TABLE VI

HYDROLYSIS OF METHYL NEOPENTYL KETAL IN 49.6% DIOXANE–50.4% WATER AT 25.0°

Acetic acid, M	Acetate, M	10^4k_1, sec.$^{-1}$	$10^{-3}k_2$, l. mole^{-1} sec.$^{-1}$
0.00268	0.00426	46.7	17.8
.00268	.00426	50.2	19.2
.00268	.00246	51.8	19.8
.00268	.00426	50.7	19.3
.00243	.01438	24.7	26.5
.00243	.01438	23.5	25.3
.00243	.01438	23.2	25.0
.00243	.01438	21.7	23.3
.000486	.00287	10.6	16.2
.000486	.00287	10.1	15.5
.000481	.000360	44.3	10.8
.000481	.000360	44.7	10.9
.000481	.000360	44.5	10.8
.00804	.01278	85.0	25.2
.00804	.01278	83.3	24.7

The mean deviation, d, in h is obtained from eq. 6

$$d = \frac{\Sigma\left[\log\left(\frac{k}{k_0}\right) + 3.600(\Sigma\sigma^*) - 0.54(\Delta n)\right]}{\Sigma(\Delta n)} \qquad (6)$$

The validity of this procedure is supported by the fact that essentially the same value of h is obtained by the method least squares, using eq. 7

$$\log\left(\frac{k}{k_0}\right) + 3.600\,(\Sigma\sigma^*) = (\Delta n)h + a \qquad (7)$$

The deviation, a, of the acetonal point by this treatment is 0.12. However, the probable error of a single point obtained in this manner is not improved over the previous one.

A slightly better fit of the data can be obtained by using eq. 8

$$\log\left(\frac{k}{k_0}\right) = \rho^*(\Sigma\sigma^*) + (\Delta n)h + a \qquad (8)$$

Three parameters, ρ^*, h and a, are simultaneously adjusted to give the best fit for all the data.[28] Values of $\rho^* = -3.751 \pm 0.101$, $h = 0.606 \pm 0.033$ and $a = 0.354$ are obtained.

The probable error of a single point is reduced to ±0.186 log unit and the correlation coefficient is raised to 0.998. It can readily be seen that the values of ρ^* and h are the same, within the combined uncertainties, as those obtained by the first procedure. The slight improvement in the probable error of a single point, in the correlation coefficient, and in the probable error of ρ^* does not seem to justify the introduction of the parameter a, and the simultaneous adjustment of h and ρ^*.

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[28] (a) R. L. Anderson and T. A. Bancroft, "Basic Statistical Theory and Analysis of Experimental Models by Least Squares," McGraw-Hill Book Co., New York, N. Y., 1952, Chapter 14; (b) We are indebted to W. A. Pavelich for setting the generalized eqs. of ref. 28(a) in a form for convenient analysis of the data by eq. (6)—*cf.* Ph.D. thesis, W. A. Pavelich, Penn State University, June, 1955.

[CONTRIBUTION FROM PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY]

The Synthesis of Long Chain α,ω-Dicarboxylic Acids

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RECEIVED JUNE 3, 1955

A series of polymethyleneketo-α,ω-dicarboxylic acids and polymethylene-α,ω-dicarboxylic acids were prepared. The polymethyleneketo-α,ω-dicarboxylic acids were prepared from sebacyl chloride utilizing the ketene polymerization synthesis. The polymethylene-α,ω-dicarboxylic acids were prepared from the above keto acids by Clemmensen reduction. The properties of these acids are discussed.

The aliphatic long chain dicarboxylic acids of 600 to 3000 molecular weight have not been prepared previously. In general, the synthetic methods[1-5] used for preparing the shorter chain α,ω-dicarboxylic acids involved many steps and resulted in poor yields. Moreover, for the molecular weight range of 600 to 3000, the synthesis of intermediates involved would be extremely difficult, if not impossible.

This paper describes the synthesis of polymethyleneketo-α,ω-dicarboxylic acids and polymethylene-α,ω-dicarboxylic acids with average molecular weights in the 600 to 3000 range. The synthesis developed for the preparation of these products is an extension of work reported by Sauer[6-8] and Blomquist and co-workers.[9-11] Sauer has shown that a polymeric ketene was obtained on the dehydrohalogenation of sebacyl chloride. Blomquist and co-workers also report that a small amount of polymeric material was obtained in the synthesis of macrocyclic ketones *via* ketene dimer formation from sebacyl chloride and triethylamine in dilute solutions. The polymeric products were not fully characterized. In the synthesis described in this paper the polymeric diketenes (I) prepared from the acid chlorides of dibasic acids were hydrolyzed to the corresponding polymethyleneketo-α,ω-di-

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[1] P. Chuit and J. Hausser, *Helv. Chim. Acta*, **12**, 850 (1929).

[2] P. Chuit, *ibid.*, **9**, 264 (1926).

[3] N. L. Drake, H. W. Carhart and R. Mozingo, THIS JOURNAL, **63**, 617 (1941).

[4] A. Kreuchunas, *ibid.*, **75**, 3339 (1953).

[5] H. Günthard, S. Heinemann and V. Prelog, *Helv. Chim. Acta*, **36**, 1147 (1953).

[6] J. C. Sauer, U. S. Patent 2,369,919.

[7] J. C. Sauer, THIS JOURNAL, **69**, 2446 (1947).

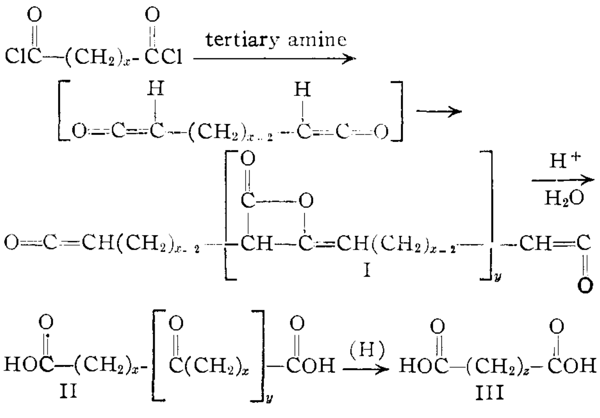
[8] J. C. Sauer, U. S. Patent 2,323,938.

[9] A. T. Blomquist and R. D. Spencer, THIS JOURNAL, **69**, 472 (1947).

[10] A. T. Blomquist and R. D. Spencer, U. S. Patent 2,584,654.

[11] A. T. Blomquist, J. R. Johnson, L. I. Diuguid, J. K. Shillington and R. D. Spencer, THIS JOURNAL, **74**, 4203 (1952).

carboxylic acids (II).[12] These acids were, in turn, converted to the polymethylene-α,ω-dicarboxylic acids (III) by the Clemmensen reduction.



The diketene polymerization reaction was carried out under a variety of conditions, and the polymeric products hydrolyzed and fully characterized. The hydrolysis products were polymethyleneketo-α,ω-dicarboxylic acids in the 600 to 3000 molecular weight range (as determined ebullioscopically in xylene). The molecular weights calculated from end-group analysis (based on 2 carboxyls/molecule) were in excellent agreement with those determined ebullioscopically. Thus, this agreement in molecular weight values indicates the difunctionality of these acids. Carbon-hydrogen data and infrared analysis coupled with the molecular weight data completely characterized these acids.

The polymethyleneketo-α,ω-dicarboxylic acids prepared in this manner have the general formula II, differing only in the number of y units. These acids were not single molecular compounds but were a mixture of acids with a certain average molecular weight. Although the molecular weight distribution has not been determined, the distribution appears to be quite sharp as judged by the solubility behavior of the acids.

Sebacyl chloride, as the diacid halide, and triethylamine, as the tertiary amine, were used in this work. From previous work[6,9] sebacyl chloride appeared to be the best intermediate as it showed little tendency to cyclize and was known to yield polymeric products. Similarly triethylamine had been found to be quite efficient in the dehydrohalogenation of diacid chlorides.[6]

In general the reaction was carried out by the addition of a solution of the diacid halide to a stirred solution of the tertiary amine. After stirring overnight, the polymeric ketene derivative was hydrolyzed with refluxing acetic-hydrochloric acid solution. The crude keto acid was purified by recrystallization from the appropriate solvent. Using this general procedure, the effect of varying reaction conditions on the molecular weight of the polymethylene-α,ω-dicarboxylic acids produced was studied.

Effect of Reaction Conditions on Molecular Weight.—When the total volume of the reaction mixture was varied from 200 to 900 ml., the molecular weight of the keto acids obtained ranged from 2000 to 500. Since in all cases, there was a precipitate of polymeric ketene derivative from practically the start of the reaction, this effect would appear to be a dilution effect rather than a solubility effect.

Changing the polarity of the solvent used in the reaction did not have any significant effect on molecular weight of the products. However, such an effect might be apparent in reaction times shorter than the 24 hours used in these experiments.

Of significance was the effect of temperature on the molecular weight of the products. As the reaction temperature was raised from room temperature to the boiling point of xylene (*ca.* 135°), the molecular weight of the keto acids decreased. Even though the polymerization reaction is favored at higher temperatures, the formation of the acyl-triethylammonium chloride complex is not, and the stability of such a complex is decreased. As a result, lower molecular weight products were obtained as the reaction temperature was increased.

Properties of the Polymethyleneketo-α,ω-dicarboxylic Acids.—The polymethyleneketo-α,ω-dicarboxylic acids in the 600 to 3000 molecular weight range were obtained in 60 to 80% yields and melted from *ca.* 120° for the 600 molecular weight acid to *ca.* 150° for the 2800 molecular weight acid. The acids were white, crystalline (by X-ray diffraction) powders which could be recrystallized from the appropriate solvents. Acids of 1000 molecular weight and above were soluble in such solvents as hot dioxane, boiling xylene and boiling acetic acid. In this molecular range, the acids were insoluble in 10% sodium hydroxide and such hydrocarbon solvents as benzene, toluene and cyclohexane even at the boil. The lower molecular weight acids (mol. wt. $>$ 1000) were soluble in the above hydrocarbons only at the boil. All of these keto acids are melt unstable, and, if heated for long periods (1 to 3 hours at or slightly above the melting point or at 200° for short periods) reacted to yield highly cross-linked gel structures.

Reduction of Keto Acids.—The reduction of carbonyl groups to methylene groups in polymethyleneketo-α,ω-dicarboxylic acids was extremely difficult. This reaction was complicated not only by the large number of carbonyls present in each molecule but by the poor solubility of the keto acids. All attempts to reduce the carbonyls catalytically with Raney nickel or ruthenium or chemically by the Wolff-Kishner reaction were unsuccessful.

The acids were reduced by a modified Clemmensen reaction using xylene-alcohol solutions as the reaction medium. Unless alcohol was used, a cross-linking reaction occurred which was probably between the intermediate reduction product and the carboxyls on the ends of the molecule. In the presence of alcohol and under the reaction conditions the carboxyls were esterified and could not undergo this cross-linking reaction.

In order to obtain a carbonyl-free acid, four successive reductions were necessary. Each reaction resulted in the reduction of ca. 50% of the carbon-

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[12] Since the completion of the work described in this paper, a similar synthesis for the preparation of polymethyleneketo-α,ω-dicarboxylic acids has been reported by H. M. Molotsky, Thesis, University of Missouri, 1953.

yls present. The course of the reduction was followed by carbon–hydrogen analysis and by infrared analysis for keto carbonyl. The over-all yield for four such reductions was *ca.* 50%.

Properties of the Polymethylene-α,ω-dicarboxylic Acids.—These acids were quite similar in behavior and appearance to the low molecular weight polyethylenes. The acids of less than 1000 molecular weight were soluble in hydrocarbon solvents (benzene, cyclohexane, toluene, etc.) but were insoluble in 10% hot sodium hydroxide solution. Acids of molecular weight above 1000 appeared to be more crystalline and were soluble in the above hydrocarbon solvents only at the boiling point.

Polymethyleneketo-α,ω-dicarboxylic acids		Polymethylene-α,ω-dicarboxylic acids	
Mol. wt.	M.p., °C.	Mol. wt.	M.p., °C.
2800	145–150	2700	90–95
2400	145–150	2100	90–95
2000	143–148	1420	80–81
1500	135–142	780	52
575	120–125	587	42

In the low molecular weight range (below 1000 molecular weight) where the carboxylic acid ends are dominant in determining properties, the acids melt higher than the corresponding polyethylenes. But as the molecular weight is increased and the polymethylene chain becomes more significant, the melting point levels off, and the physical characteristics of these acids (m.p., solubility, etc.) approach that of the polyethylene of comparable molecular weight.

As in the case of the keto acid, the molecular weights determined ebullioscopically and those calculated from end-group analysis were in excellent agreement.

Experimental

Sebacyl chloride and triethylamine were purchased from Eastman Kodak Company. The acid chloride was distilled in small portions from a 500-ml. round bottom flask immersed in an oil-bath. In this manner, sebacyl chloride, boiling at 146 to 147° (1 mm.), was obtained. Triethylamine was purified by drying over caustic followed by distillation from 10% of its weight of α-naphthyl isocyanate.

Preparation of Polymethyleneketo-α,ω-dicarboxylic Acid from Sebacyl Chloride.—A solution of 23.9 g. (0.1 mole) of sebacyl chloride in 100 ml. of dry benzene was added over 2 hr. to a stirred solution, protected from atmospheric moisture, of 24 g. (0.25 mole) of triethylamine in 200 ml. of dry benzene. After stirring an additional 16 hr., the benzene was removed by slow distillation while 500 ml. of acetic acid–hydrochloric acid (4:1) was slowly added. The acetic acid solution was refluxed overnight and poured into 1 l. of ice-water. The precipitated crude keto acid was separated and recrystallized from boiling xylene to give 11.5 g. (66%) of keto acid having m.p. 145–150°.

Anal. Calcd. for $C_{138}H_{266}O_{18}$: C, 74.9; H, 12.03; mol. wt., 2400. Found: C, 75.00; H, 12.05; mol. wt. (ebullioscopically in xylene), 2398, 2378; carboxyls/10^6 g., 834, 839; molecular weight (calcd. from 2 carboxyls/molecule), 2400.

By varying the total volume of solvent used, from 200 to 900 ml., keto acids with molecular weights from 2800 to 610 were obtained. No effect on the molecular weight of the keto acid was observed when benzene was replaced as the solvent by chloroform, dioxane, nitrobenzene, and/or xylene. There was a progressive decrease in molecular weight from 2800 to 610 when the reaction temperature was raised from room temperature to 135°.

Clemmensen Reduction of Polymethyleneketo-α,ω-dicarboxylic Acids.—Into a refluxing reaction mixture containing 24 g. of polymethyleneketo-α,ω-dicarboxylic acid (molecular weight, 2400), 110 g. of amalgamated zinc, 100 ml. of ethanol and 500 ml. of xylene was bubbled hydrogen chloride (dry) for 24 hours. The resulting mixture was poured into 2 liters of water and xylene and alcohol removed by steam distillation. The residual solid was recrystallized from hot benzene and dried overnight in a vacuum oven. Approximately 20 g. (85% of theory) of the partially reduced keto acid ester was obtained.

The free acid was obtained by refluxing for 24 hours a stirred mixture of 20 g. of the ester, 300 ml. of 10% hydrochloride acid solution and 50 ml. of benzene. The resulting mixture was slowly distilled until all the benzene and approximately one-half of the aqueous solution was removed. The residual solution was cooled to 0°, and the crude acid precipitated and filtered off. On recrystallization from benzene, approximately 19 g. of the dicarboxylic acid, melting 125 to 130°, was obtained.

Anal. For the partially reduced keto acid. Calcd. for $C_{138}H_{266}O_{10}$: C, 79.9; H, 12.7; mol. wt., 2300. Found: C, 80.1; H, 12.8; mol. wt. (ebullioscopically in benzene), 2200, 2300; carboxyls/10^6 g., 900, 910; mol. wt. (calcd. from 2 carboxyls/molecule), 2200.

The carbon–hydrogen analysis agrees for a polymethyleneketo-α,ω-dicarboxylic acid in which approximately 50% of the carbonyls have been reduced. Similarly, infrared analysis indicated the reduction of approximately 50% of the keto carbonyl groups.

In order to produce a dicarboxylic acid essentially free of keto groups, the above reduction had to be repeated on a particular sample four times. In each of these consecutive reductions approximately 50% of the carbonyls were reduced in approximately 80% yields. Over-all yield for four such consecutive reductions was 48%.

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