[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

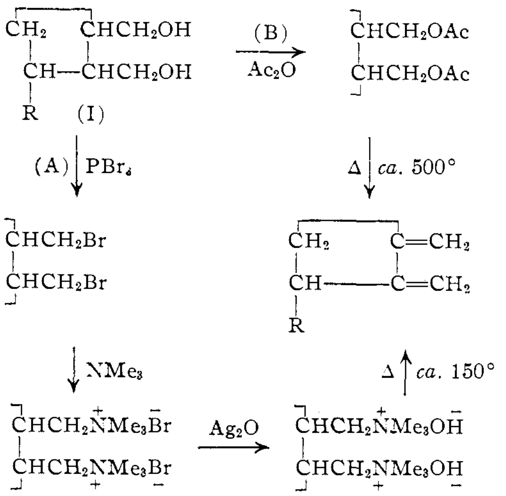
1,2-Dimethylenecyclohexane. Synthesis and Polymerization[1]

BY A. T. BLOMQUIST AND D. T. LONGONE

RECEIVED FEBRUARY 6, 1957

1,2-Dimethylenecyclohexane has been obtained by the thermal decomposition of 1,2-bis-(dimethylaminomethyl)-cyclohexane dimethohydroxide. The syntheses of the precursors for the diene involved standard classical transformations starting with diethyl phthalate. The over-all yield was 27%. A number of polymerizations utilizing several systems and for various reaction times showed that the monomer was much less reactive than its smaller ring homologs, 1,2-dimethylenecyclobutane and 1,2-dimethylenecyclopentane. Polymers obtained were either oils or highly crystalline non-rubbery solids. On the basis of infrared spectra the polymers appeared to be comprised of all *cis*-1,4-units. The polymerization characteristics of this diene appear to be due, at least in part, to its six-membered ring structure.

Previous investigations carried out in this Laboratory concerning the study of conjugated exocyclic dienes have utilized two quite different preparative methods. Both methods may be viewed as starting with the same appropriate glycol I and proceeding as



Path A involves the Hofmann degradation of the appropriate bis-quaternary ammonium hydroxide and path B the pyrolytic decomposition of the requisite diacetate.

On comparing the two methods of preparation it has been found that the Hofmann elimination affords a product of greater purity and in higher yield. It also gives a single product, whereas with acetate pyrolysis a large forerun must be carefully removed in the purification of the diene.

The high pyrolytic temperatures (*ca.* 500°) required in the latter method may lead to ring cleavage in more sterically strained cyclic systems. Thus it has been shown that pyrolysis of 1,2-bis-(acetoxymethyl)-cyclobutane at 485° gives only 2-vinyl-1,3-butadiene while the desired product, 1,2-dimethylenecyclobutane, may be obtained *via* the Hofmann method in 28% yield.[2]

More recently[3] a direct comparison of both methods was made in the synthesis of 1,2-dimethylenecyclopentane and its 3-methyl homolog. Yields and product purity were superior using the Hofmann method.

Because of the encouraging results obtained in these earlier studies it seemed desirable to restudy the synthesis of 1,2-dimethylenecyclohexane (II). This diene has been prepared previously in this Laboratory *via* the acetate pyrolysis at 525° in 29% yield.[4] Emulsion polymerization of the diene, using potassium persulfate as initiator, was carried out at 53° and gave a 53% conversion to a highly crystalline polymer with no rubber characteristics whatsoever. The synthesis and polymerization of II also has been reported by two other groups of investigators. Wicklatz and Short[5] first prepared this diene by dehydrohalogenation of 1,2-bis-(iodomethyl)-cyclohexane and by diacetate pyrolysis at 300–500°; while Bailey and Golden[6] repeated the diacetate pyrolysis at 520°.

Wicklatz and Short[7] obtained a homopolymer of II and described the product as a brittle resin. They also report the ionic polymerization of II using aluminum trichloride at −70° to produce "oily polymers." Bailey and Golden[6] obtained a white crystalline homopolymer melting at 165° using a peroxide-catalyzed emulsion system, an identical polymer from ionic polymerization using boron trifluoride etherate, and a viscous oil using boron trifluoride gas.

The physical properties of the homopolymers of II obtained in the work summarized above are in marked contrast to those of the homopolymers of the smaller ring homologs prepared in this Laboratory. 1,2-Dimethylenecyclobutane[2] and 1,2-dimethylenecyclopentane[3] readily gave elastomeric homopolymers using a persulfate emulsion system. Both monomeric dienes were prepared *via* the Hofmann method. Of further interest is the fact that Bailey obtained only a highly crystalline, nonrubber homopolymer of 1,2-dimethylenecyclopentane using monomer prepared *via* the acetate pyrolysis.[8]

These anomalies led us to suspect that traces of impurities might be present in the monomeric dienes prepared *via* the more drastic acetate py-

---

[1] The work reported here was done as part of a general research program in organic chemistry at Cornell University sponsored by the B. F. Goodrich Co.

[2] A. T. Blomquist and J. A. Verdol, THIS JOURNAL, **77**, 1806 (1955).

[3] A. T. Blomquist, J. Wolinsky, Y. C. Meinwald and D. T. Longone, *ibid.*, **78**, 6057 (1956).

[4] J. A. Verdol, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1955.

[5] J. E. Wicklatz and J. N. Short, U. S. Patent 2,601,075; *C.A.*, **47**, 4366 (1953).

[6] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[7] J. E. Wicklatz and J. N. Short, U. S. Patent, 2,600,454 (1952); *C. A.*, **46**, 11769 (1952).

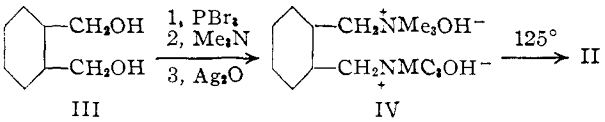
[8] W. J. Bailey, "Conference on Elastomer Research and Development," National Academy of Sciences and National Research Council Publication 370, January 12–13, 1954, p. 115.

rolysis. Olefinic impurities, inherent in the latter method of preparation, would be expected to affect the polymerization of the dienes in a number of possible ways—retarder or inhibitor action, etc.

Since, 1,2-dimethylenecyclohexane (II) had not been prepared by the Hofmann method and information was available concerning its preparation *via* acetate pyrolysis and subsequent polymerization, this investigation was initiated.

The immediate goal was to determine whether the highly crystalline, non-rubber characteristics of the homopolymer II were due to impurities in the monomer prepared *via* the acetate pyrolysis or were unique to this particular six-membered ring system.

1,2-Dimethylenecyclohexane (II).—The synthesis of II was achieved as indicated below.



The glycol 1,2-bis-(hydroxymethyl)-cyclohexane (III) was made by lithium aluminum hydride reduction of diethyl 1,2-cyclohexanedicarboxylate obtained from the catalytic reduction of diethyl phthalate. The over-all yield of III from diethyl phthalate was 84%. Treatment of III with phosphorustribromide gave 1,2-bis-(bromomethyl)-cyclohexane in 90% yield. Conversion of the dibromide to the bis-quaternary ammonium hydroxide IV was effected by treatment with methanolic trimethylamine followed by reaction with freshly prepared moist silver oxide.

Thermal decomposition of IV at 120–125° gave II (40%). After one distillation under nitrogen and reduced pressure the pure diene showed b.p. 73–74° (139 mm.), $n^{25}\text{D}$ 1.4717, and an ultraviolet spectrum maximum (in isoöctane) at 220 mμ with log ϵ 3.82.

Polymerization of II.—Freshly prepared and purified diene was subjected to a number of free radical initiated polymerizations using conventional emulsion and oxidation–reduction recipes and one typical Ziegler recipe. The rate of polymerization in all cases was very slow and homopolymer products were either oils or brittle, powdery solids depending upon extent of polymerization time.

The solid homopolymers were highly crystalline as evidenced by their complete insolubility in all common organic solvents and high melting points. The comparatively narrow melting point ranges indicate absence of extensive crosslinking. The polymerization results are summarized in Table I.

Infrared spectra of the solids (KBr) show the absence of terminal methylene groups and indicate all *cis*-1,4-units in the polymers. Molecular weight estimations either by the Signer—Barger ebullioscopic method, applicable to molecular weights of about 5000, or by intrinsic viscosity measurements could not be made because of solvent difficulties.

The homopolymers reported here are thus very similar to the oils and brittle resins of Wicklatz and Short and the high-melting crystalline solids of Bailey and Golden.

TABLE I

HOMOPOLYMERS OF 1,2-DIMETHYLENECYCLOHEXANE

System	Temp., °C.	Time	Conversion, %	M.p., °C.
Emulsion	50	20 hr.	Oil	.....
Emulsion	50	50 hr.	Oil	.....
Emulsion	50	60 hr.	100	148–152
Emulsion	50	80 hr.	100	148–152
Emulsion	50	135 hr.	100	148–152
Emulsion	50	144 hr.	100	148–152
Oxidation–reduction	50	117 hr.	100	135–144
Oxidation–reduction	5	5 wk.	Oil	.....
Mass (benzoyl peroxide)	50	2 wk.	29	132–135
Ziegler	50	24 hr.	0	.....

Since the diene II was prepared and purified by the same methods used for 1,2-dimethylenecyclopentane and 3-methyl-1,2-dimethylenecyclopentane, its extremely slow rate of polymerization appears to be peculiar to the six-membered ring system. In addition to the increased steric effect present in going from the five-carbon to the six-carbon cyclic monomer a more significant structural difference is the spatial relationship of the exocyclic double bonds. In 1,2-dimethylenecyclobutane and the 1,2-dimethylenecyclopentanes, which polymerize rapidly, the exocyclic double bonds are forced to be coplanar by the steric requirements of the cyclobutane and cyclopentane rings. In 1,2-dimethylenecyclohexane, however, there is a large deviation from coplanarity of the double bond system when the cyclohexane ring is in the chair conformation. The angle between the planes of the double bonds approaches 60° in this conformation. Cyclohexane is known to exist predominantly in the chair form at moderate temperatures and only at elevated temperatures is the boat form important. The ultraviolet absorption maxima of the dienes are a measure of the relative coplanarity of the double bond system. 1,2-Dimethylenecyclohexane has a maximum absorption about 30 mμ lower than the corresponding four- and five-membered ring dienes.

This non-coplanarity of the conjugated system would be expected to decrease the reactivity of the monomer toward 1,4-addition. Free radical addition to one of the exocyclic methylene groups and resultant formation of the endocyclic double bond (1,4-addition) requires twisting the ring system so that the originally non-planar methylene carbon atoms become coplanar. In the smaller ring analogs no such ring contortions are required in the formation of the internal double bond.

Whether this factor is significant enough to account entirely for the marked decrease in the reactivity of the monomer cannot be ascertained at the present time. It is pertinent, however, to mention the extreme difficulty Laughlin[9] encountered in attempting to polymerize 4-neopentyl-1,2-dimethylenecyclohexane in a wide variety of systems; and the low conversions (29–75%) Wolinsky[10] obtained on polymerization of 1,2-dimethylene-4-methylcyclohexane.

[9] R. G. Laughlin, Ph.D. Thesis, Cornell University, 1955.

[10] J. Wolinsky, Ph.D. Thesis, Cornell University, 1956.

Experimental Part

Diethyl 1,2-Cyclohexanedicarboxylate (V).—In a stainless steel hydrogenation bomb diethyl phthalate, 236 g. (1.06 moles), was reduced over Raney nickel at 170° to give crude V. The crude was fractionated through a 60-cm. Vigreux column to give pure diester (94%), b.p. 124–125° (5.4 mm.), n^{25}D 1.4503 (Bailey and Golden[6] reported b.p. 150–152° (23 mm.), n^{25}D 1.4505).

1,2-Bis-(hydroxymethyl)-cyclohexane (III).—Lithium aluminum hydride reduction of 122 g. (0.53 mole) of V carried out in the usual way gave 67 g. (89%) of III, b.p. 142–143° (3.8 mm.), n^{25}D 1.4905 (Haggis and Owen[11] reported b.p. 110–130° (0.3 mm.), n^{20}D 1.4914; Bailey and Golden[6] found b.p. 134–136° (3 mm.), and Wicklatz and Short[5] reported b.p. 145–146° (5 mm.), n^{25}D 1.4880).

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.73; H, 11.13.

1,2-Bis-(bromomethyl)-cyclohexane (VI).—Using the procedure described for the preparation of 1,2-bis-(bromomethyl)-cyclopentane,[3] from 76 g. (0.53 mole) of III there was obtained pure dibromide (90%), b.p. 112–113° (2.5 mm.), n^{25}D 1.5413, d^{25}_4 1.6276; *M*D calcd. for $C_8H_{14}Br_2$ 52.5, found 52.2 (no correction for exaltation due to the six-membered ring).

Anal. Calcd. for $C_8H_{14}Br_2$: C, 35.58; H, 5.23; Br, 59.19. Found: C, 35.63; H, 5.32; Br, 59.33.

1,2-Bis-(dimethylaminomethyl)-cyclohexane Dimethobromide (VII).—A mixture of 59 g. (1.00 mole) of trimethylamine, 44 g. (0.16 mole) of VI and 10 ml. of methanol was kept in a sealed Pyrex bomb at room temperature until separation of solid precipitate was complete. Evaporation of the reaction mixture to dryness *in vacuo* gave the bis-quaternary ammonium bromide (88%). Attempted recrystallization of the crude salt was unsuccessful. A portion of it was converted to the quaternary ammonium picrate which was recrystallized from 95% ethanol. Two picrates were obtained: A, difficultly soluble in hot ethanol and B, very soluble in hot ethanol. Picrate A had m.p. 192–194° and B a m.p. of 166–167°.

Anal. Calcd. for $C_{26}H_{36}O_{14}N_8$: C, 45.61; H, 5.30; N, 16.37. Found: A: C, 45.28; H, 5.11; N, 16.41; B: C, 45.35; H, 5.13; N, 16.18.

1,2-Dimethylenecyclohexane (II).—The crude quaternary ammonium bromide VII (38.2 g., 0.098 mole) was dissolved in a minimum amount of water. Freshly prepared silver oxide was added to the aqueous solution in small portions with stirring. The reaction vessel was cooled with an ice-bath. An immediate exothermic reaction occurred with the formation of yellow silver bromide. The addition of silver oxide was continued until the formation of silver bromide ceased, as was evidenced by the persistence of the dark brown color due to excess oxide. The solid mixture of silver bromide and silver oxide was filtered off and the filtrate, an aqueous solution of 1,2-bis-(dimethylaminomethyl)-cyclohexane dimethohydroxide, was transferred directly into a 200-ml. round-bottomed flask for pyrolysis. The flask was equipped with a Vigreux head and condenser take-off which led to a receiver immersed in an ice-bath. The cold receiver had an outlet leading to a trap immersed in Dry Ice. Hydroquinone was added to the pyrolysis flask and the receiver and the entire system purged with nitrogen. The flask was heated slowly with an oil-bath and under reduced pressure (142–146 mm.). At bath temperature from 90 to 115° mostly water came over at a vapor temperature 66–68°. In the range 115 to 125° oil and water co-distilled at *ca.* 68°. The oil-bath was kept at 125° until the decomposition was complete. The ice-bath receiver contained all the crude diene (upper layer) and it was separated from the water layer and washed with 10% hydrochloric acid to convert the trimethylamine, formed during pyrolysis, to its ammonium salt. After washing with water, until neutral to litmus, and drying over magnesium sulfate the crude diene was distilled from a 25-ml. pear-shaped flask. Distillation was carried out in an atmosphere of nitrogen and in the presence of hydroquinone. Pure diene (5.0 g., 40%) showed b.p. 73–74° (136 mm.), n^{25}D 1.4717 (Wicklatz and Short[5] reported b.p. 48.8–49.4° (55 mm.), n^{25}D 1.4710; Bailey and Golden[6] found b.p. 60–61° (90 mm.), 124° (740 mm.), n^{25}D 1.4718; Verdol[4] gave b.p. 80–81° (130 mm.), n^{20}D 1.4741).

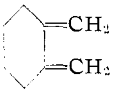
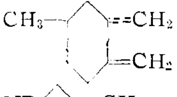
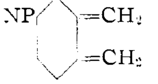
Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.85; H, 11.30.

Reaction of II with Maleic Anhydride.—Maleic anhydride (1.42 g., 0.0145 mole) and 25 ml. of ether were placed in a 50-ml. round-bottomed flask equipped with a reflux condenser. After the addition of 1.57 g. (0.0145 mole) of pure diene II the mixture was allowed to stand overnight during which time a white crystalline solid separated. The ether was evaporated, using a water aspirator, and the crude product recrystallized from ether to give pure $\Delta^{9,10}$-octahydronaphthalene-2,3-dicarboxylic acid anhydride, m.p. 139.5–140.0° (Bailey and Golden[6] reported m.p. 139–140° and Verdol[4] gave m.p. 142–143°).

Absorption Spectra of II.—The infrared spectrum of II was similar to those reported for the smaller ring analogs.[3] Strong absorption is present at 3.26 and 6.08 μ indicative of unsaturation and at 11.35 μ characteristic of the terminal methylene group.

The ultraviolet spectrum of II shows only one peak, λ_{max} (isoöctane) 220 mμ, log ε 3.82 (Bailey and Golden[6] reported λ_{max} 220, log ε 4.00 and Verdol[4] λ_{max} 220, log ε 3.74).

The log ε value reported by Bailey and Golden appears to be somewhat high. Examination of several other compounds containing the same chromophoric group gives values which are in the range 3.7 to 3.8.

Diene	λ_{max}, mμ	log ε	Reference
	220	3·82	This work
	220	4·00	6
	220	3·74	4
	218 (Ethanol)	3·80	10
	217 (Isoöctane)	3·77	10
 NP = neopentyl	221	3·69	9

Homopolymerization of II.—All polymerizations were carried out on about one-gram samples of freshly prepared and purified diene in sealed glass tubes. All polymerizations but one were at 50° in a rotating constant-temperature water-bath. The oxidation–reduction charge at 5° was kept in a refrigerator and frequently hand-agitated. In all cases before sealing, the glass tubes were purged with purified nitrogen to remove oxygen.

The recipes used were

(a) Emulsion
  Monomer, 1.0 g.
  Ivory soap, 0.1 g.
  Initiator solution, 0.1 ml. (3% potassium persulfate soln.)
  Water, 2.5 ml.

(b) Oxidation–reduction emulsion

Monomer	1.0 g.
Water	3.3 ml.
Ivory soap	0.03 g.
Catalyst ($K_2S_2O_8$)	.33 ml. (3% soln.)
Activator (Na_2SO_3)	.005 g.

(c) Mass

Monomer	1.0 g.
Benzoyl peroxide	0.01 g.

(d) Ziegler[12]

Benzene	21.5 ml.
Triisobutylaluminum	0.063 ml. (added as 10% soln. in benzene)
Titanium tetrachloride	0.027 ml. (5% soln. in benzene)
Diene	2.0 ml.

In the Ziegler system no visible change occurred after 24

---

[11] G. A. Haggis and L. N. Owen, *J. Chem. Soc.*, 389 (1953).

[12] We are indebted to C. E. Brockway of the B. F. Goodrich Research Center who carried out this polymerization.

hours at 50°. Addition of 50 ml. of methanol did not precipitate polymer; only a trace of flocculent white solid separated. On standing overnight in an open heater, the solvent evaporated off, leaving a clear yellow sticky wax, evidently very low molecular weight polymer or air oxidation product of monomer.

All other reactions were quenched by chilling the tubes before opening and pouring the contents into a 2% sol. of PBNA in absolute ethanol. Where solid polymers were obtained, they precipitated as gummy particles which on stirring balled up into one mass. After drying at room temperature *in vacuo* the solids were hard, brittle white resins. They were found to be completely insoluble and generally unswollen in all common organic solvents.

Where oils were obtained, unreacted monomer could be recovered as its maleic anhydride adduct from an ether extract of the coagulating solution. The presence of monomer rather than dimer, even after heating at 50° for 50 hours (see Table I), indicates further the decreased activity of this diene. 1,2-Dimethylenecyclopentane, in comparison, dimerizes very readily above 90° or on contact with silica gel to form a self Diels–Alder adduct.[3]

The homopolymers obtained as oils were not further investigated.

Anal. of polymer (solid). Calcd. for $(C_8H_{12})_x$: C, 88.82; H, 11.18. Found: C, 89.09; H, 10.98.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES]

Preparation and Properties of Some Hexadecyl Hydrogen Esters of Dibasic Acids

BY W. FREDERICK HUBER AND E. S. LUTTON

RECEIVED MARCH 4, 1957

Hexadecyl hydrogen esters of the dibasic acids succinic, glutaric, pimelic, maleic and itaconic were prepared and their crystallization behavior studied by means of X-ray diffraction. The compounds melt in the range of 59–77° and show only one crystal form whether from solvent or melt. Each appears to crystallize in double chain-length structure; each shows rather individualistic diffraction behavior except the similar homologous pair, the glutarate and the pimelate.

Introduction

Little is known of the preparation and properties of the longer monoalkyl hydrogen esters of dibasic acids. The preparation of hexadecyl hydrogen succinate by the reaction of succinic anhydride with hexadecanol has been reported.[1] Herein are reported the preparation and X-ray diffraction patterns of the hexadecyl hydrogen esters of succinic, glutaric, pimelic, maleic and itaconic acid.

Experimental

M.p.'s and analyses of the products appear in Table I.

TABLE I

M.P.'S AND ANALYSES OF HEXADECYL HYDROGEN ESTERS

n-Hexadecyl hydrogen ester	M.p., °C.	Analyses, % Neut. equiv. Calcd.	Found	Sapn. equiv. Calcd.	Found
Succinate	63.5–64.5	342.5	340.0	171.3	172.2
Maleate	70–71.5	340.5	338.8	170.3	172.1
Itaconate	76–76.5	354.5	356.0	177.3	175.8
Glutarate	68.5–69.5	356.5	356.7	178.3	177.7
Pimelate	58–59	384.6	382.5	192.3	191.4

The succinate, maleate and itaconate were prepared by heating molar equivalents of the requisite acid anhydride with hexadecyl alcohol at 130–140° for 10 minutes. Hexadecyl hydrogen glutarate and pimelate were obtained by refluxing hexadecanol with excess dibasic acid for about 10 hr. in benzene with *p*-toluenesulfonic acid as a catalyst. The products were purified by recrystallization from hexane. In the case of the pimelate it was necessary to wash the hexane solution with warm water to remove pimelic acid. The structure of the products is unequivocal with the exception of hexadecyl hydrogen itaconate. In this case, esterification can open the anhydride to form either hexadecyl hydrogen α-methylenesuccinate or hexadecyl β-methylenesuccinate. The chemical structure of the itaconate was not explored.

Thermal and X-Ray Diffraction Technique.—Rapid complete m.p.'s and regular complete m.p.'s[2] were determined, the latter on both melted-chilled and solvent-crystallized samples. The single melting-level has been reported under sample preparation. "Rod pellets" of both solvent-crystallized and melted-chilled samples were X-rayed and found to have substantially identical patterns. Flat-film patterns were obtained with a General Electric XRD-1 unit employing nickel-filtered CuKα radiation and a 0.025-in. pinhole system. Sample-to-film distance was normally 10 cm.

X-Ray diffraction data are listed in the following order: compound; long spacing, L.S. (in Å.); short spacings, S.S. (in Å.). Relative intensities of diffraction lines are indicated by (V.S.) = very strong, (S) = strong, (M) = medium, (W) = weak.

Hexadecyl H succinate: L.S. 42.8; S.S. 4.54(S+), 3.98(S), 3.77(W), 3.63(S+)

Hexadecyl H glutarate: L.S. 45.2; S.S. 4.63(W), 4.4(W), 4.11(V.S.), 3.76(S)

Hexadecyl H pimelate: L.S. 50.8; S.S. 4.60(W), 4.14(V.S.), 3.79 (S)

Hexadecyl H maleate: L.S. 29.4; S.S. 5.28(W), 4.64(S), 3.78(V.S.)

Hexadecyl H itaconate: L.S. 40.7; S.S. 4.68(M), 4.44(W), 4.16(V.S.), 3.74(S)

Discussion

While the dibasic acids from which these hexadecyl monoesters were made show a range of m.p.'s covering 90°, the esters show a spread of only 18° with little correlation between relative melting level in the acid and ester series. Each ester shows the same single solid phase whether from solvent or from melt. The several compounds are quite individualistic in X-ray diffraction behavior except for the glutarate and pimelate which are adjacent odd homologs; they show a beta prime-type of pattern rather similar to those exhibited by palmitic and stearic acids. It is a little surprising that the higher homolog melts 10° lower, especially when the acid m.p.'s are in the reverse order.

The chain lengths of these hexadecyl esters should be of the order 28–30 Å. The long spacings which mostly run from 40–50 Å. bespeak tilted double-chain length structures. The maleate long

---

(1) J. T. Davies and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A194**, 417 (1948).

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