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STUDIES ON POLYMERIZATION AND RING FORMATION. II. POLY-ESTERS

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An example of a bi-bifunctional reaction is found in the reaction between a dibasic acid and a dihydric alcohol, HOOC—R′—COOH + HO—R″—OH, which, if it is conducted so as to involve both functional groups of each reactant, must lead to an ester having the structural unit, —OC—R′—CO—O—R″—O— = —R—. In accordance with the thesis developed in the previous paper, esters formed in this way will be polymeric unless the number of atoms in the chain of the structural unit is less than seven. In this paper esters are described in which the number of atoms in the chain of the structural unit is 7, 8, 9, 10, 11, 12, 14, 15, 16, 18 and 22 atoms. All these esters are highly polymeric, and, although some of them have been prepared by various methods, no monomeric form of any of them has as yet been isolated.

Preparation of the Esters

The following method was used for the preparation of the solid esters whose properties are listed in the table. The acid together with a 5% excess of the glycol was placed in a Claisen flask provided with a receiver and condenser, and the flask was heated in a metal-bath. At about 160° (bath temperature) reaction set in. Water distilled off freely during the first hour (temp., 175–185°) and very slowly if at all during the succeeding two hours at the same temperature. The receiver was now changed, the flask provided with a very fine capillary and heating continued under a good vacuum (usually less than 0.2 mm.) for about three hours, the temperature of the bath being raised to 200–250°. During this period little or no distillate collected (provided only a 5% excess of glycol was used). The residue, which was a slightly dark and, at 150°, more or less viscous liquid, was poured from the flask. The amount of this residue corresponded with the theoretical (based on the acid used), and the amount of water actually collected approached the calculated more closely the larger the sample used (60–90%). The esters were purified by crystallization.

Ethylene malonate was prepared by heating ethyl malonate and glycol in the same fashion. There was some decomposition (evolution of gas) when the residue was heated to 240° *in vacuo*. This residue was a thick sirup which could not be induced to crystallize. It was dissolved in acetone, filtered and heated for several hours at 175–190° in high vacuum. Nothing corresponding to a monomeric ethylene malonate was found on redistilling the distillates from this preparation.

The preparation and properties of some esters not included in the table are described in the Experimental Part of this paper.

Structure of the Esters

The conclusion that these compounds are esters and that they contain the structural unit —R— indicated above follows directly from the method of preparation and is supported by the analytical data and chemical behavior. Comparison of Cols. 4 and 5 in Table I shows that the carbon and hydrogen percentages in general agree with those calculated for —R—. So also did saponification numbers where these were determined. The products of saponification of the esters are the acids and glycols from which they were prepared.

That the esters are not monomeric 7-, 8-, 9-, . . ., 22-membered rings is indicated by their physical properties and by their molecular weights. In Col. 7 are given the molecular weights calculated from the observed boiling point elevations or freezing point lowerings, and in Col. 8 the solvents and methods used. The solvents used in the ebullioscopic determinations include chloroform, ethylene chloride, benzene and acetone. Those used in the cryoscopic determinations include benzene, glacial acetic acid and diphenyl ether.

In these determinations it was necessary to use rather large samples to obtain boiling point or freezing point changes of 0.02 to 0.05°. Judged by their self-consistency, the values obtained with the use of freezing benzene have about the same relative accuracy as is ordinarily attained with simple compounds. With other solvents, and especially in the boiling point determinations, observations were much less consistent. This was due in part at least to changes of surface tension, associated no doubt with molecular size, since there was much foaming. The values obtained by this method are recorded, since for some of the esters they are the only ones available, and for others they clearly indicate that the order of magnitude of the apparent molecular weights is quite independent of the character of the solvent used.

The lowest molecular weight observed for any of the solid esters was 2300 and the highest 5000. The mean of all the determinations is 3200, and for purposes of calculation the molecular weight of each ester has been assumed to be approximately 3000. Such a molecular weight corresponds with a value of 8 to 20 (depending on the length of the chain of the structural unit) for n in the general formula $—(—CO—R'—CO—O—R''—O—)—_n$. It can scarcely be supposed that the molecules present in a given sample are all identical so far as the values of n are concerned, but their crystallinity and a certain homogeneity in such physical behavior as solubility indicate that the varieties of molecular species present in a given sample probably do not include a very wide range.

The disposition of the valences at the ends of the chains in the above formula cannot as yet be definitely decided. A cyclic structure is rendered improbable by the same considerations which led us to expect that these esters would be polymeric and which have been discussed in the previous paper. Esters prepared by the method indicated above are definitely not acidic, and since the detection of a carboxyl group in a molecule having a weight of 3000 to 5000 should present no difficulties, no carboxyl groups can be present at the ends of the chains. Attempts to detect the presence of hydroxyl groups have not as yet succeeded. Ethylene succinate crystallizes unchanged from acetic anhydride, and is not affected by phenyl or naphthyl isocyanate. Nevertheless we are inclined to assume that hydroxyl groups are present at each end of the chain due to the presence of one more molecule of glycol than acid: $HO—R''—O—(—CO—R'—CO—O—R''—O—)_n—H$. The failure of these groups to react with reagents may be ascribed to the operation of the same factors which set a limit to the size of the molecules formed.

In general the analytical values agree more closely for such a formula than for a cyclic formula. In Col. 6 of Table I are given the carbon and hydrogen percentages calculated for this formula assuming a molecular weight as close as possible to 3000. The means of the deviations between the carbon and hydrogen percentages found and those calculated for the $—(—R—)—_n$ formula are -0.48 and -0.01%; while the deviations calculated for the $HO—(—R—)_n—R'—OH$ formula are -0.31 and -0.11%.

Assuming a molecular weight of 3000 the chains, $H—[—O—(CH_2)_y—O—CO—(CH_2)_x—CO—]_n—O—(CH_2)_y—OH$, would contain 170–200 atoms and their lengths would lie between 240 and 280 Å.[1] Their lengths are therefore of the same order of magnitude as that assumed by Meyer[1] for the cellulose chains (100 glucose units per chain = 510 Å.). The molecular cohesions calculated from the data presented by Meyer[2] lie between 250,000 and 300,000 cal. or 3.3 to 4 times the heat of separation of a carbon–carbon bond (75,000 cal.). These molecular cohesions are, however, only about 10% of those calculated for a cellulose chain of 500 Å.

The structure of these esters will be discussed in more detail later in the light of experimental work which is not yet completed.

Properties of the Esters

All the esters of the type $—(—CO—(CH_2)_x—CO—O—(CH_2)_y—O—)—$ with the exception of ethylene malonate are crystalline solids. The property of crystallinity is not very highly developed, but it is quite definitely present.[3] This fact is of interest because examples of crystalline highly polymeric substances are not very numerous. As with all crystalline substances of this class, it is not possible to develop large crystals. Ethylene succinate when it separates from a melt or from concentrated solutions (in chloroform) crystallizes in doubly refracting spherolites (microscopic) which grow to what appear to be star-like groups of needles.

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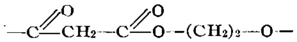
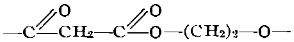
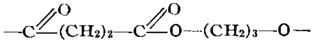
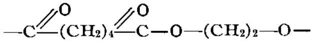
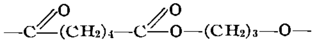
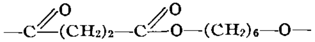
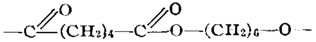
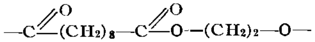
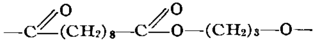
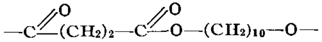
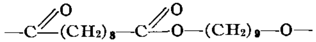
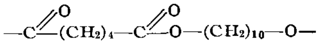
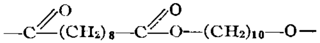
[1] The values C = 1.5 Å. and O = 1.1 Å. are taken from Meyer, *Naturwissenschaften*, **42,** 782 (1928).

[2] Ref. 1, p. 790.

[3] So far as they have been examined in this respect, all these esters give sharp x-ray diffraction patterns.

Table I

Poly-esters

Compound	Formula of structural unit —R—	Atoms in chain of str. unit	Analyses Found, % C	Found, % H	Calcd. for —R—, % C	Calcd. for —R—, % H	Anal. calcd. for HO—(R)$_n$—R″—OH assuming for M. w. the nearest value to 3000 C, %	H, %	n	M. w.	App. mean M. w. obs.	Solvent and method	M. p., °C.
Ethylene malonate	 $-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-$	7	46.42 46.46	4.85 4.84	46.15	4.65					2700, 2500 3500, 2700, 2300	B. p., AcMe, B. p., CHCl$_3$	Liquid
Ethylene succinate	 $-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-$	8	49.75 49.82	5.71 5.61	49.97	5.58	49.75	5.69	20	2943	3400, 3500, 2500 2900, 2500, 2300	B. p., CHCl$_3$ B. p. (ClCH$_2$)$_2$	108
Trimethylene succinate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-O-$	9	52.95 52.72	6.45 6.32	53.13	6.38	52.99	6.48	19	3080	4300, 3500	F. p., AcOH	52
Ethylene adipate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-$	10	55.23 55.28	7.08 7.06	55.78	7.03	55.42	7.08	17	2988	3600, 3900 3400 2700, 2900 2700	B. p ., C$_6$H$_6$ F. p., AcOH F. p., C$_6$H$_6$	50
Trimethylene adipate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-O-$	11	57.42 57.21	7.62 7.50	58.03	7.58	57.76	7.66	16	3054	3600, 3300, 3200 4300, 2400	B. p., C$_6$H$_6$ F. p., AcOH	45
Hexamethylene succinate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_6-O-$	12	59.41 59.32	7.95 7.92	59.97	8.05	60.00	8.22	14	2920	3200, 3500	B. p., C$_6$H$_6$	57
Hexamethylene adipate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_6-O-$	14	62.67 62.57	8.82 8.86	63.10	8.85	63.09	8.96	13	3084	3300	F. p., AcOH	56
Ethylene sebacate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O-$	14	62.37 62.38	8.96 8.81	63.10	8.85	62.62	8.86	13	3028	3100, 3100	F. p., C$_6$H$_6$	79
Trimethylene sebacate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-O-$	15	64.20	9.09	64.41	9.17	63.98	9.20	12	2982	4600, 5000 3100, 3100	B. p. (ClCH$_2$)$_2$ F. p., C$_6$H$_6$	56
Decamethylene succinate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_{10}-O-$	16	64.62 64.67	9.53 9.28	65.57	9.45	65.78	9.63	11	2992	3500, 3400, 3200	B. p., C$_6$H$_6$	68
Hexamethylene sebacate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-(CH_2)_9-O-$	18	66.72 66.97	9.81 9.94	67.56	9.92	67.30	10.01	10	2960	2700, 2600	F. p., C$_6$H$_6$	67
Decamethylene adipate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_{10}-O-$	18	67.23 67.01 67.27	9.82 9.93 9.94	67.56	9.92	67.64	10.09	10	3016	3300, 3200	F. p., C$_6$H$_6$	77
Decamethylene sebacate	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-(CH_2)_{10}-O-$	22	70.32 70.76	10.70 10.73	70.53	10.67	70.44	10.79	8	2896	3000, 3000	F. p., C$_6$H$_6$	74

From dilute alcohol solutions it separates in discrete microscopic needles.[4]

Crystallized ethylene succinate and decamethylene sebacate are dusty powders which have a great tendency to become electrified. Some of the intervening members are quite soft and even somewhat sticky. Ethylene succinate solidifies from a melt as a hard, brittle, opaque, white mass. Decamethylene sebacate solidifies to a white, brittle, waxy solid.

The non-crystalline members include ethylene malonate, ethylene fumarate and ethylene, trimethylene, hexamethylene and decamethylene phthalates. The phthalates and the fumarate evidently have less symmetry than the saturated straight-chain purely aliphatic type. The lack of crystallinity of the malonate may be associated with the low melting point of the malonic acid; or it may be due to the fact that considerable decomposition occurred during the process of esterification.

The melting points of the solid esters are not very sharp and they depend somewhat upon the rate of heating. This latter effect is noticed especially with ethylene succinate.

When the crude reaction mixture is dissolved in chloroform and precipitated with benzene, the resulting dusty white powder melts in a capillary tube at about 102°. If, however, the tube is placed in a bath which has already been heated to 96° the sample melts at once. The two melting points are called the slow and instantaneous melting points, respectively, and they are best observed on a bloc Maquenne. Samples which are dusted on the bloc when it is below 96° do not melt until it reaches 102°, but as soon as the bloc reaches 96° samples melt the instant they touch it. Both these temperatures may be changed somewhat by repeated crystallization, but a sample whose melting point has been raised by repeated crystallization may suddenly show the original melting point on further crystallization. By long extraction with boiling absolute alcohol in which it is practically insoluble, ethylene succinate is modified so that the instantaneous and slow melting points coincide at about 107–108°, and from the extracts may be isolated a very small amount of lower-melting material. When such a high-melting sample is again crystallized from a mixture of chloroform and benzene or ether, the melting point usually drops, and one observes again the instantaneous melting point of 96° and the slow melting point 102°. The melting point of such samples may also be raised by long heating just below 100°, and both melting points then gradually approach 107°. When a 96, 102° sample is quickly melted, then allowed to solidify in an agate mortar and powdered, the instantaneous melting point is lowered somewhat, and the slow melting point may be either raised or lowered, depending upon the time during which the molten material is heated.

Attempts to define the melting point more clearly by heating or cooling curves on fairly large samples were unsuccessful.[5] Apparently the viscosity of the melt is so great

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[4] Incidentally these are the forms in which Hess' trimethylcellulose crystallizes, and the photomicrographs (Figs. 78, 80 and 81) which he presents ("Die Chemie der Zellulose," Leipzig, **1928**, p. 432) for this substance would serve almost perfectly as pictures of ethylene succinate. The crystallinity of this trimethylcellulose therefore provides no guarantee either than it contains only a single molecular species, or that the molecules present are not very large.

[5] Some experiments were kindly made for us by Dr. E. L. Skau with the special apparatus which he has devised for the precise determination of the melting points of pure organic compounds.

as to make the process of crystallization slow even in the presence of previously formed crystals and under a considerable temperature gradient.

The erratic behavior of the melting points may be associated with the fact that all these esters are hygroscopic, but the absorption of water cannot be the sole cause for this behavior, for samples of ethylene succinate having various melting points were stored over 20% sulfuric acid for ten days and all of them gained considerably in weight without changing in physical appearance or melting point.

Anomalies in melting points are not unknown among compounds of definite constitutions and relatively low molecular weights. One may cite, for example, the fact that sucrose separates from methyl alcohol in crystals melting at 169–170° and from other solvents in crystals melting at 179–180°, and these two forms do not show any detectable chemical differences.[6] But the case of ethylene succinate appears to be more complicated and confused than this. Its melting point depends upon its history in a fashion which can as yet be defined only to the following extent—it always rises and approaches 107° as it is, while still in the solid state, heated or extracted with boiling absolute alcohol.

Among the other esters these irregularities were less pronounced. Nevertheless, the melting points are not very characteristic and no attempt was made to crystallize them to constant melting points. Instead they were crystallized two to six times depending upon the color and softness of the sample. The melting points recorded are the highest observed for complete melting and are usually within 5° of the lowest observed for any sample of the same material. The melting range was usually less than 2°. The melting point of the decamethylene ester of a given acid was higher than that of the hexamethylene ester. The melting point of the hexamethylene ester was higher than that of the trimethylene ester, which was in turn lower than that of the ethylene ester. With one exception, the adipic ester of each glycol melted lower than either its succinic or sebacic ester.

All of these esters are, when molten, quite viscous. Those which do not crystallize on cooling become more or less hard, tough and glassy. The use as resins of esters formed by the action of polybasic acids on polyhydric alcohols has been covered by numerous patents.[7] The impression seems to prevail that all such esters are resins. Of the esters described in this paper the majority are crystalline. The phthalates which we have prepared are, however, all resinous. Ethylene phthalate is quite tough and moderately hard. Neither this ester nor the trimethylene, hexamethylene nor decamethylene esters of the same acid have been described in the scientific literature. As the length of the alcohol chain increases, these phthalates become progressively softer. Decamethylene phthalate has the consistency of a moderately thick sirup.

None of these esters is volatile. Each of them has been heated to

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[6] Pictet and Vogel, *Helv. Chim. Acta*, **11**, 901 (1928).

[7] See for example U. S. Patents Nos. 1,108,332; 1,091,627; 1,091,628; 1,091,732 1,108,329; 1,108,330; 1,108,331; 1,642,079; 1,678,105; 1,098,776; 1,098,777; 1,424,137; 1,413,144; 1,413,145; 1,667,199; 1,667,200; 1,119,592; 1,141,944; 1,663,183.

200° *in vacuo* without showing any tendency to distil. Ethylene succinate heated for three hours at 250° under a pressure of 2 mm. is not changed in properties, and its analytical composition (carbon, hydrogen and saponification number) is not changed. It shows no tendency to distil or to evolve any volatile products when heated to 280° at a pressure of 1 *micron*. At 350° ethylene succinate undergoes complete thermal decomposition, the products being ethylene, acetaldehyde, succinic anhydride, carbon, etc.[8]

All of these esters are insoluble, or nearly so in water, alcohol, petroleum ether and ether.[9] The least soluble of the saturated aliphatic esters is ethylene succinate. It is more or less soluble in hot ethyl acetate, acetic acid, acetic anhydride, ethyl succinate and acetone, and it crystallizes from these solvents on cooling. It is insoluble in benzene. The other saturated aliphatic esters with the exception of ethylene malonate are readily soluble in cold benzene and at least moderately soluble in acetone, ethyl acetate and glacial acetic acid. The solutions are noticeably viscous only when fairly concentrated (*e. g.*, 10% or stronger). This fact and the rapidity with which solution occurs lead us to believe that the solutions are true molecular dispersions.

Although none of these esters is soluble in water they are all somewhat hygroscopic. This property is especially pronounced in those poly-esters which are not crystalline. The drying of these resins was very difficult and, as the analytical results indicate, was not always successful. Drying to constant weight was complicated by the tendency to foam when heated *in vacuo*.[10]

Other Methods of Preparation

The only detailed study of poly-esters of the type here described which we have found is reported in a paper by Vorländer.[11]

Ethylene succinate was first prepared by Lourenço[12] by heating succinic acid and ethylene glycol to 300° (m. p. about 90°). Subsequently Davidoff[13] prepared Lourenço's ester and identified it with one which he obtained by heating silver succinate with ethylene bromide. Vorländer

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[8] Tilitschejew, *J. Russ. Phys.-Chem. Soc.*, **57**, 143 (1925).

[9] It is interesting to note that Freudenberg and Braun's trimethylcellulose, like ethylene succinate, is insoluble in ether and carbon tetrachloride, but quite soluble in chloroform [*Ann.*, **460**, 288 (1928)].

[10] It is interesting to observe that inulin, a polymeric substance of a different type, but probably of the same degree of molecular complexity as the esters here described is also quite hygroscopic. *Cf.* Drew and Haworth, *J. Chem. Soc.*, 2690 (1928).

[11] Vorländer, *Ann.*, **280**, 167 (1894). See also Bischoff, *Ber.*, **27**, 2940 (1894); **40**, 2779, 2803 (1907). Glycol esters of adipic acid are referred to in German patent 318,222, *Chem. Zentr.*, II, 536 (1920).

[12] Lourenço, *Ann. chim. phys.*, 293 (1863).

[13] Davidoff, *Ber.*, **19**, 406 (1886).

studied this latter compound in detail and showed that its chemical behavior was in all respects what would be expected of an ethylene ester of succinic acid. He also identified it with Lourenço's ester and with one obtained by the action of succinyl chloride on the disodium derivative of ethylene glycol.

Vorländer found that his ethylene succinates prepared from silver succinate and from succinyl chloride had apparent molecular weights ranging from 265 to 321 in freezing phenol and in freezing acetic acid. He supposed them to be dimeric, and in accordance with this view was able to prepare the same compound from silver succinate and di-(β-chloro-ethyl)-succinate. This method of synthesis evidently merely establishes that the compound was probably not monomeric.

The properties which Vorländer records for ethylene succinate agree in general with those which we have observed. We have found that it is possible to prepare ethylene succinates having, within certain limits, various melting points (and molecular weights) by heating succinic acid and glycol in various proportions. The highest melting (102°) is that described above. It was prepared from acid and excess glycol. Vorländer and other writers on this subject ascribe to ethylene succinate a melting point of 88–90°. We have obtained samples showing this melting point by using the acid and glycol in equivalent amounts; and, by using excess acid, have obtained lower-melting samples. These ethylene succinates differ somewhat in solubility, but they are alike in physical appearance, in their lack of volatility and in their viscous character when molten. All of these materials are highly polymeric. We have also prepared ethylene succinate from silver succinate and ethylene bromide according to Vorländer's directions. This reaction does not proceed smoothly, and our product was slightly colored and melted at 75° instead of at 90°. Nevertheless, molecular weight determinations in boiling ethylene chloride gave values ranging from 1400 to 2000. We think, therefore, that Vorländer's molecular weight determinations must be in error; and this conclusion is supported by the fact that the properties which he records and which we have observed are not consistent with so low a molecular weight as 288.

We have also prepared ethylene succinate from ethyl succinate and glycol. It is also highly polymeric. Thus the methods which have been used for the preparation of this compound include four separate and distinct methods commonly used in the preparation of esters. They all lead to products of the expected composition but of high molecular weights. There is not the slightest reason for supposing that the monomeric ethylene succinate should be incapable of existence, or even that it should be unstable, but it still remains unknown. These facts find their explanation in the thesis developed in the previous paper.

Vorländer also prepared ethylene maleate and ethylene fumarate by the silver salt method. He could not obtain any consistent values for the molecular weights of these materials. We have prepared the fumarate from ethyl fumarate and the maleate from maleic anhydride. Our preparations differ from those of Vorländer in several respects. Thus, our maleate was crystalline and our fumarate resinous. The reverse was true for Vorländer's compounds. Neither our analytical values nor his agree well with the calculated. These esters appear to be much more complicated in their behavior than ethylene succinate. They both become completely insoluble on heating.

Experimental Part

Ethylene Phthalate No. 1.—Ethylene glycol 62 g. (1 mole) and phthalic anhydride 74 g. (0.5 mole) were heated together for eight hours at 190° under ordinary pressure and for three hours at 300° under 3 mm. The viscous residue was heated with boiling water for twenty minutes, dissolved in chloroform, filtered and precipitated with ether, and then dissolved in acetone, filtered and precipitated with water. It was then dried by heating to 160–170°. The resulting glassy resin was fairly hard when cold, and became softer on heating. All attempts to induce it to crystallize failed. It was neutral: 2 g. required 0.03 cc. of 0.23 *N* NaOH for alkalinity toward phenolphthalein. It was soluble in chloroform, acetone, ethyl acetate and acetic acid; insoluble in petroleum ether, ether, benzene, alcohol and water.

Anal. Substance dried to constant weight in high vacuum at 70°. Calcd. for $C_{10}H_8O_4$: C, 62.48; H, 4.19; molecular weight, 192; saponification number, 96. Calcd. for $H[O(CH_2)_2OOCC_6H_4CO]_{25}O(CH_2)_2OH = C_{252}H_{206}O_{102}$: C, 62.15; H, 4.28; molecular weight, 4864; saponification number, 97.3. Found: C, 61.86, 61.95; H, 4.29, 4.30; molecular weight by micro boiling point method in ethylene chloride, 4830, 5070, 4680, 4690; saponification number, 95.7.

Ethylene Phthalate No. 2.—This was prepared in the same way as No. 1, but with a 20% excess of phthalic anhydride and was purified in a similar fashion. Appearance and solubility were the same as for No. 1.

Anal. After drying to constant weight in high vacuum at 70°. Found: C, 62.11, 62.07; H, 4.29, 4.33; molecular weight, by method of Menzies and Wright in ethylene chloride, 2940, 2700, 3020; by micro boiling point method in ethylene chloride, 3030, 2930; saponification number, 96.2.

Ethylene Phthalate No. 3.—Prepared by heating diethyl phthalate (0.5 mole) with ethylene glycol (1 mole) in the same fashion and purified as before. Appearance and solubility were the same as for No. 1.

Anal. after drying to constant weight in high vacuum at 70°. Found: C, 62.35, 62.14; H, 4.40, 4.37; molecular weight, by freezing point lowering in diphenyl ether, 2070, 2030; by method of Menzies and Wright in ethylene chloride, 1990, 2100, 2050, 1770; by micro boiling point method in ethylene chloride, 2100, 1870.

Ethylene Phthalate No. 4.—This was prepared by stirring vigorously 19 g. of glycol (added slowly) with 60 g. of phthalyl chloride and 51 g. of dry pyridine in 125 cc. of chloroform at 0–5°. The reaction mixture was washed thoroughly with dilute acid and dilute sodium carbonate and water, and decolorized with Darco. After drying the chloroform solution the ester was precipitated with ether. The yield was 53 g. It resembled the other ethylene phthalates, but its solutions in chloroform were less viscous —0.016 poise for a 20% solution at 27° as compared with 0.027–0.031 poise for the other ethylene phthalates. Its apparent molecular weight was also lower.

Anal. after drying to constant weight in high vacuum at 70°. Found: C, 61.64, 61.64; H, 4.28, 4.30; molecular weight, by method of Menzies and Wright in ethylene chloride, 1550, 1610; saponification number, 99.5, 99.6.

Hydrolysis of Ethylene Phthalate.—Twenty grams of ethylene phthalate was refluxed for sixty-four hours with 60 g. of 48% hydrobromic acid. After neutralization with sodium carbonate, the reaction mixture was steam distilled. From the distillate was isolated 16.7 g. or 86.6% of the calculated amount of ethylene bromide, b. p. 131–134°. The residue on acidification gave 16.3 g. or 93.6% of the calculated amount of phthalic acid. This on conversion to the anhydride melted at 130–131°.

Trimethylene Phthalate.—Seventy-four grams (0.5 mole) of phthalic anhydride and 38 g. (0.5 mole) of trimethylene glycol were heated at 250° for two hours under ordinary pressure and under diminished pressure for two hours. The residue was dissolved in benzene, treated with Darco, filtered and precipitated with ether. When cold it was a clear, glassy solid, somewhat softer than ethylene phthalate. It was soluble in chloroform, benzene, acetone, ethyl acetate and acetic acid; slightly soluble in alcohol; insoluble in ether, petroleum ether and water.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.08; H, 4.89; molecular weight, 206. Calcd. for $H[OOCC_6H_4COO(CH_2)_3]_{15}O(CH_2)_3OH = C_{168}H_{158}O_{62}$: C, 63.63; H, 5.05; molecular weight, 3168. Found: C, 63.68, 63.51; H, 5.17, 5.12; molecular weight by micro boiling point method in ethylene chloride, 3180, 3030.

Hexamethylene Phthalate.—Twenty-nine and six-tenths g. of phthalic anhydride and 23.6 g. of hexamethylene glycol were heated to 180–190° under atmospheric pressure for two and one-half hours and then for one and one-half hours at 250° under 5 mm. In addition to the water, some phthalic anhydride collected in the receiver. The residual dark gum was purified by dissolving in benzene, decolorizing with Darco, and precipitating with ether. It formed a clear, light brown, sticky gum. Solubility: solvents are the same as for trimethylene phthalate, but hexamethylene phthalate is more soluble.

Anal. after drying to constant weight in high vacuum at 70°. Calcd. for $C_{14}H_{16}O_4$: C, 67.75; H, 6.50; molecular weight, 248. Calcd. for $H[O(CH_2)_6OOCC_6H_4CO]_7O-(CH_2)_6OH = C_{194}H_{126}O_{30}$: C, 67.35; H, 6.85; molecular weight, 1855. Found: C, 66.74, 66.84; H, 6.75, 6.85; molecular weight by freezing point lowering in benzene, 1700, 1830.

Decamethylene Phthalate.—Seven and four-tenths g. of phthalic anhydride and 9 g. of decamethylene glycol were heated at 190–200° for two hours under atmospheric pressure, and at 210–220° for one and one-half hours at 5 mm. The residue was dissolved in benzene, decolorized with Darco and precipitated by petroleum ether. It was a clear, light brown, thick, sticky sirup. Solubility: solvents for decamethylene phthalate are the same as for hexamethylene phthalate, but the former is more soluble.

Anal. after drying to constant weight in high vacuum at 70°. Calcd. for $C_{18}H_{24}O_4$: C, 71.01; H, 7.95; molecular weight, 304. Calcd. for $H[O(CH_2)_{10}OOCC_6H_4CO]_7O-(CH_2)_{10}OH = C_{136}H_{190}O_{30}$: C, 70.80; H, 8.39; mol. wt. 2303. Found: C, 70.66, 70.44; H, 8.21, 8.26; molecular weight by freezing point lowering in benzene, 2250, 2060.

Ethylene Fumarate.—Fifty-seven and three-tenths g. of diethyl fumarate (0.33 mole) and 25 g. of ethylene glycol (0.4 mole) were heated for ten hours in a stream of nitrogen, the temperature being gradually raised from 190 to 230° and the pressure being reduced at the end to 4 mm. The residue weighed 35 g. or 75% of the calculated amount. It was accompanied by some insoluble material from which it was freed by solution in chloroform, filtration and precipitation with ether. It was washed several times with dry ether. It formed a transparent, slightly yellow, moderately tough mass. After drying it became insoluble in the common solvents.

Anal. after drying to constant weight in high vacuum at 70°. Calcd. for $C_6H_6O_4$: C, 50.70; H, 4.22. Found: C, 51.95, 51.89. H, 6.06, 6.12. Molecular weight determinations could not be made because of the lack of solubility after drying.

Ethylene Maleate.—Thirty-two and five-tenths g. of maleic anhydride (0.33 mole) and 18.6 g. (0.30 mole) of glycol were heated at 195–200° for four hours, and then for some time at 210–215° under reduced pressure. The residue (40 g.) was separated from some insoluble material by solution in warm ethylene chloride and filtration. It was precipitated by cold ether. The product separated as an oil but solidified on standing at 5–10° for two hours. It was a white powder. Most of it melted between 88 and 95°. After drying *in vacuo* it had become insoluble in the common solvents including ethylene chloride and it did not melt below 250°.

Anal. after drying to constant weight in high vacuum at 70°. Calcd. for $C_6H_6O_4$: C, 50.70; H, 4.22. Found: C, 49.87, 49.70; H, 4.36, 4.28. Molecular weight determinations could not be made because of the lack of solubility after drying.

For his kind assistance in the analytical work we here express our thanks to Mr. Wendell H. Taylor.

Summary

The following esters have been prepared: ethylene malonate, ethylene succinate, trimethylene succinate, ethylene adipate, trimethylene adipate, hexamethylene succinate, hexamethylene adipate, ethylene sebacate, trimethylene sebacate, decamethylene succinate, hexamethylene sebacate, decamethylene adipate, decamethylene sebacate, ethylene maleate, ethylene fumarate, ethylene phthalate, trimethylene phthalate, hexamethylene phthalate and decamethylene phthalate. Their molecular weights have been determined. They are all highly polymeric. Their properties are described and their structures are discussed.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SHARP AND DOHME]

A NEW SERIES OF ANESTHETICS. ACYLANILINE DERIVATIVES

BY WALTER H. HARTUNG AND J. C. MUNCH

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While working in these Laboratories with *m*-aminobutyrophenone, it was found that this compound produced anesthesia in the lips and tongue. Examination revealed further that an aqueous solution of its hydrochloride also was anesthetic to the lips and tongue and when injected subcutaneously into animals. This fact was of sufficient interest to warrant investigation of other bases, and their salts, of the same general type as aminobutyrophenone. Accordingly, a series of acylanilines and acyltoluidines was prepared, a series of anesthetics to which no previous reference has been found.

Table I lists those compounds that have been prepared and established by analysis, for only the first two have been previously recorded; the table also includes preliminary data on the toxicity and anesthetic potency of the