250. *The Preparation and Properties of Some Hydrocarbons with Recurrent Groups.*

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Six hydrocarbons of high molecular weight, with methyl, tetramethylene, and pentamethylene substituent groups attached to a paraffin chain, have been prepared from the corresponding long-chain dicarboxylic esters *via* the glycols and dibromides. The esters were obtained by anodic oxidation of the acid esters of ββ-disubstituted glutaric acids. Physical properties of the hydrocarbons are described.

ATTEMPTS to correlate the physical properties of hydrocarbons with structure have been considerably hampered by lack of reliable data for the higher and more complex members. We have prepared a series of hydrocarbons in which a recurrent group occurs as in certain types of polymers. Our recurrent groups were (I), (II), and (III).

$-CH_2\cdot CMe_2\cdot CH_2-$ (I)

$[CH_2]_5>C(CH_2-)_2$ (II)

$[CH_2]_4>C(CH_2-)_2$ (III)

Hydrocarbons based on (II) and (III) form a new series.

We prepared six hydrocarbons—three containing two and three containing four of these repeating units. The method of preparation was anodic oxidation of the sodium salt of the acid ester of a dibasic organic acid :

$$2RO_2C\cdot[CH_2]_n\cdot CO_2H \longrightarrow RO_2C\cdot[CH_2]_{2n}\cdot CO_2R + 2CO_2 + H_2$$

followed by reduction of the diesters to the glycols, conversion of the latter into dibromides, and finally reduction to the hydrocarbons. The yields were 50—70% overall from the esters.

There are several practical limitations to building up a molecule of relatively high molecular weight by successive electrolyses. At each succeeding electrolysis, the yield decreases owing to increased formation of by-products. These are difficult to separate when they boil outside the range of normal distillation, but might be removed by use of, *e.g.*, selective solvents. Another difficulty is due to the decreasing solubility of the intermediate derivatives.

Our starting materials were ββ-dimethylglutaric, *cyclo*hexane- and *cyclo*pentane-1 : 1-diacetic acids. With acetic anhydride these gave the anhydrides from which the methyl hydrogen esters were obtained by treatment with sodium methoxide solution. In the preliminary work, ethyl esters were employed for electrolysis with absolute methanol as electrolyte but the exchange of methyl and ethyl groups between ester and electrolyte caused difficulty. The exclusive use of methyl esters obviated this. A further modification was the replacement of pure methanol as electrolyte by a mixture of equal parts of methanol and light petroleum. The resulting increase in solubility of esters in the electrolyte enabled more concentrated solutions to be electrolysed with consequent decrease in undesirable reaction products. Also, cooling of the reaction vessel became unnecessary since the temperature was controlled at the reflux temperature (50—54°). Electrolysis of the above three methyl hydrogen esters yielded the substituted dimethyl suberates. Conversion of these into the methyl hydrogen esters, followed by electrolysis of the sodium salts yielded the dimethyl dodecane-1 : 12-dicarboxylates.

The six dimethyl esters were reduced to the glycols by lithium aluminium hydride (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197), then converted into the dibromide by anhydrous hydrogen bromide, and reduced with zinc dust and refluxing glacial acetic acid to the hydrocarbons, the physical properties of which are tabulated below. The only recorded reference to these hydrocarbons is that Whitmore and Carney (*ibid.*, 1941, **63**, 2633) isolated a small amount of impure 3 : 3 : 6 : 6-tetramethyloctane after reaction of sodium with 1-chloro-2 : 2-dimethylbutane.

EXPERIMENTAL

Analyses were carried out by Drs. Weiler and Strauss, Oxford.

General Method of Electrolysis.—A 2-l. wide-mouthed bottle was fitted with a cork supporting a reflux condenser, a thermometer, and a glass rack as an electrode support. The electrodes consisted of a sheet platinum anode (4 × 6 cm.) with two sheet iron cathodes of similar dimensions spaced 5 mm. away on either side, all held firmly in the glass rack. The respective electrode leads were of stout platinum and iron wire spot-welded to the electrodes and sealed into glass tubes passing through the cork. The current was taken from the 100-v D.C. supply through a rheostat and ammeter.

Electrolysis of each acid ester was carried out in a mixture of methanol and light petroleum (b. p. 70—90°) to which a small amount (3 g.) of metallic sodium * had been added. The reaction proceeded under reflux at a current of 2—3 amp. until a 25% excess over the theoretical amount of electricity had been used.

Ref.	Hydrocarbon	B. p.°/mm.	M. p.		d^{20}	d^{25}	Purity, mol.% ^{b}
			Found ^{b}	Calc.^{a}			
A	3 : 3 : 6 : 6-Tetramethyloctane	189·7°/760 130°/140	−73·59°	−73·28°	0·7617	0·7570	99·0
B	3 : 3 : 6 : 6 : 9 : 9 : 12 : 12-Octamethyltetradecane	191·3°/23·3	Glass	—	0·8061	0·8030	—
C	3 : 3-6 : 6-Di(pentamethylene)-octane	218·7°/20·5	+ 7·06	+ 7·40	0·9025	0·8992	99·0
D	3 : 3-6 : 6-9 : 9-12 : 12-Tetra-(pentamethylene)tetradecane	—	+70—71	—	—	—	—
E	3 : 3-6 : 6 - Di(tetramethylene)-octane	105°/1·5	−15·66	−14·83	0·8808	0·8775	97·5
F	3 : 3-6 : 6-9 : 9-12 : 12-Tetra-(tetramethylene)tetradecane	—	+65	—	—	—	—

^{a} Calc. for zero impurity. ^{b} Freezing points were determined by the method of Mair, Glasgow, and Rossini (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 591) and purity was estimated by the method of Glasgow, Streiff, and Rossini (*ibid.*, 1945, **35**, 355).

Refractive indices at various wave-lengths (Å).

Hydro-carbon ref.	Hydrogen (6562)		Sodium (5893)		Mercury (5460)		Hydrogen (4861)		Mercury (4358)		Kinematic viscosity, centistokes/deg.		
	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°	20°	37·8°	98·9°
A	1·4242	1·4222	1·4265	1·4244	1·4284	1·4263	1·4316	1·4296	1·4360	1·4338	2·15	1·615	0·795
B	1·4475	1·4457	1·4498	1·4481	1·4519	1·4501	1·4554	1·4534	1·4598	1·4581	60·37	22·51	3·66
C	1·4868	1·4852	1·4894	1·4875	1·4914	1·4897	1·4954	1·4935	1·5002	1·4985	51·82	20·61	3·57
E	1·4745	1·4729	1·4768	1·4755	1·4789	1·4778	1·4827	1·4810	1·4873	1·4868	—	—	—

Methyl Hydrogen ββ-*Dimethylglutarate.*—ββ-Dimethylglutaric acid (800 g.) was refluxed for 1 hour with acetic anhydride (430 g.). The excess of the latter, together with the acetic acid formed, was removed by distillation and the residual ββ-dimethylglutaric anhydride distilled at atmospheric pressure. The anhydride, m. p. 121°, was obtained in theoretical yield and converted into the acid ester by slowly adding the finely-ground material (710 g.) to a well-stirred solution of sodium methoxide (116 g. of sodium in 3 l. of methanol) at 0°. The mixture was allowed to warm slowly to room temperature and, after a further hour, gently refluxed for 1 hour. After addition of water (3 l.) the methanol was removed on the water-bath and the acid ester liberated by the addition of excess of hydrochloric acid. The crude product was dried by distillation with benzene, the last traces of which were removed under reduced pressure. The acid ester (850 g., 100%) was used for the next stage without further treatment.

Dimethyl ββββ'β'-*Tetramethylsuberate.*—Methyl hydrogen ββ-dimethylglutarate (104 g.) was dissolved in 1 : 1 mixture (1·3 l.) of methanol and light petroleum to which metallic sodium (3 g.) had been added. Electrolysis was allowed to proceed at reflux temperature (54°) until a 25% theoretical excess of electricity had been passed. The product was filtered from deposited sodium carbonate and, after evaporation of the filtrate on the water bath, the residue was dissolved in benzene (100 ml.). After being washed with 5N-hydrochloric acid (100 ml.), the benzene solutions from eight such electrolyses were combined and evaporated and the residue

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[*] The use of potassium in recent work has proved advantageous.

fractionated at reduced pressure through a short column. Dimethyl ββ′β′-tetramethylsuberate distilled at 143·5°/10 mm. and 292°/760 mm., with n_D^{20} 1·4435, in 75% yield (Walker and Wood, *J.*, 1906, **89**, 598, obtained a 40% yield) (Found: C, 65·1; H, 10·1. Calc. for $C_{14}H_{26}O_4$: C, 65·1; H, 10·4%).

The free acid, obtained by hydrolysis with alcoholic potassium hydroxide and crystallised from methanol, melted at 169·5° (Walker and Wood gave 164—165°) (Found: C, 62·8; H, 9·6. Calc. for $C_{12}H_{20}O_4$: C, 62·6; H, 9·6%).

3 : 3 : 6 : 6-*Tetramethyloctane*-1 : 8-*diol*.—Lithium aluminium hydride (38 g.; 1 mole) was dissolved in dry ether (1 l.) in a 3-l. three-necked round-bottomed flask fitted with a sealed Hershberg stirrer, dropping funnel, and an efficient reflux condenser (calcium chloride tube). A solution of dimethyl tetramethylsuberate (194 g., 0·75 mole) in ether (500 ml.) was added to the vigorously stirred solution as fast as the exothermic reaction would allow. Stirring was continued for an hour after the addition was complete and the excess of hydride destroyed by careful addition of water. Hydrolysis was carried out with 10% sulphuric acid (1500 ml.) and, after separation of the ether layer, the aqueous layer was thoroughly extracted with ether. The combined ethereal layers were washed with sodium hydrogen carbonate solution, dried, and filtered, and the ether was removed on the water-bath. The residue distilled at 156—158°/3 mm. and the distillate crystallised at low temperature from ether, yielding the pure *glycol* (112 g., 74·5%), m. p. 48—49° (Found: C, 71·4; H, 13·1. $C_{12}H_{26}O_2$ requires C, 71·2; H, 13·0%).

The material recovered from the mother-liquors was re-treated with lithium aluminium hydride, the final yield of 3 : 3 : 6 : 6-*tetramethyloctane*-1 : 8-*diol* being 92·5% (140 g.). The *phenylurethane* derivative, crystallised from light petroleum, melted at 101·5—102·5° (Found: C, 71·0; H, 7·9; N, 6·4. $C_{26}H_{36}O_4N_2$ requires C, 70·9; H, 8·2; N, 6·4%). The 3 : 5-*dinitrobenzoate* melted at 134—135° (Found: C, 53·3; H, 5·4; N, 9·3. $C_{26}H_{30}O_{12}N_4$ requires C, 52·9; H, 5·1; N, 9·5%).

1 : 8-*Dibromo*-3 : 3 : 6 : 6-*tetramethyloctane*.—The glycol (135 g.) was treated at 120° with hydrogen bromide till absorption was complete and the product extracted with light petroleum. After successive washing with water, concentrated sulphuric acid, and sodium hydrogen carbonate solution, the extract was dried ($CaCl_2$) and filtered and the solvent removed. The crude product (187 g., 85%) was purified by crystallisation from light petroleum, to yield 1 : 8-*dibromo*-3 : 3 : 6 : 6-*tetramethyloctane*, m. p. 21·5° (Found: C, 44·5; H, 6·6; Br, 48·8. $C_{12}H_{24}Br_2$ requies C, 43·9; H, 7·4; Br, 48·7%).

3 : 3 : 6 : 6-*Tetramethyloctane*.—The dibromide (164 g., 0·5 mole) and glacial acetic acid (1·5 l.) were placed in a 3-l. flask fitted with a Hershberg stirrer and a reflux condenser. Zinc dust (500 g.) was added to the vigorously stirred solution which was refluxed for 48 hours with the addition of more zinc dust (100 g.) after 24 hours. The solution was diluted with an equal volume of water and steam-distilled, to yield the crude hydrocarbon which was dissolved in light petroleum and washed with concentrated sulphuric acid, 10% sodium hydroxide solution, and water. After drying (K_2CO_3), the solvent was removed, and the 3 : 3 : 6 : 6-tetramethyloctane (70 g., 82·5%) distilled as a colourless oil at 74°/12 mm. (Found: C, 85·0; H, 15·2. Calc. for $C_{12}H_{26}$: C, 84·6; H, 15·4%).

Methyl Hydrogen ββ′β′-*Tetramethylsuberate*.—Dimethyl tetramethylsuberate (378 g.) was refluxed with an equimolecular quantity of acetic acid (88 ml.) and concentrated hydrochloric acid (20 ml.). Methyl acetate was removed as formed through a short column until 0·33 equiv. had distilled. Further reaction was stopped by adding benzene (200 ml.), and the water removed by distillation with the benzene. Acetic acid was then distilled off and the residue fractionated at reduced pressure, to yield unchanged dimethyl ester, b. p. 142—146°/11 mm., n_D^{20} 1·4437, and the required acid methyl ester, b. p. 183°/10 mm., n_D^{20} 1·4530, m. p. 27°. The residue of tetramethylsuberic acid was combined with the unchanged dimethyl ester and, after addition of the calculated quantity of acetic and hydrochloric acids, the procedure was repeated several times. The final yield of acid ester was 83% (297 g.) with only a small residue (21 g.) of neutral ester and acid.

Dimethyl 2 : 2 : 5 : 5 : 8 : 8 : 11 : 11-*Octamethyldodecane*-1 : 12-*dicarboxylate*.—The methyl hydrogen ββ′β′-tetramethylsuberate (344 g.) was electrolysed under the conditions previously described. After removal of solvent, the residue was dissolved in benzene and washed with sodium hydrogen carbonate solution. The solution was dried by distilling the benzene, and the residue distilled through a small column to an overhead temperature of 162°. The residual oil was finally fractionated at reduced pressure, to give the *dodecanedicarboxylate* (205 g., 75%), b. p. 137°/0·5 mm., n_D^{20} 1·4560 (Found: C, 72·3; H, 11·6. $C_{24}H_{46}O_4$ requires C, 72·8; H, 11·7%). The free *acid*, liberated from the potassium salt after saponification, crystallised from methanol as a white microcrystalline powder, m. p. 135° (Found : C, 71·2; H, 11·4. $C_{22}H_{42}O_4$ requires C, 71·3; H, 11·4%).

3 : 3 : 6 : 6 : 9 : 9 : 12 : 12-*Octamethyltetradecane*-1 : 14-*diol*.—The above ester (279 g., 0·7 mol.) was reduced with lithium aluminium hydride (38 g.; 1 mol.) in ether (3 l.). The crude product (235 g., 98%), on crystallisation from ether, yielded the *diol*, m. p. 82—83° (Found : C, 77·2; H, 13·3. $C_{22}H_{46}O_2$ requires C, 77·2; H, 13·5%). The *phenylurethane* derivative crystallised from light petroleum as fine needles, m. p. 112—113° (Found : C, 74·1; H, 9·6; N, 5·2. $C_{36}H_{56}O_4N_2$ requires C, 74·4; H, 9·7; N, 4·8%).

1 : 14-*Dibromo*-3 : 3 : 6 : 6 : 9 : 9 : 12 : 12-*octamethyltetradecane*.—The glycol (230 g.) was esterified as above. The crude dibromide (315 g.) was obtained in theoretical yield. After repeated crystallisations from light petroleum at low temperature, the 1 : 14-*dibromo*-3 : 3 : 6 : 6 : 9 : 9 : 12 : 12-*octamethyltetradecane* (210 g.) melted at 42·0—42·5° (Found : C, 56·5; H, 9·3; Br, 34·3. $C_{22}H_{44}Br_2$ requires C, 56·4; H, 9·5; Br, 34·1%).

3 : 3 : 6 : 6 : 9 : 9 : 12 : 12-*Octamethyltetradecane*.—The dibromide (234 g.) was stirred with zinc dust and refluxing glacial acetic acid for 48 hours. After dilution with water, the solution was extracted with light petroleum and the extract washed with concentrated sulphuric acid, 10% sodium hydroxide, and water, before drying ($CaCl_2$). The solvent was removed and 3 : 3 : 6 : 6 : 9 : 9 : 12 : 12-*octamethyltetradecane* (132 g., 85%) distilled as a viscous oil at 115°/0·4 mm. (Found : C, 85·2; H, 14·9. $C_{22}H_{46}$ requires C, 85·1; H, 14·9%).

Methyl Hydrogen cyclo*Pentane*-1 : 1-*diacetate*.—*cyclo*Pentane-1 : 1-diacetic acid was refluxed for 3 hours with excess of acetic anhydride; after distillation of acetic acid and acetic anhydride, the residual *cyclo*pentane-1 : 1-diacetic anhydride was obtained as a brown solid. Crystallisation from light petroleum gave fine colourless needles, m. p. 68°. The anhydride (568 g.) was added with shaking to a solution of sodium (78 g.) in methanol (3 l.) which was cooled in an ice-bath till dissolution was complete. The solution was allowed to warm overnight to room temperature and, after 2 hours' refluxing, water (3 l.) was added. Methanol was removed by distillation and the acid ester liberated by the addition of hydrochloric acid, separated, and dried by distillation with benzene. On removal of the benzene the acid ester was obtained in theoretical yield (661 g.).

Dimethyl 2 : 2-5 : 5-*Di*(*tetramethylene*)*hexane*-1 : 6-*dicarboxylate*.—Methyl hydrogen *cyclo*pentane-1 : 1-diacetate (661 g.) was electrolysed as previously described and worked up in the normal way. The product was distilled to 122°/12·5 mm. and the residue (330 g.) distilled in the range 105—110°/0·04 mm. Fractionation in a 16-plate spinning-band column (Birch, Gripp, and Nathan, *J. Soc. Chem. Ind.*, 1947, **66**, 33) yielded a fraction (170 g.), b. p. 139°/0·5 mm., n_D^{20} 1·4793, which proved to be the required diester. It was dissolved in ether and washed with sodium hydrogen carbonate solution to remove traces of *cyclo*pentane-1 : 1-diacetic acid. The *dimethyl* ester was finally refractionated and obtained as a colourless oil, n_D^{20} 1·4790, d^{20} 1·043 (Found : C, 69·7; H, 9·8. $C_{18}H_{30}O_4$ requires C, 69·6; H, 9·8%). A small quantity of the ester was hydrolysed to yield the free *acid* which crystallised from acetone as rhombic crystals, m. p. 170° (Found : C, 68·2; H, 9·0. $C_{16}H_{26}O_4$ requires C, 68·1; H, 9·3%).

3 : 3-6 : 6-*Di*(*tetramethylene*)*octane*-1 : 8-*diol*.—The above ester (31 g., 0·1 mol.) was reduced with lithium aluminium hydride to the *glycol* (22 g., 87%) which crystallised from ether as a microcrystalline powder, m. p. 110—111° (Found : C, 75·9; H, 11·9. $C_{16}H_{30}O_2$ requires C, 75·5; H, 11·9%).

1 : 8-*Dibromo*-3 : 3-6 : 6-*di*(*tetramethylene*)*octane*.—This *dibromide* (25 g., 80%), obtained from the above glycol (21 g.) and crystallised from light petroleum at low temperature, had m. p. 59—60° (Found : C, 51·2; H, 7·5; Br, 41·7. $C_{16}H_{28}Br_2$ requires C, 50·5; H, 7·4; Br, 42·0%).

3 : 3-6 : 6-*Di*(*tetramethylene*)*octane*.—The dibromide (22 g.) was reduced with zinc dust and refluxing glacial acetic acid and the resultant hydrocarbon treated as described previously. The 3 : 3-6 : 6-*di*(*tetramethylene*)*octane* (9·5 g., 75%) distilled at 105°/1·5 mm. as a colourless oil (Found : C, 86·7; H, 13·4. $C_{16}H_{30}$ requires C, 86·4; H, 13·6%).

Methyl Hydrogen 2 : 2-5 : 5-*Di*(*tetramethylene*)*hexane*-1 : 6-*dicarboxylate*.—Dimethyl 2 : 2-5 : 5-di(tetramethylene)hexane-1 : 6-dicarboxylate (157 g.) was dissolved at 5° in a solution of potassium hydroxide (28·5 g.) in methanol (450 ml.). The mixture was held at this temperature for 36 hours in a refrigerator, allowed to attain room temperature for 12 hours, and finally refluxed for 3 hours. After addition of water (500 ml.), methanol was distilled off and unchanged ester separated by extraction of the aqueous solution with light petroleum. The aqueous layer was then acidified with hydrochloric acid and extracted with warm light petroleum, and the extract cooled overnight at 5°. The required acid ester (83 g.) was obtained by removal of the solvent. The recovered acid was dissolved in methanol (100 ml.) and esterified, with sulphuric acid (10 ml.) as catalyst. The total bulk of recovered diester was then reprocessed and the bulked crude acid ester was fractionated in a 16-plate spinning-band column, to give methyl hydrogen 2 : 2-5 : 5-di(tetramethylene)hexane-1 : 6-dicarboxylate (108·5 g.), b. p. 150°/0·25 mm., n_D^{20} 1·4891.

Dimethyl 2 : 2-5 : 5-8 : 8-11 : 11-*Tetra(tetramethylene)dodecane*-1 : 12-*dicarboxylate*.—The acid ester (108 g.) was electrolysed, 50% excess current being used, and the product processed in the usual way. On fractionation in a spinning-band column, a high-boiling fraction was obtained at 172—180°/0·02 mm., which slowly crystallised. This solid (24·5 g.) was resolved into three components by crystallisation from dilute methanol at low temperature. They were a viscous oil, a trace (0·5 g.) of a microcrystalline powder, m. p. 145°, and *dimethyl* 2 : 2-5 : 5-8 : 8-11 : 11-*tetra(tetramethylene)dodecane*-1 : 12-*dicarboxylate* (18 g.), colourless needles, m. p. 56° (Found : 76·4; H, 10·8. $C_{32}H_{54}O_4$ requires C, 76·6; H, 10·8%). A small quantity of the free *acid* was obtained which crystallised from acetone as colourless needles, m. p. 175° (Found : C, 75·4; H, 10·2. $C_{30}H_{50}O_4$ requires C, 75·9; H, 10·6%).

3 : 3-6 : 6-9 : 9-12 : 12-*Tetra(tetramethylene)tetradecane*-1 : 14-*diol*.—The ester (15 g., 0·03 mol.) was reduced by lithium aluminium hydride (5 g.) in ether (300 ml.), the ester being dissolved from the thimble of a Soxhlet extractor fitted between the flask and reflux condenser by the refluxing solvent. The *diol* (13 g.) crystallised from ether as a microcrystalline powder, m. p. 110—111° (Found : C, 80·4; H, 12·1. $C_{30}H_{54}O_2$ requires C, 80·65; H, 12·2%).

1 : 14-*Dibromo*-3 : 3-6 : 6-9 : 9-12 : 12-*tetra(tetramethylene)tetradecane*.—The diol (12 g.) yielded the *dibromide* (14·5 g., 94%) which, crystallised from light petroleum at low temperature, had m. p. 71—72° (Found : C, 62·8; H, 9·4; Br, 27·6. $C_{30}H_{52}Br_2$ requires C, 62·9; H, 9·2; Br, 27·9%).

3 : 3-6 : 6-9 : 9-12 : 12-*Tetra(tetramethylene)tetradecane*.—The dibromide (13 g.) was reduced by zinc dust and refluxing glacial acetic acid and the product isolated as before. The *hydrocarbon* (6·5 g., 70%) crystallised from methylene chloride at low temperature as colourless needles, m. p. 65° (Found : C, 87·0; H, 12·9. $C_{30}H_{54}$ requires C, 86·9; H, 13·1%).

Methyl Hydrogen cyclo*Hexane*-1 : 1-*diacetate*.—*cyclo*Hexane-1 : 1-diacetic anhydride was prepared in 85% yield from *cyclo*hexanediacetic acid as described for *cyclo*pentanediacetic anhydride. The finely powdered anhydride, m. p. 69°, was slowly added to a stirred solution of sodium (95 g.) in methanol (3 l.) at 0°. When dissolution was complete the mixture was allowed to warm to room temperature and then refluxed for 2 hours. Excess of methanol was distilled off, the residue dissolved in water (3 l.), and the acid ester liberated with a slight excess of hydrochloric acid. It was extracted with benzene and dried by distillation of the benzene. The methyl hydrogen *cyclo*hexane-1 : 1-diacetate was obtained in theoretical yield (879 g.).

Dimethyl 2 : 2-5 : 5-*Di(pentamethylene)hexane*-1 : 6-*dicarboxylate*.—The acid ester described above was electrolysed in batches (145 g.) in the usual way. Distillation of the crude product to 200°/16 mm. removed the by-products and the residue was fractionated in a spinning-band column. The *dimethyl* ester, b. p. 148—152°/0·3 mm., crystallised from acetone at low temperature as large prisms (265 g.), m. p. 40·5°, in 38% yield (Found : C, 71·2; H, 9·9. $C_{20}H_{34}O_4$ requires C, 71·0; H, 10·1%). The free *acid* crystallised from acetone as small colourless prisms, m. p. 194° (Found : C, 69·4; H, 9·6. $C_{18}H_{30}O_4$ requires C, 69·7; H, 9·7%).

3 : 3-6 : 6-*Di(pentamethylene)octane*-1 : 8-*diol*.—The ester (253·5 g., 0·75 mol.) was reduced with lithium aluminium hydride and the resultant diol (168 g.) obtained by crystallisation from ethereal solution. The crude solid (50 g.) recovered from the mother-liquors was reprocessed with lithium aluminium hydride, to give a total quantity of 200 g. (94·5%) of *diol*, m. p. 108—109° (Found : C, 76·9; H, 11·9. $C_{18}H_{34}O_2$ requires C, 76·5; H, 12·1%). The *phenylurethane* derivative crystallised from methanol as fine needles, m. p. 171—172° (Found : C, 73·6; H, 8·4; N, 5·5. $C_{32}H_{44}O_4N_2$ requires C, 73·8; H, 8·5; N, 5·4%).

1 : 8-*Dibromo*-3 : 3-6 : 6-*di(pentamethylene)octane*.—The diol (188 g.) yielded crude dibromide which, being insoluble in light petroleum, was dissolved in hot benzene (2 l.). The solution was washed with hot water and sodium hydrogen carbonate solution and dried by distilling off the benzene. The residue crystallised from benzene–light petroleum, yieding 1 : 8-*dibromo*-3 : 3-6 : 6-*di(pentamethylene)octane* (216 g., 80%) as minute needles, m. p. 104·5—105·5° (Found : C, 53·0; H, 7·9; Br, 38·8. $C_{18}H_{32}Br_2$ requires C, 52·95; H, 7·9; Br, 39·15%).

3 : 3-6 : 6-*Di(pentamethylene)octane*.—The dibromide (184 g.) was reduced to the hydrocarbon by the prolonged action of zinc dust and refluxing acetic acid. The 3 : 3-6 : 6-*di(pentamethylene)octane* (88 g., 78%), isolated as described previously, distilled as a colourless oil at 130°/0·8 mm. (Found : C, 86·1; H, 13·7. $C_{18}H_{34}$ requires C, 86·3; H, 13·7%).

Methyl Hydrogen 2 : 2-5 : 5-*Di(pentamethylene)hexane*-1 : 6-*dicarboxylate*.—This substance was prepared by partial hydrolysis of the dimethyl ester (400 g.) with acetic acid (145 g.) and hydrochloric acid (30 ml.). The mixture was refluxed in an oil-bath and the methyl acetate distilled off through a small column as it formed. When the theoretical quantity of methyl acetate had been removed, benzene (100 ml.) was added and the water removed as the benzene-water azeotrope. The residue was fractionated at reduced pressure, to give unchanged ester at 148°/0·6 mm., acid ester at 168°/0·6 mm., and a residue of diacid. This residue was combined with unchanged ester and heated to 180° till homogeneous; then it was cooled to 100° and hydrochloric acid and dibutyl ether were added in the proportions required for the acid ester synthesis (*Org. Synth.*, **19**, 45). After 5 hours' refluxing, the product was again isolated and fractionated, any diacid and diester being returned for further treatment. In this way the acid ester (280 g.) was obtained in 73% yield as a highly viscous oil

Dimethyl 2 : 2-5 : 5-8 : 8-11 : 11-*Tetra(pentamethylene)dodecane*-1 : 12-*dicarboxylate*.—The acid ester was electrolysed under the conditions already described and the product was fractionated in a spinning-band column. The final fraction (62 g.), b. p. 180—195°/0·05 mm., slowly deposited crystals of the required ester. On crystallisation from methanol, the *dimethyl* ester (35 g., 14·5%) formed large colourless needles, m. p. 94·5° (Found : C, 77·3; H, 11·1. $C_{36}H_{62}O_4$ requires C, 77·4; H, 11·2%). The corresponding *acid* crystallised from dioxan as a white powder, m. p. 202° (Found : C, 76·7; H, 11·0. $C_{34}H_{58}O_4$ requires C, 76·7; H, 11·0%).

3 : 3-6 : 6-9 : 9-12 : 12-*Tetra(pentamethylene)tetradecane*-1 : 14-*diol*.—The ester (30 g.) was reduced by lithium aluminium hydride (5 g.) in ether (600 ml.). The ester was not very soluble in ether and was therefore placed in the thimble of a Soxhlet extractor and dissolved by the refluxing solvent. The solution was finally concentrated. The *diol* (27 g.) separated as a powder, m. p. 117—118° (Found : C, 80·9; H, 12·2. $C_{34}H_{62}O_2$ requires C, 81·2; H, 12·4%).

1 : 14-*Dibromo*-3 : 3-6 : 6-9 : 9-12 : 12-*tetra(pentamethylene)tetradecane*.—The *dibromide* (30 g.) crystallised at low temperature from light petroleum as small needles, m. p. 99—100° (Found: C, 65·5; H, 9·5; Br, 25·3. $C_{34}H_{60}Br_2$ requires C, 65·0; H, 9·6; Br, 25·4%).

3 : 3-6 : 6-9 : 9-12 : 12-*Tetra(pentamethylene)tetradecane*.—The dibromide (24 g.) with zinc dust and glacial acetic acid gave 3 : 3-6 : 6-9 : 9-12 : 12-*tetra(pentamethylene)tetradecane* (10 g., 63%) which crystallised from methylene chloride at low temperature as fine needles, m. p. 70—71° (Found : C, 86·7; H, 13·2. $C_{34}H_{62}$ requires C, 86·7; H, 13·3%).

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