treatment with potassium hydroxide and refluxing at 350° for ten hours in the presence of copper as catalyst. A yield of 33% was obtained, distilling at 326–329°. It has a pleasant odor, crystallizes in small cubical crystals which melt at 33–34° and is soluble in most solvents, though only slightly soluble in ligroin, It is not affected by potassium hydroxide in aqueous solution and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.09. Found: C, 72.82, 73.18; H, 6.14, 6.02.

Summary

1. Five new alkoxy derivatives of diphenyl oxide were prepared. They are compounds of great stability to alkalies or acids and to heat, of pleasant odor and of low surface tension.

2. In the preparation of phenols for condensation, a new method of procedure was discovered, namely, the hydrolysis of diazonium salts in hot acid solution under a layer of inert solvent, which prevents the formation of tarry by-products by removing the phenol from the acid hydrolyzing solution as rapidly as it is formed.

3. Of several catalysts used, finely divided freshly reduced copper gave the best yields.

PULLMAN, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OMEGA-HYDROXY ALIPHATIC ACIDS. II. CONVERSION OF OMEGA-HYDROXYDECANOIC ACID TO CHAIN POLY-INTERMOLECULAR ESTERS AND TO A DIMERIC CYCLIC ESTER[1]

BY W. H. LYCAN[2] AND ROGER ADAMS

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In a previous paper a satisfactory method of preparation for many ω-hydroxy aliphatic acids was described. Attention was called to the fact that by the action of heat on such acids compounds were produced which appeared to be of high molecular weight. In this investigation these latter compounds are described in more detail. Several other reactions of ω-hydroxy acids have been studied.

A recent paper by W. H. Carothers[3] has given a very clear exposition on polymerization: a proper definition, conditions of ring formation and an introduction to the theory of condensation polymers. The terminology in that publication has been adopted here. As pointed out in a general discussion by Carothers, bi-functional reactions may be either intramolecular or intermolecular. In the first case, the products will be monomeric

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[1] Lycan and Adams, THIS JOURNAL, 51, 625 (1929).

[2] This paper is an abstract of a thesis submitted by W. H. Lycan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Carothers, THIS JOURNAL, 51, 2548 (1929).

rings; in the second case the products will be polymeric rings or long chains. Intramolecular reaction takes place with readiness only when five- or six-membered rings are possible; whenever an intramolecular reaction would lead to rings of greater size, the reaction almost invariably proceeds intermolecularly with the formation of chain polymers.

The sole products of heating ω-hydroxydecanoic acid alone or with solvents, with or without a catalyst, were chain poly-esters. A lactone was never detected among the products. The general structure of these high molecular weight compounds may be represented by the formula

$$HO(CH_2)_xCO_2—[(CH_2)_x—CO_2—]_n(CH_2)_x—COOH$$

The poly-esters were obtained as complex mixtures and crystallized from solvents as fine white powders. The crystals were less than microscopic in dimension but were definitely crystalline, inasmuch as sharp x-ray diffraction patterns were readily obtained.[4] The mixtures were, in general, soluble in the hot in acetone, alcohol, chloroform, benzene, toluene and ethyl acetate, but were only sparingly soluble in the cold. They were completely insoluble in water and ether.

The presence of the free carboxyl group in these molecules was demonstrated by the fact that their potassium salts were completely soluble in hot water. Furthermore, the exactly neutral potassium salt was perfectly stable in hot water. This was shown by the fact that a polymer recovered from its potassium salt by acidification with mineral acid had exactly the same properties and the same molecular weight as it had before neutralization. If ring compounds were present in the original polymer, either it would not be completely soluble in alkali or it would be partially hydrolyzed. In the latter event the recovered polymer might be expected to give a different average molecular weight determination, and different properties from the original polymer. There was no evidence that either of these things occurred.

The presence of a free hydroxyl group was also demonstrated beyond reasonable doubt. A polymeric mixture of average molecular weight of about 1100 yielded an acetyl derivative upon heating with acetic anhydride in boiling benzene. The fact that the average molecular weight of the product increased to about 1800 during the course of this reaction was not entirely unexpected. In addition to acting as an acetylating reagent the acetic anhydride might readily have acted as a catalyst for further intermolecular esterification. Intermolecular esters prepared in boiling benzene, using *p*-toluenesulfonic acid as a catalyst, had average molecular weights of about 2500. Thus the reactions of acetylation and further intermolecular esterification may be regarded as competing re-

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[4] Dr. G. L. Clark of the Chemistry Department of the University of Illinois has been kind enough to take x-ray photographs of some of these polymers. The detailed results will be published independently in a later communication.

actions. The acetyl polymer was characterized by its lower melting point (68–72° as compared to 74–76° for unacetylated derivative) and increased solubility in solvents. After hydrolysis with aqueous alkali and acidification with phosphoric acid, distillation yielded an acidic distillate. That this acetic acid could not have resulted from combination of the acetic anhydride with the free carboxyl group in the form of mixed anhydride is indicated by the increased molecular weight of the product. If it be assumed that acetic anhydride does not catalyze intermolecular esterification to a greater extent than *p*-toluenesulfonic acid, a decrease in average molecular weight would result from mixed anhydride formation.

The ordinary methods of molecular weight determination have never been extremely satisfactory for compounds of high molecular weight. In most cases the high polymers have not been sufficiently soluble in solvents to produce differences in boiling points, freezing points or vapor pressure large enough to permit of accurate measurement. Furthermore, it has not been possible to show that high molecular weight values thus obtained have not resulted from some kind of abnormal association in solution. Several attempts were made to determine average molecular weight values for a polymeric mixture, both by the boiling-point and freezing-point methods in benzene. The results varied from 1500 to 3000 in successive readings, and the same values could not be duplicated with any degree of accuracy. Average molecular weights were determined on the same material by titration of the free carboxyl group and these values never varied more than 5–8% from a mean of 2800. Inasmuch as free hydroxyl and free carboxyl groups often lead to abnormal molecular weights by the ordinary methods, it need not necessarily be inferred that the varying results obtained above are the limits of accuracy for other polymers.

The average molecular weights of these poly-esters were obtained easily by titration of the free carboxyl group. Large samples were titrated with fiftieth normal alkali solutions and from the values thus obtained average molecular weights were calculated. Inasmuch as the results of these titrations could be duplicated fairly closely with successive samples of the same mixture of polymers, it seems reasonable to assume that these were close approximations of the correct values. Furthermore, the values obtained from successively recrystallized samples increased in the regular manner expected; that is, the recrystallizations resulted in the concentration of the less soluble and more highly polymerized molecules. The filtrates yielded the more soluble fractions, which were constituted of fewer molecules of the parent acid, and the molecular weights determined for these fractions were characterized by a corresponding decrease. As the molecular weight of the polymer increased, the values obtained were subject to increased error. Even with polymers of average molecular weight as high as 9000, however, the error was not over 10%. The error in the values obtained for the lower polymers was ordinarily considerably less than 10%.

It has been previously intimated that the samples of poly-esters used for the molecular weight determinations were mixtures rather than individual compounds. It was impossible to obtain pure definite components from the highly complex mixtures in the reaction products because of the wide number of possible combinations and the similarity in solubility between each of them. The difference in solubility between a polymer constituted of twenty structural units and one constituted of ten is great enough to permit of separation, but when the mixture is made up of molecules containing every possible constituent from five or six to thirty structural units, separation becomes impossible. These mixtures were separated into fractions in which the components of each fraction were constituted of members of the same order of magnitude of structural units. However, the solubilities of the individual compounds of any one of these fractions were so similar that separation into individual components could not be effected. The molecular weight values observed, therefore, represent average values for a mixture constituted of a number of very similar components.

The addition polymers of Staudinger[5] result from equilibrium reactions and higher temperatures usually lead to lower polymers, whereas the poly-esters are formed by the elimination of molecules of water, and higher temperatures always lead to higher polymers. The lower temperature limit for the formation of polymers of ω-hydroxydecanoic acid without the presence of catalyst, was in the neighborhood of 100°. At any rate, heating the fused acid by itself at this temperature resulted in the formation of polymers composed of an average of between five and six structural units. Heating in a solvent required a somewhat higher temperature, perhaps because the alcohol–acid molecules were more widely dispersed. Heating in boiling toluene (b. p. 110°) over a considerable period of time resulted in only the very beginning of esterification. However, heating in cymene (b. p. 175°) resulted in a polymeric mixture of molecules constituted of an average of about six structural units. Other polymeric fractions were obtained by heating the fused acid over long periods of time at 200–210° and at 220–250°, respectively. The latter experiment produced polymers of average molecular weight of about 9000. In other words, these mixtures were composed of molecules constituted of in the neighborhood of fifty structural units.

[5] Staudinger and co-workers, *Helv. Chim. Acta.*, **5**, 785 (1922); **7**, 23, 842 (1924); **8**, 41, 65, 67 (1925); **9**, 529 (1926); *Ber.*, **53**, 1073 (1920); **57**, 1203 (1924); **59**, 3019 (1926); **60**, 1782 (1927); **61**, 2427 (1928); **62**, 241, 263, 442 (1929); *Ann.*, **447**, 97, 110 (1926); *Z. physik. Chem.*, **126**, 425 (1927); *Kautschuk*, 237 (1927).

The use of *p*-toluenesulfonic acid permitted the reaction to proceed at a considerably lower temperature and resulted in a higher degree of poly-intermolecular esterification. The reaction proceeded smoothly in boiling benzene (b. p. 80°) with the production of a polymer of average molecular weight of about 2000. About the same results were obtained by its use in boiling toluene (b. p. 110°) but in cymene (b. p. 175°) polymers of much higher molecular weight were formed.

A few words should be said concerning the nature of one of these reaction mixtures from any of the sources described. The original mixture might have, for example, an average molecular weight of 2000. This product would then be recrystallized repeatedly and samples titrated during the progress of their recrystallizations. The values obtained for the less soluble material continually increased, and after ten recrystallizations the average molecular weight would be in the neighborhood of 4000. The first few filtrates yielded samples whose average molecular weights were in the neighborhood of 1000. In other words, the mixtures all contained compounds constituted of a large number of degrees of esterification, and heating at increased temperature and the presence of a catalyst resulted in an increased predominance of the more highly esterified compounds.

The polymers obtained by these poly-intermolecular esterification reactions are obviously analogous to the natural "etholides" obtained by Bougault and Bourdier[6] from the waxes of a variety of conifers. These natural poly-esters were extracted from the desiccated leaves of the conifers with alcohol, and were purified by repeated crystallizations from the same solvent. As has been the case with their synthetic analogs, no pure components were isolated. They were characterized as being white powders and had, in general, the same solubilities that have been observed for the poly-esters of ω-hydroxydecanoic acid. These compounds yielded, upon hydrolysis, the two natural acids, juniperic and sabinic acids, mentioned in the previous paper.[1] It is entirely possible that both acids are combined in the single complex compounds which constitute the polymeric mixture. The following general structure was assigned to the polymer as a result of their experiments.

$$HO(CH_2)_x—CO[O(CH_2)_y—CO—]_nO(CH_2)_zCO_2H$$

Titration values indicated that the average molecular weight of the natural substances was between 1000 and 2000. The only products of complete hydrolysis were the alcohol–acids and the saponification numbers experimentally determined corresponded closely to the values calculated on this assumption. Furthermore, it was possible to prepare an acetyl derivative and the saponification number was modified an amount corresponding to the theoretical amount calculated, assuming the presence of one free hydroxyl group.

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[6] Bougault and Bourdier, *J. pharm. chim.* [6] **29**, 561 (1909); [6] **30**, 10 (1909).

One anomalous fact presents itself with respect to the melting points observed for both the natural etholides and the synthetic polymers. Bougault and Bourdier recorded that, although they were unable to separate the natural mixture into pure definite compounds, they found that the melting points tended to group themselves around certain definite temperatures, namely, 68, 72, 78 and 82°. They assumed that this fact indicated that they were dealing with a mixture containing but a few components. It was found in these researches, however, that after the mixtures attained an average molecular weight of 2000, further increases in average molecular weight up to one of 9000 had no effect on the melting point. Every sample melted over 2° ranges between 74 and 77°. Several samples whose average molecular weights were of the magnitude of about 1000 melted over a range of only 2 or 3° around 65°.[6a] Bougault and Bourdier had recrystallized their etholides repeatedly before molecular weight determinations were made, so it is impossible to say whether or not the lower melting fractions also had lower average molecular weights.

The mixtures obtained from the conifers were composed of molecules constituted chiefly of a sixteen carbon and a twelve carbon hydroxy acid. The highest melting fraction, which had an average molecular weight of about 2000, melted around 80°. Since the two components, juniperic acid and sabinic acid, melt at 95 and 84°, respectively, it will be seen that the mixture melts considerably lower than either of the two component parent substances. This was true also in the case of the synthetic polymers of ω-hydroxydecanoic acid where the low fractions melted at 10° lower than, and the higher fractions at almost the same temperature as, the parent molecule.

An entirely satisfactory explanation of these facts does not present

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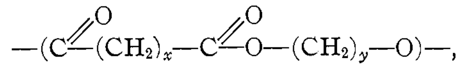
[6a] After the manuscript of this communication was in the hands of the printer, the article by Chuit and Hausser appeared [*Helv. Chim. Acta*, **12**, 463 (1929)] entitled "Sur les acides-alcools polyméthylène-carboniques de 8 a 21 atomes de carbone." These authors have stated that upon heating ω-hydroxydecanoic acid at various temperatures, no definite products were obtained but merely mixtures of etholides of various size. After heating the hydroxy acid at 125° for ten hours they report that a material was isolated from the product which melted at 72.5–73°. The carbon–hydrogen analysis of this material indicated the presence of about six structural units in the molecule. All of the polymers studied and described in this communication which melted at approximately the point mentioned by Chuit were shown by molecular weight to contain ten or more structural units, while molecules of lower molecular weight (5–8 structural units) melted somewhat lower. As a consequence, Chuit's experiment was repeated and led to a product which melted at 74 to 76° and gave by neutral equivalent a molecular weight of about 2000 (12 structural units). Since minor details of experimentation frequently affect the size of the polymer materially, the difference between Chuit's results and those in this investigation may, probably, be accounted for in this way. Chuit found that ω-hydroxynonanoic acid gave entirely different results when subjected to polymerizing conditions. A careful comparison of the polymerization of the various ω-hydroxy acids is now under way in this Laboratory.

itself. Inasmuch as the polymers are mixtures, they might be expected to melt at lower temperatures than individual components of the mixture but, unfortunately, the latter may not be determined. The only plausible idea that suggests itself is based upon a consideration of the fundamental principle of the melting point. The temperature at which any substance melts depends only upon the forces operating between the molecules within the crystal. Whenever the temperature is sufficiently high to overcome these forces, then the substance fuses or melts. It is probable that any individual crystal of the poly-esters of ω-hydroxydecanoic acid is composed of molecules constituted of unequal numbers of structural units. In fact the preliminary x-ray examination,[4] mentioned above, indicates this to be a fact. Other examples of the same phenomenon have been observed, particularly in the case of the polyoxymethylenes.[7] Inasmuch as the homologous molecules in each individual crystal are so similar, it may be assumed that the forces operating between two homologous molecules are of the same order of magnitude as those which would operate between two identical molecules. It must also be assumed that beyond certain limits of dimension of molecules, the magnitude of the operating forces is constant. If these two assumptions are correct, the melting points of the various fractions of the poly-esters might be expected to be constant. It is realized that this explanation is not entirely satisfactory, but more data are necessary before indulging in further speculation.

Carothers and Arvin[8] have prepared a large number of poly-esters by heating dibasic acids with glycols. The structure assigned to these compounds,  $-(\overset{O}{\overset{/\!/}{C}}-(CH_2)_x-\overset{O}{\overset{/\!/}{C}}-O-(CH_2)_y-O)-$, is very similar to that of the poly-esters of ω-hydroxydecanoic acid. It is not surprising, therefore, that many properties are common to these two series of compounds. The various fractions of both series are crystalline, although this property is not highly developed in either case. The property of crystallinity in general seems to be more highly developed in these compounds where the recurring ester groups are separated by shorter carbon chains. Decamethylene sebacate, which is most similar in structure to the poly-esters of ω-hydroxydecanoic acid, is described as a dusty powder which has a great tendency to become electrified. The same general description applies to the various fractions of the present series, and the tendency to become electrified is quite pronounced.

The solubilities of the two series are also somewhat similar. The poly-esters produced from ethylene glycol and the lower dibasic acids such as succinic acid are the least soluble of those described by Carothers and Arvin. Decamethylene sebacate is more soluble and in this respect is

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[7] Hengstenberg, *Ann. phys.*, **84**, 245 (1928).

[8] Carothers and Arvin, THIS JOURNAL, 51, 2560 (1929).

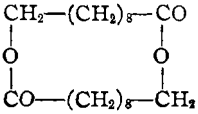
again more similar to the poly-esters of ω-hydroxydecanoic acid. The previous authors point out that the behavior of their compounds on going into solution is indicative of the fact that the solutions are true molecular dispersions. This conclusion was drawn from the facts that solutions of their compounds in acetone, ethyl acetate, and glacial acetic acid were noticeably viscous only when fairly concentrated, and that the rate of solution was very rapid. The concentrated solutions of the poly-esters of ω-hydroxydecanoic acid were not at all viscous and solution in hot solvents was almost instantaneous. These compounds, therefore, present another group of substances of very high molecular weight which give normal solutions in contrast to the apparently colloidal solutions obtained from the polymers of high molecular weight of cyclopentadiene, *iso*propene and styrene.

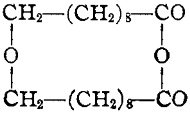
Carothers and Arvin also reported certain anomalies with respect to the melting points of their compounds. They found that the rate of heating had a marked effect on the melting point. Furthermore, they observed that the highest melting point obtained for any sample was within 5° of the lowest and that range was ordinarily within 2°. The effect of rate of heating on the melting points of poly-esters of ω-hydroxydecanoic acid is not so pronounced but the short ranges and constancy for various fractions of the same material are similar. These phenomena have already been discussed. It is interesting to observe that the melting point recorded by Carothers and Arvin for decamethylene sebacate is 74°. This checks very closely the mean value of 74–76° obtained for all of the fractions of average molecular weights of between 2000 and 9000 of the polyesters of ω-hydroxydecanoic acid.

An acetyl derivative of ω-hydroxydecanoic acid was obtained by the action of acetic anhydride on the pure acid. The reaction product consisted, in fact, of a mixture of the acetyl derivative of the acid with the diacetyl derivative of its anhydride. The diacetyl anhydride was readily converted to the acetyl derivative of the acid by shaking with water at ordinary temperatures. Although the free ω-hydroxydecanoic acid could not be distilled at any pressure and temperature, its acetyl derivative was easily distilled without change under diminished pressures. In other words, the tendency to eliminate acetic acid from this molecule was considerably less than the tendency to eliminate water from its parent substance.

It has been pointed out that the bi-functional condensations present the possibility of proceeding either intramolecularly to form monomeric rings, or intermolecularly to form either chains or large rings. Carothers has pointed out that with dibasic acids and glycols ring formation occurred only when five- or six-membered rings could result. In a similar manner chain intermolecular esterification of ω-hydroxydecanoic acid has been found to occur so readily that no cyclic compounds were isolated. It seemed, however, possible that if the chain intermolecular condensation could be inhibited, intramolecular or ring intermolecular condensation might occur. With this in mind, the potassium salt of ω-hydroxydecanoic acid was heated first with acetic anhydride and the product after removal of the acetic anhydride by distillation was dry distilled in a vacuum. If chain intermolecular condensation occurred the products would be non-volatile, not only because of their high molecular weight, but also because the potassium salt would be produced. On the other hand, the monomeric lactone produced by intramolecular condensation and the lower members of the products of ring intermolecular condensation might be expected to be volatile and could thus be isolated from the reaction mixture.

By carrying out the reaction as mentioned, a white crystalline material distilled, accompanied by a few drops of a high-boiling liquid. Traces of acetic anhydride and the few drops of high-boiling material were decanted from the crystals. These proved to be surprisingly pure, as shown by the sharp melting point, 95–95.5°, and by the fact that recrystallization did not alter this value. This substance by analysis and molecular weight determination corresponded to a dimeric lactone of Formula I.

I



II

Furthermore, it was readily saponified with aqueous alkali to yield ω-hydroxydecanoic acid, the original starting material. It also proved to be perfectly stable to water, inasmuch as it was recovered unaltered after shaking with water overnight. These latter two properties exclude the possibility that the compound may have a cyclic ether anhydride formula, II. It is impossible to say whether the dilactone results from the combination of two simple molecules or from the heat decomposition of higher chain polymers.

The dilactone is differentiated from the intermolecular chains by its higher melting point and greater solubility in solvents. It is, apparently, perfectly stable and reacts, in fact, as a normal ester.

The yields obtained in a number of experiments were approximately 5% of the theoretical amount and this value compares favorably with the yields obtained by Ruzicka,[9] in the preparation of large membered cyclic ketones. It should be pointed out that this is the second type of a very large ring which has been capable of direct preparation, and that it conforms to the present idea of the stability of large rings as embodied in the Sachse–Mohr theory.

Such a small amount of the high-boiling liquid accompanying the

[9] Ruzicka, *Helv. Chim. Acta*, 9, 249 (1926).

crystals has as yet been isolated, that a determination of its composition has not been effected. It appears to be a mixture and a preliminary examination has indicated that it is not a monomeric lactone. A mixture closely resembling this high-boiling material was obtained by the dry distillation of the potassium salt of ω-hydroxydecanoic acid itself. Apparently, no dilactone was formed during the course of this reaction.

Experimental

ω-Hydroxydecanoic acid was chosen for the study of intermolecular esterification as it was the most readily available of the homologs previously described. It was found, in fact, that this acid could be obtained in yields of 65–75% of the theoretical amount, calculated from the weight of methyl undecylenate.

Intermolecular Esterification of ω-Hydroxydecanoic Acid.—The general method employed for the intermolecular esterification of ω-hydroxydecanoic acid consisted in heating the acid alone at various temperatures and in various inert solvents at their boiling points, with and without a catalyst. Heating was continued from eight to sixty-five hours and chain poly-esters resulted. In the experiments where no catalyst was used, the products were recovered directly by merely cooling the fused mass or by cooling the solvent in ice and salt. When *p*-toluenesulfonic acid was used to catalyze the reaction the product was obtained as follows. The solvent was cooled in ice and salt, whereupon the product and catalyst separated together. The mixture was removed by filtration and sucked and pressed dry on the filter. The lumps were then crushed and powdered and suspended in a large excess of water at room temperature. After shaking vigorously for several minutes, the suspension was filtered and the product washed with many successive portions of water. It was then dried and an average molecular weight determination made. Both the products of the reactions wherein the catalyst was used, and wherein the acid was heated alone, were recrystallized repeatedly from successive portions of ethyl acetate and average molecular weight determinations were made at intervals during this process.

Molecular-Weight Determinations.—The average molecular weights of the various fractions were obtained by titrations. The general procedure employed consisted in dissolving a weighed sample (0.4–1.2 g.) of the poly-ester in 100 cc. of boiling alcohol which had been distilled over lime. Four drops of phenolphthalein indicator solution was added and an excess of fiftieth normal potassium hydroxide in 75% alcohol solution was run rapidly into the hot solution from a standard buret. About 100 cc. of cold water was added at once, and the resulting alkaline solution was back titrated with standard fiftieth normal aqueous potassium acid phthalate solution. It was found possible to obtain duplicate results within a maximum limit of 10%.

Intermolecular Esterification of ω-Hydroxydecanoic Acid in Boiling Benzene.—A 10-g. sample of ω-hydroxydecanoic acid was recovered practically unchanged after heating in boiling benzene without a catalyst over a period of eight hours. When 0.2 g. of *p*-toluenesulfonic acid was added to a solution of 10 g. of the acid in 75 cc. of anhydrous benzene and refluxing was continued for twelve hours, a different result was obtained. To the resulting solution, 75 cc. of petroleum ether (b. p. 25–40°) was added, and a fine white precipitate was obtained by cooling to −10°. After filtering and drying the product was powdered and suspended and shaken vigorously with 250 cc. of water at room temperature. It was filtered, washed in the filter with three additional 100-cc. portions of water and finally dried. The melting range of the dry polymer was 74.5–76.5° and titration gave an average molecular weight value of 2572.

The remainder of the product was recrystallized from 100 cc. of hot ethyl acetate.

This was accomplished by dissolving the material in 100 cc. of boiling ethyl acetate and cooling immediately in a flow of tap water of an average temperature of about 20°. The precipitate was filtered and dried and an average molecular weight determination made. To the filtrate was added 100 cc. of petroleum ether (b. p. 25–40°) and the resulting solution was cooled to −10°. In this manner additional polymer was recovered and another molecular weight determination made.

The main product was recrystallized four more times from ethyl acetate in the manner described and another average molecular weight determination was made. The combined filtrates from these recrystallizations yielded another fraction. The main product was again four times recrystallized from 100-cc. portions of ethyl acetate. An analysis for carbon and hydrogen and an average molecular weight determination were made on the 9-times recrystallized product. Table I will summarize the results of this experiment.

TABLE I

DATA ON RECRYSTALLIZED PRODUCT

	Times recryst.	Av. mol. wt.	Subs., g.	0.0158 *N* alk., cc.	0.0219 *N* acid, cc.	M. p., °C. (corr.)
1	0	2572	0.4456	15.2	1.9	74.5–76.5
2	1	3329	.4362	14.05	3.0	74.5–76.5
3	Filtrate	1047	.3085	23.85	3.3	62–66
4	5	3621	.6203	13.2	1.7	74.5–76.5
5	Filtrate	1474	.2426	12.9	1.8	34–51
6	9	4476	1.0812	19.6	3.1	74.5–76.5

Anal. Subs., 0.1805: CO_2, 0.4659; H_2O, 0.1771. Calcd. for $(C_{10}H_{18}O_2)_{26}\cdot H_2O = C_{260}H_{470}O_{53}$: C, 70.30; H, 10.52. Found: C, 70.39; H, 11.01.

Intermolecular Esterification of ω-Hydroxydecanoic Acid in Boiling Toluene.—A 5-g. sample of ω-hydroxydecanoic acid was heated in 50 cc. of boiling anhydrous toluene for fifteen hours. The resulting product consisted chiefly of unchanged acid melting at 58–67°. This was shown by the fact that its neutral equivalent was 204 as compared with the theoretical value 180 for the pure acid. In a second experiment, 10 g. of ω-hydroxydecanoic acid was heated in a boiling solution of 0.2 g. of *p*-toluenesulfonic acid in 75 cc. of anhydrous toluene through a period of sixty-five hours. The product was recovered and subjected to the same process as that obtained in the previous experiment with benzene as a solvent. In this experiment duplicate titrations were made on two fractions. In addition a sample of neutralized polymer was recovered from the neutral titration mixture by shaking with an excess of very dilute hydrochloric acid. This product was once recrystallized from hot ethyl acetate by cooling to −10° and a second molecular weight determination was made. The results are tabulated below. An analysis was made on a fraction obtained after five crystallizations.

TABLE II

ANALYTICAL DATA

	Times recryst.	Av. mol. wt.	Subs., g.	0.0158 *N* alk., cc.	0.0219 *N* acid, cc.	M. p., °C. (corr.)
1	0	2608	0.4362	18.9	6.0	75–77
	0	2409	.9918	34.1	5.8	75–77
Recov. from 1st 2 titrns.		2572	.8482	27.8	5.0	75–77
2	1	3443	.8392	21.6	4.45	75–77
	1	3268	.6412	18.1	4.1	75–77
3	5	4683	.6097	12.5	3.55	75–77
4	9	5563	.6893	12.0	3.0	75–77

Anal. Subs., 0.1835: CO_2, 0.4732; H_2O, 0.1807. Calcd. for $(C_{10}H_{18}O_2)_{27}\cdot H_2O$ = $C_{270}H_{488}O_{55}$: C, 70.31; H, 10.59. Found: C, 70.33; H, 11.01.

A second experiment was conducted in which 10 g. of ω-hydroxydecanoic acid was heated for thirteen hours in a solution of 0.2 g. of *p*-toluenesulfonic acid in 60 cc. of anhydrous toluene. The product was recovered in the same manner as in the previous experiments. The titrations were conducted as follows. The sample was dissolved in 100 cc. of alcohol which had been distilled over lime and the acid was directly titrated to phenolphthalein with twentieth normal alkali. The results of this experiment are summarized in Table III.

TABLE III

RESULTS OF EXPERIMENT

	Times recryst.	Av. mol. wt.	Subs., g.	0.0522 *N* alk., cc.	M. p., °C. (corr.)
1	0	2334	0.9019	7.4	72–76
2	1	2604	.7341	5.4	74–76
3	2	2846	.6613	4.45	74–76
4	3	3075	.6273	4.1	74–76

Intermolecular Esterification of ω-Hydroxydecanoic Acid in Boiling Cymene.—A 5-g. sample of ω-hydroxydecanoic acid was heated in boiling cymene for ten hours. The product was recovered by cooling the solution to −10° and the cymene mother liquors were completely recovered by recrystallizing once from a 100-cc. portion of ethyl acetate. The dried material melted at 64–67°. An analysis for carbon and hydrogen and an average molecular weight determination were run.

Neutral equivalent. Subs., 0.2045: cc. 0.0158 *N* alk., 14.2; cc. 0.0219 *N* acid, 2.0. Neut. equiv., 1132.

Anal. Subs., 0.1806: CO_2, 0.4585; H_2O, 0.1719. Calcd. for $(C_{10}H_{18}O_2)_6\cdot H_2O$ = $C_{60}H_{110}O_{13}$: C, 69.36; H, 10.59. Found: C, 69.24; H, 10.65.

A second experiment was conducted in which 10 g. of ω-hydroxydecanoic acid was heated in a boiling solution of 0.2 g. of *p*-toluenesulfonic acid in 75 cc. of anhydrous cymene. The product was recovered and treated in the usual manner and yielded the fractions recorded in Table IV. An analysis was made after five recrystallizations.

TABLE IV

EXPERIMENTAL RESULTS

	Times recryst.	Av. mol. wt.	Subs., g.	0.0158 *N* alk., cc.	0.0219 *N* acid, cc.	M. p., °C. (corr.)
1	0	5061	0.3381	5.2	0.7	73.5–74.5
2	1	7530	0.5324	6.0	1.1	74–76
3	5	7906	1.3938	15.9	4.6	74–76
4	9	8600	0.7312	8.9	2.4	74–76

Anal. Subs., 0.1575: CO_2, 0.4080; H_2O, 0.1564. Calcd. for $(C_{10}H_{18}O_2)_{46}\cdot H_2O$ = $C_{460}H_{830}O_{93}$: C, 70.42; H, 10.59. Found: C, 70.65, H, 11.11.

Upon heating ω-hydroxydecanoic acid with *p*-toluenesulfonic acid in ether, the acid was recovered essentially unchanged.

Intermolecular Esterification of ω-Hydroxydecanoic Acid without a Solvent.—A 5-g. portion of ω-hydroxydecanoic acid was heated in a test-tube at 100° for ten hours under a pressure of 100 mm. After one recrystallization from ethyl acetate, the product melted at 63–67° and gave the following value for neutral equivalent.

Neutral equivalent. Subs., 0.4240: cc. 0.0158 *N* alk., 27.8; cc. 0.0219 *N* acid, 1.5. Neut. equiv., 1043.

A second sample of 10 g. of ω-hydroxydecanoic acid was heated for ten hours at 200–210° in a test-tube. This product was recrystallized twenty times from 100-cc. portions of ethyl acetate after which it melted at 74–76° and gave a value of 6618 for average molecular weight.

Neutral equivalent. Subs., 0.9651: cc. 0.0158 *N* alk., 12.1; cc. 0.0219 *N* acid, 2.1. Neut. equiv., 6618.

A third experiment was conducted in which 10 g. of ω-hydroxydecanoic acid was heated at 220–250° in a test-tube for fifteen hours. The material, upon cooling, was an amber-colored wax which could be readily recrystallized from ethyl acetate. The fractions obtained by recrystallizing this product are summarized in Table V. A sample was analyzed after the first crystallization.

TABLE V

ANALYTICAL AND OTHER DATA

	Times recryst.	Av. mol. wt.	Subs., g.	0.0158 *N* alk., cc.	0.0219 *N* acid, cc.	M. p., °C. (corr.)
1	0	5250	0.9241	12.8	1.2	...
2	1	7455	.5219	4.7	0.2	74–76
3	5	8733	.7772	6.9	.9	74–76

Anal. Subs., 0.1539: CO_2, 0.3968; H_2O, 0.1463. Calcd. for $(C_{10}H_{18}O_2)_{31}\cdot H_2O$ = $C_{310}H_{560}O_{63}$: C, 70.53; H, 10.59. Found: C, 70.32; H, 10.64.

An attempt was made to prepare poly-esters of higher average molecular weight by heating a fused sample of ω-hydroxydecanoic acid with *p*-toluenesulfonic acid, but only charring resulted at 240°.

ω-Acetoxydecanoic Acid.—Twenty grams of ω-hydroxydecanoic acid was added slowly to 150 cc. of ice-cold acetic anhydride. There was no apparent evolution of heat during the addition. The solution was transferred to a 500-cc. round-bottomed flask and was stirred overnight. After heating at 90° for three-quarters of an hour, the resulting solution was distilled under diminished pressure. After the acetic anhydride and the acetic acid were removed, no constant boiling fraction was obtained, but the entire product distilled from 190–220° (1 mm.) and solidified in the receiving flask. It had a pleasant, fruit-like odor and did not lend itself to crystallization from any of the variety of solvents. An analysis indicated the probability that the product consisted of a mixture of the acetyl derivative of the simple acid with the diacetyl derivative of its anhydride.

Anal. Subs., 0.1855: CO_2, 0.4337; H_2O, 0.1592. Calcd. for $C_{12}H_{22}O_4$: C, 62.56; H, 9.63. Found: C, 63.85; H, 9.55.

Fifteen grams of this mixture was shaken with 100 cc. of water overnight. An emulsion was formed but the product was easily removed by extraction with 150 cc. of absolute ether. The ether solution was dried with anhydrous magnesium sulfate, filtered and distilled. The product boiled at 168–170° (1 mm.) and was finally recrystallized several times from 100-cc. portions of petroleum ether (b. p. 60–70°). It was thus obtained in shining white plates which melted at 35–36° (corr.). The neutral equivalent and analysis correspond to the theoretical values calculated for the acetyl derivative of ω-hydroxydecanoic acid.

Neutral equivalent. Subs., 0.2395: cc. 0.0733 *N* alk., 14.1. Calcd. for $C_{12}H_{22}O_4$: 230.2. Found: 231.

Anal. Subs., 0.2029: CO_2, 0.4670; H_2O, 0.1751. Calcd. for $C_{12}H_{22}O_4$: C, 62.56; H, 9.63. Found: C, 62.77; H, 9.65.

Action of Acetic Anhydride on Poly-esters of ω-Hydroxydecanoic Acid.—A 2-g. sample of poly-esters of average molecular weight of 1100 (obtained by melting pure ω-hydroxydecanoic acid in boiling cymene) was introduced into a solution of 1.0 cc. of acetic anhydride in 50 cc. of anhydrous benzene. The resulting solution was refluxed for one hour and then cooled in ice water. The resulting precipitate was filtered and recrystallized once from ethyl acetate. It was observed that this product was more soluble both in benzene and ethyl acetate than the corresponding simple poly-ester. The dried product melted at 68–72° and gave the following values for analysis and neutral equivalent.

Neutral equivalent. Subs., 0.3780: cc. 0.0158 *N* alk., 15.0; cc. 0.0219 *N* acid. 1.3. Neut. equiv., 1812.

Anal. Subs., 0.2067: CO_2, 0.5262; H_2O, 0.1948. Calcd. for $CH_3CO_2(CH_2)_9CO$-$[O(CH_2)_9CO]_8$-$O(CH_2)_9CO_2H$: C, 69.48: H, 10.47. Found: C, 69.43; H, 10.54.

This product was then refluxed for two hours with 10% aqueous potassium hydroxide solution. The alkaline solution was cooled and acidified with an excess of phosphoric acid. Upon distillation the distillate was strongly acidic to litmus.

Preparation of the Dimeric Lactone of ω-Hydroxydecanoic Acid.—In a small Claisen distilling flask, 10 g. of the pure potassium salt of ω-hydroxydecanoic acid was covered with acetic anhydride. This mixture was heated just below the boiling point of acetic anhydride for about one hour. The excess acetic anhydride was then removed from the solution on a water pump and the dry potassium salts distilled under a pressure of about 5 mm. A liquid–air trap between the receiving flask and the vacuum pump protected the latter. During the distillation the solid salts fused between 350 and 400° (estimated temperature) and distillation occurred between 400–500°. Two products resulted. One of these was an oil which boiled in the neighborhood of 170–190° and was obtained only in small quantities. It was never identified. The second product was a crystalline solid which readily could be recrystallized from acetone and was obtained thus pure as fine, white needles, melting at 95–95.5°. The yield was from 0.3–0.35 g. and was about the same in each of a number of experiments.

A molecular weight determination in benzene agreed with the theoretical value within 4%. *Mol. wt.* Subs., 0.4714; wt. of benzene, 18.61; lowering of f. p. 0.395°. Calcd. for $C_{20}H_{36}O_4$, 340. Found: 328.

The values obtained upon analysis for carbon and hydrogen also checked the calculated values. *Anal.* Subs., 0.1881: CO_2, 0.4854; H_2O, 0.1790. Calcd. for $C_{20}H_{36}O_4$: C, 70.58; H, 10.67. Found: C, 70.40; H, 10.59.

A 0.2-g. sample of this material was hydrolyzed in 10 cc. of 5% alcohol in potassium hydroxide solution. Water was added and the alcohol removed by distillation. Upon cooling and acidifying with dilute hydrochloric acid, ω-hydroxydecanoic acid precipitated, which was recovered and identified as follows. The aqueous suspension was extracted with several 5-cc. portions of alcohol-free ether. The combined ethereal solutions were washed with water and dried with anhydrous magnesium sulfate. After filtering, the ether was removed under diminished pressure and the product was recrystallized from ethyl acetate. It melted at 75–76° and a mixed melting point with pure ω-hydroxydecanoic acid (m. p. 75–76°) showed absolutely no depression.

A 0.1-g. sample of this product was shaken with 25 cc. of water overnight at a temperature of 20–30°. The product was filtered and recrystallized once from acetone. The melting point remained unchanged at 95–95.5° and a mixed melting point with some of the original material showed no depression.

The dry distillation of the potassium salt of ω-hydroxydecanoic acid led to the formation of water and a high-boiling oil. After separating from the water, the oil was distilled, but no constant boiling fraction was obtained, although the major portion boiled at 170–190°. Attempts were made to hydrolyze this product and to condense it with phenylhydrazine and semicarbazide, but no pure products were isolated.

Summary

1. The intermolecular esterification of ω-hydroxydecanoic acid has been studied and found to proceed easily with the formation of mixtures of chain polymers. These mixtures were separated by crystallization into fractions of average molecular weights ranging from 1000 to 9000.

2. These poly-esters were titrated quantitatively with standard alcoholic potash solutions and average molecular weights thus determined. By boiling with excess alcoholic potassium hydroxide, they were converted back to the original acid.

3. A twenty-two-membered dimeric lactone of ω-hydroxydecanoic acid was prepared by dry distillation of the product obtained by the action of acetic anhydride on its potassium salt.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE APPARENT RACEMIZATION OF PINENE

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The thermal decomposition of *d*-pinene was noted by Wallach[1] many years ago in connection with his study of the action of heat on a variety of essential oils. He showed that at 250–270° the final products were dipentene and polymerized material. Very recently Smith[2] has made a quantitative study of the loss of optical activity of pinene at somewhat lower temperatures (185–237°) and concludes that the reaction consists for the most part of a simple racemization. This view he supported by distillation of a sample which had been heated until it had lost about a third of its original optical activity. This evidence did not seem to us conclusive, however, and we decided to determine, if possible, whether the loss of optical activity of pinene was the result of racemization or rearrangement. From a physico-chemical point of view the question is probably of relatively little significance and most of Smith's conclusions are not affected by our final results, which establish that the process he was measuring was in reality a rearrangement and not a racemization. From the standpoint of the organic chemist, however, the point at issue is obviously of importance.

A few experiments convinced us that a definite answer to the problem could not be obtained by fractional distillation. Although there is a 20° difference in the boiling points of pinene (155°) and dipentene (176°), a mixture of equal amounts of the compounds was very incompletely separated by several fractionations through an efficient Widmer column.

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[1] Wallach, *Ann.*, **227**, 282 (1885).

[2] Smith, THIS JOURNAL, **49**, 43 (1927).