is removed by distillation, more is formed in an attempt to maintain this equilibrium. Although Carothers, *et al.*,[2] suggested that thermolysis of condensation polymers should be a rather general preparative method for macrocycles with practical advantages over high dilution techniques, it appears to have received little subsequent attention.[4-6] The only reference to *o*-phthalate macrocycles is a patent[3] giving melting points of the "monomeric" and "dimeric" macrocyclic ethylene *o*-phthalates (**5** and **6**); however, no other specific information was disclosed. This paper reports on the preparation of *o*-phthalate macrocycles by the polyester thermolysis method.

Polyester Preparation.—Because *o*-phthalic acid is eliminated from carboxy terminated chains as phthalic anhydride, which sublimes and clogs the apparatus, it is expedient to prepare polyesters with acid numbers of less than about five before subjecting them to thermolysis (Chart I).

Although *o*-phthalic acid is relatively difficult to esterify completely, such polyesters have been obtained in 2–6 hr by a melt polymerization technique which employs efficient esterification catalysts, a 20–40% molar excess of the glycol, and precautions to minimize

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[1] Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] W. H. Carothers, *et al.*, in "Collected Papers of Wallace H. Carothers on Polymerization," H. Mark and G. S. Whitby, Ed., Interscience Publishers, Inc., New York, N. Y., 1940.

[3] E. W. Spanagel, U. S. Patent 2,092,031 (1937).

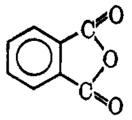
[4] L. I. Belenkii, *Russ. Chem. Rev.*, **33**, 551 (1964).

[5] C. E. Berr, *J. Polym. Sci.*, **15**, 591 (1955).

[6] S. D. Ross, E. R. Coburn, W. A. Leach, and W. B. Robinson, *ibid.*, **13**, 406 (1954).

TABLE I

ESTERIFICATION AND THERMOLYSIS CONDITIONS

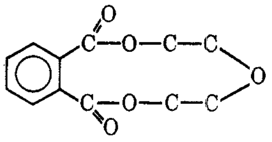


$+ \ 1.2\text{HOROH} \xrightleftharpoons{-H_2O} \text{hydroxy terminated polyester} \rightleftharpoons \text{macrocyclic esters(s)} + 0.2\text{HOROH}$

	Esterification[a]		Thermolysis				
R	Max temp, °C	Time, hr	Temp, °C	Pressure, mm	Time, hr	Product(s)	Yield, % (theoretical)
$-(CH_2)_2O(CH_2)_2-$	220	3.0	220–230	1–2	6.5	**1**	89
$-(CH_2)_2O(CH_2)_2O(CH_2)_2-$	220	3.7	250–260	1–2	5.0	**2**	90
$-(CH_2)_5-$	235	1.3	235–260	1–2	5.25	**3**	94
$-(CH_2)_6-$	235	1.3	235–260	1–2	8.5	**4**	88
$-(CH_2)_2-$	235	4.2	235–275	1–2	4.2	**5, 6**	3, 0.5
$-CH(CH_3)CH_2CH_2-$	225	4.0	240	2–5	7.0	**7**	5
$-(CH_2)_2S(CH_2)_2-$	200	*a*	220–240	2–5	1.1	**8**	2

[a] Reactions catalyzed by 0.36% $Ti(OBu)_4$. Fusion cooks using molar ratio of glycol to anhydride of 1.2/1.0 for all but the last example. This was a solvent (xylene) cook using a 1.4:1.0 ratio of glycol to anhydride and refluxed 4 hr (temp 145–200°). Xylene was removed prior to thermolysis.

CHART I



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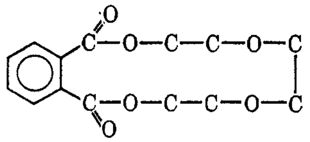

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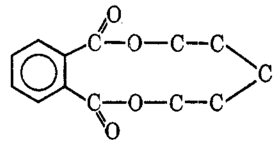

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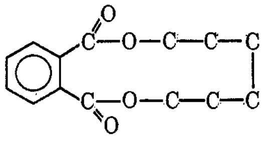

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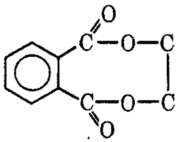

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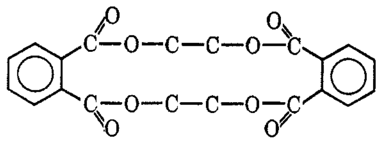

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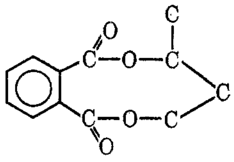

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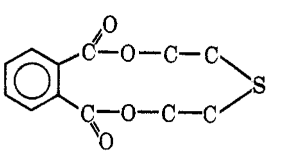

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glycol loss. Catalysts used serve subsequently as thermolysis catalysts. Specific esterification data are included in Table I.

Thermolysis of *o*-Phthalate Polyesters of "Simple" Glycols.—Tables I and II summarize those thermolyses conducted on *o*-phthalate polyesters of "simple" glycols. Preliminary thermolyses were conducted in most cases to find the appropriate temperature range. Distillation was always rapid until most of the excess glycol was removed. As the distillation subsided the temperature was generally raised further in an attempt to maintain a reasonable rate. The occurrence of side reactions dictated against going above 240° in the last two thermolyses. In the first four reactions listed, conversion of the respective polyesters into 1,3,4,6,-7,9-hexahydro-2,5,8-benzotrioxacycloundecin-1,9-dione (**1**), 1,3,4,6,7,9,10,12-octahydro-2,5,8,11-benzotetraoxacyclotetradecin-1,12-dione (**2**), 1,4,5,6,7,9-hexahydro-3(H)-2,8-benzodioxacycloundecin-1,9-dione (**3**) and 1,3,-4,5,6,7,8,10-octahydro-2,9-benzodioxacyclododecin-1,10-dione (**4**) was essentially quantitative. The higher thermolysis temperature required for **3**, as compared to that required for **1**, may be due to the additional nonbonded interactions incurred when oxygen is replaced by methylene in the ring. Lower volatilities and statistical probabilities of formation may explain why a higher temperature had to be employed to obtain **2** than was needed for **1** and why **4** was obtained more slowly than **3** under the same conditions. In the case of poly(ethylene *o*-phthalate), after most of the excess glycol had distilled, the distillation practically stopped and raising the temperature to 275° did not noticeably accelerate it. The distillate did, however, contain small amounts of 1,3,4,6-tetrahydro-2,5-benzodioxacyclooctin-1,6-dione[3] (**5**) and 5,7,8,10,15,17,18,20-octahydrodibenzo[*c*,*k*]-1,6,9,14-tetraoxacyclohexadecin-5,10,-15,20-tetrone[3] (**6**). Compound **6** was the only "dimer" detected in this study, perhaps because the other dimers are too high boiling to distill under the conditions employed. Unlike the larger ring compounds, **5**, which has an eight-membered ring, could be constructed with Fisher–Taylor–Hirschfelder atomic models only by twisting the carbonyl groups well out of the plane of the benzene ring. This provides a rationale for the poor yield. 3-Methyl-1,4,5,7-tetrahydro-3(H)-2,6-benzodioxacyclononin-1,7-dione (**7**) and 1,3,4,6,7,9,-hexahydro-2,8-benzodioxa-5-thiacycloundecin-1,9-dione (**8**) were obtained only in poor yield and were accompanied by other decomposition products.

Tetrabutyl *o*-titanate reacts with water and/or end groups during the esterification (*n*-butyl alcohol is evolved) so that the active esterification and thermolysis catalyst is titanium in some other form (probably a complex polymeric structure).

Thermolysis of "Poly(dipropylene *o*-phthalate)."—Commercial dipropylene glycol (DPG) is reported to be a mixture of the three positional isomers 1-(2-hydroxypropoxy)-2-propanol (A), 2-(2-hydroxypropoxy)-1-propanol (B), and 2-(1-hydroxypropoxy)-1-propanol (C).[7-10]

Each positional isomer is composed of two diastereoisomers. Havlik and Lawson[9,10] have separated Union Carbide Corp. DPG into four significant frac-

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[7] British Patent 835,717 (1960); *Chem. Abstr.*, **55**, 2696*f* (1961).

[8] A. J. Havlik and A. F. Hildebrandt, *J. Polym. Sci.*, **41**, 533 (1959).

[9] A. J. Havlik and D. D. Lawson, Research Summary 36-14 (B), 145–8, Jet Propulsion Laboratory, Pasadena, 1962.

[10] D. D. Lawson and A. J. Havlik, Space Programs Summary 37-22 (D), 94–6, Jet Propulsion Laboratory, Pasadena, 1963.

TABLE II

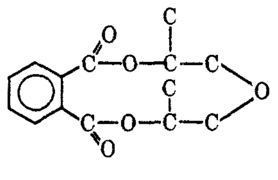
PRODUCT CHARACTERIZATION[a]

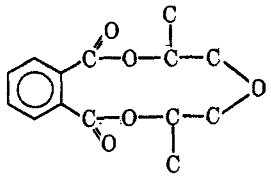
Compd	Recrystn solvents[b]	Mp, °C	Calcd C	Calcd H	Calcd Sapon equiv	Calcd Mol wt	Found C	Found H	Found Sapon equiv[c]	Found Mol wt
1[d]	1.33 e:p	61.5–62.5	61.01	5.12	118.1	236	60.83	5.06	121.0	232
2[e]	1 b:n, 1.5 m:w	119.5–121.0	59.99	5.76	140.7	280	59.78	5.58	143.0	275
3	4 h:b, n	100.8–102.3	66.66	6.02	117.1	234	66.90	6.16	117.4	230
4	m, e	63.7–64.5	67.73	6.50	124.2	248	67.76	6.56	125.5	239
5	10 e:p	59.5–61.8[f]								
6	1.5 n:a	193.0–195.0[f]								
7	n, 10 h:b	78.6–78.8	65.45	5.49	110.1	220	65.18	5.30	112.6	217
8[g]	e, 2 h:b, m	107.2–107.7	57.13	4.79	126.2	252	56.98	4.69	127.2	250

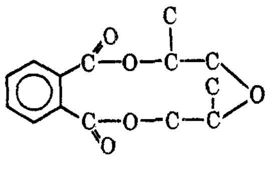
[a] The ir spectra of **1**–**8** all had strong bands near 5.77, 7.85, 8.90, 9.35, and 13.45 μ typical of *o*-phthalate esters and no OH bands. [b] Solvents: p = petroleum ether; m = methanol; n = naphtha (bp 160–200°); w = water; h = hexane; b = benzene; e = ether; a = acetone; 4 h:b = four volumes of h to one of b; etc. [c] Phthalic acid and the parent glycol were isolated upon saponification of all the new macrocycles by the method of J. F. Shay, S. Skilling, and R. W. Stafford, *Anal. Chem.*, **26**, 652 (1954). Identification by comparison of ir spectra with spectra of authentic samples. [d] Nmr signals ($CDCl_3$) at δ 3.89 (4 H half of $A_2'B_2'$ pattern, 2 (CCH_2O)), at 4.43 (4 H half of $A_2'B_2'$ pattern, 2 ($COOCH_2C$)), at 7.65 (4 H $A_2'B_2'$ pattern, aromatic protons). [e] Nmr signals ($CDCl_3$) at δ 3.58 (4 H single peak, $O(CH_2)_2O$), at 3.77 (4 H half of $A_2'B_2'$ pattern, 2(CCH_2O), at 4.47 (4 H half of $A_2'B_2'$ pattern, 2 ($COOCH_2C$)), at 7.62 (4 H $A_2'B_2'$ pattern, aromatic protons). [f] Lit.[3] mp of **5** is 55° and **6** is 198°. [g] *Anal.* Calcd for **8**: S, 12.71. Found: S, 12.50.

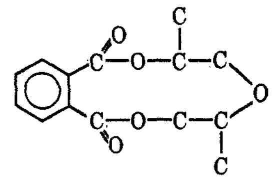
tions by glpc. From their assignments for these fractions and the relative peak areas the approximate composition is deduced to be 43% A, 47% B, 5.7% C, and 4.5% unknown. Whether or not the 5.7 and the 4.5% fractions which have similar retention times could be the individual diastereoisomers of positional isomer C is not clear. We have repeated this work and obtained the same four fractions in similar percentages.

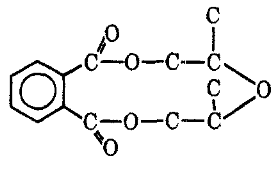
Thermolysis of "poly(dipropylene *o*-phthalate)" gave an alkali insoluble liquid–crystal paste believed to be a mixture of the six macrocyclic *o*-phthalates **9a**–**11b**.

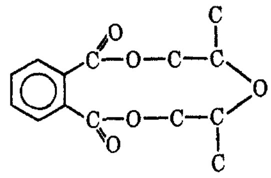

meso cis (**9a**)


racemic *trans* (**9b**)


racemic *cis* (**10a**)


racemic *trans* (**10b**)


meso cis (**11a**)


racemic *trans* (**11b**)

The crystalline portion of this mixture was separated from the oil and a combination of fractional crystallization and chromatography separated this portion into two pure isomers. These have been shown to be the diastereoisomers of 3,6-dimethyl-1,3,4,6,7,9-hexahydro-2,5,8-benzotrioxacycloundecin-1,9-dione (**10a** and **10b**); however, differentiation between them has not been accomplished.

Saponification of **10a** and **10b** produced the two diastereoisomers of 2-(2-hydroxypropoxy)-1-propanol (B) which have been characterized for the first time as their bis-*p*-nitrobenzoate derivatives. Glpc assay of the isomeric mixture of glycols obtained upon saponification of the total macrocyclic mixture indicated that **10a** and **10b** comprise about 65% of this mixture.

Experimental Section

General.—Melting points were determined in a capillary using a Laboratory Devices Mel-Temp apparatus and are corrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were obtained by Nuclear Magnetic Resonance Specialties, Inc., using a Varian Model A-60 spectrometer operating at 60 Mc. Chemical shifts are expressed in parts per million from the internal standard tetramethylsilane (δ). Molecular weights were determined using a Mechrolab vapor pressure osmometer, Model 301 (solvent, benzene). Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer, Model 137. Nujol mulls were prepared for solids and liquids were used neat except for the dipropylene glycols (1% carbon disulfide solutions).

Materials.—The following materials were purchased from the indicated suppliers in the purest available grades and used, without further purification: phthalic anhydride, Koppers Co., Inc.; tetrabutyl *o*-titanate, E. I. du Pont de Nemours and Co.; 1,3-butanediol and 1,6-hexanediol, Celanese Chemical Co.; 1,5-pentanediol, ethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, and bis(2-hydroxyethyl sulfide), Union Carbide Corp.

Preparation and Thermolysis of "Simple" Poly(*o*-phthalates).—Into a 3-l., five-necked flask was placed 2200 g of a 1.2:1.0 *M* mixture of the respective glycol and phthalic anhydride along with 8.0 g of tetrabutyl *o*-titanate.

The flask was equipped with a heating mantle, mechanical stirrer, thermometer, temperature controller, gas inlet tube, and a vacuum jacketed fractionating column (length = 47 cm, i.d. = 1.5 cm) filled with $^1/_8$ in. i.d. glass helices.[11] A still head with thermometer and take-off condenser was mounted on the fractionating column. Carbon dioxide was bubbled through the mixture at a rate of 1.8 l./min. The temperature was raised to that indicated in Table I as fast as possible without driving the temperature of the distilling vapors at the top of the column above about 100°. This temperature was held for the indicated time (Table I) during which the acid number had dropped to <5. The gas inlet tube was then replaced by a hose adapter (with stopcock) to which was attached a McLeod gauge and the fractionating column by a still head and short air condenser leading to a receiver (a 3-l. two-necked round-bottom flask) in an ice–water bath. The flask and still head were insulated and

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[11] This type of partial condenser proved ideal as it allows water to escape easily, returns glycol and anhydride almost quantitatively to the vessel, and resists clogging in most cases.

the system was evacuated[12] to 1–4 mm. When the initial thermolysis temperature, as given in Table I, is higher than the maximum esterification temperature, the initial thermolysis temperature was approached rapidly. Once reached, this temperature was held for a time and then gradually increased to the maximum indicated in an effort to maintain a reasonable distillation rate.

In the preparation of **1–4** the distillations were continued until the polyester was practically gone. In the preparation of **5** and **6** the distillation essentially stopped after the excess glycol distilled and was terminated when the rate could not be increased by gradually raising the temperature to 275°. In the preparation of **7** and **8** the reactions were stopped arbitrarily as it became evident that side reactions were predominating. The distillates were melted and poured into water (vigorous agitation) and sodium carbonate was added to bring the pH to 9–10. Compounds **1–4** were isolated by filtration, washing, and drying. The white crystals thus obtained had melting points only 1–4° lower than those of the subsequent analytical samples and the yields reported are based on these materials. Compounds **5** and **6** were isolated by ether extraction of the aqueous suspension (partial evaporation of the ether extract caused precipitation of **6** and evaporation to near dryness gave **5**). Compound **7** was isolated by filtration, followed by recrystallization from methanol. Compound **8** was isolated by chloroform extraction, evaporation of the chloroform, and recrystallization of the residue from methanol. Analytical samples of **1–8** were obtained by recrystallization to constant melting point using the solvents indicated in Table II.

Preparation and Thermolysis of "Poly(dipropylene *o*-phthalate)."—Using the same apparatus and procedure as described above, a polyester of acid number <3 was prepared (maximum temperature 225°, 5.5 hr) from 1080 g (7.3 mol) of phthalic anhydride, 1205 g (9.0 mol) of dipropylene glycol (DPG), and 6.0 g of stannous oxalate. The system was modified and evacuated to 1–2 mm; the temperature was raised gradually to and kept at 235° for 3.8 hr. The distillate (577 g) was melted, poured into ice water in a Waring Blendor, and neutralized with sodium carbonate. The aqueous phase was decanted from an oil. This oil was washed with two 2.8-l. portions of ice water which resulted in its partial crystallization. The sludge was dissolved in 500 ml of chloroform. This solution was distilled and a 289 g (15%) fraction boiling at 130–135° (0.15 mm) was collected. This became predominantly crystalline upon cooling. Its origin, saponification equivalent (134.0; calcd 132.2), ir spectrum,[13] and chromatographic behavior[14a] suggest that it is a mixture of the isomeric macrocycles **9a–11b**. A portion of this mixture (140 g) was triturated with 3:1 DPG–methanol. Filtration produced 105 g of white crystals, mp 82–112°. Recrystallization from 3:2 petroleum ether–benzene gave a 42-g fraction (F_1) melting at 125–130°. Evaporation of the mother liquor produced an oily crystalline mass. This was triturated with petroleum ether and the crystals were collected by filtration, washed with a little ether, and recrystd from 4:1 methanol–water to give 31 g of another fraction (F_2) melting at 96–99°. Further recrystallization of F_1 (twice from 3:2 petroleum ether–benzene and once from naphtha (bp 160–200°) afforded an analytical sample, mp 134.5–136.5°. Further recrystallization of F_2 (from 4:1 methanol–water and 4:3 ether–petroleum ether) raised its mp to a constant 99.3–101.3°. Efforts to resolve F_1 into additional fractions failed; however, F_2 (a solid solution or molecular complex) was separated into two fractions by preparative glpc and by elution from a column of neutral alumina with benzene. One of these fractions (approximately 25% of F_2) was identical with F_1 (mixture melting point and ir) and the other (approximately 75% of F_2) was a new substance, F_3, that melted at 106.6–107.9° after recrystallization from hexane–ether. The nmr spectra ($CDCl_3$) of F_1 and F_3 are complex; however, both have single proton multiplets (δ 5.5 and 5.03, respectively) which could be assigned only to methine protons adjacent to ester linkages. Since isomers **9a** and **9b** would have two such protons each and since isomers **11a** and **11b** would have none, isomers **10a** and **10b** are the only compatible structures.

Anal. of F_1 and F_3 Calcd for $C_{14}H_{16}O_5$ (**10a** or **10b**): C, 63.62; H, 6.10; sapon equiv, 132.2; mol wt, 264. Found (F_1): C, 63.56; H, 6.04; sapon equiv, 132.5; mol wt, 270. Found (F_3): C, 63.92; H, 6.12; sapon equiv, 130.0; mol wt, 254.

There was isolated, upon saponification of F_1 and saponification of F_3, phthalic acid and a glycol which formed bis-*p*-nitrobenzoate derivatives D_1 (mp 110–111°) and D_2 (mp 99.8–100.8°), respectively. The glycols obtained by saponification of F_1 and F_3 had almost identical infrared spectra, essentially identical with the published spectrum[15] of DPG positional isomer B (mixed diastereoisomers). They also exhibited identical glpc retention times[16] which corresponded to that of the 47% peak of DPG, reported by Havlik and Lawson[9] to be DPG isomer B (mixed diastereoisomers). A 1:1 mixture (by weight) of the glycol derivatives (D_1 and D_2) was recrystallized from ethanol yielding a solid solution or molecular complex melting at 83.1–85.3° (identical with that reported[15] for the ethanol recrystallized bis-*p*-nitrobenzoate of DPG positional isomer B).

Anal. of D_1 and D_2 Calcd for $C_{20}H_{20}N_2O_9$ (D_1 or D_2): C, 55.55; H, 4.66; N, 6.48. Found for D_1: C, 55.66; H, 4.76; N, 6.45. Found for D_2: C, 55.76; H, 4.66; N, 6.35.

The bis-*p*-nitrobenzoates of the diastereoisomers of DPG positional isomer A melt at 119–120 and 148.5–149.5°[10,17] (different from D_1 and D_2 above).

Another DPG polyester was prepared and thermolyzed in a similar manner to that above except that 8.0 g of tetrabutyl *o*-titanate was used as catalyst and the thermolysis was conducted for 12 hr at 225–240°. The chloroform solution obtained upon work-up of the distillate (as before) was simply washed with water and evaporated giving a 44% yield of mixed isomers. Glpc of this mixture and of the glycols isolated upon its saponification revealed no impurities and indicated that it also contained about 65% **10a** and **10b**.

Registry No.—**1**, 13988-26-6; **2**, 16709-48-1; **3**, 16709-49-2; **4**, 16709-50-5; **5**, 4196-98-9; **6**, 16709-52-7; **7**, 16720-20-0; **8**, 16709-53-8; **10a**, 16709-54-9; **10b**, 16709-55-0; 2-(2-hydroxypropoxy)-1-propanol bis-*p*-nitrobenzoate (a), 16709-56-1; 2-(2-hydroxypropoxy)-1-propanol bis-*p*-nitrobenzoate (b), 16709-57-2.

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[12] It is important that the system be evacuated gradually, that the vacuum train is free of narrow restrictions, and/or that the McLeod gauge be connected directly to the flask. These precautions tend to prevent and/or allow the detection of clogging.

[13] Strong bands were at 5.78, 7.76, 8.77, 9.33, and 13.34 μ, consistent with *o*-phthalate ester; there was no OH absorption.

[14] (a) The mixture of macrocycles **9a–11b** was eluted from an Aerograph Autoprep gas chromatograph as five overlapping peaks and shoulders. Conditions were as follows: sample size, 0.10 ml of a 25% benzene solution; column, 30 ft × 3/8 in. aluminum, packed with 15% Carbowax 20M-TPA on acid-washed Chromosorb W; carrier gas rate, 170 ml/min; column temperature, 255°. (b) The diastereoisomers **10a** and **10b** were separated on a preparative scale using the same apparatus and conditions as in a, except that the column used was only 18 ft long. Retention times were 69 (mp 134.5°) and 75 min (mp 106.6°).

[15] A. R. Sexton and E. C. Britton, *J. Amer. Chem. Soc.*, **75**, 4357 (1953).

[16] The isomeric dipropylene glycols were resolved on an F & M Scientific Model 500 gas chromatograph using a 2.5 ft × 0.25 in. o.d. stainless-steel column packed with 10% Carbowax 20M-TPA on 60–80 mesh Chromosorb W (acid washed) at 150°.

[17] R. K. Summerbell, D. M. Jerina, and R. J. Grula, *J. Org. Chem.*, **27**, 4433 (1962).