oration of the ether left *p*-*N*,*N*-dimethylaminoaniline, identified as the phenylthiourea (0.304 g., 49%) by mixed melting point with an authentic sample, m.p. 147.5°. The infrared spectra of the samples were identical.

p-Nitroso-*N*,*N*-dimethylaniline (1.40 g., 0.00934 mole) and 1-benzyl-1,4-dihydronicotinamide (1.00 g., 0.00468 mole) were dissolved in 15 ml. of ethanol, and the solution was boiled for 10 min. Water was added to bring the total volume to 50 ml. The mixture was chilled in an ice bath, and 50 ml. of water was added. Filtration gave a red-brown crystalline solid (1.27 g.). One recrystallization from alcohol and two recrystallizations from 50% acetone gave fine yellow plates (0.086 g., 8%) m.p. 137–140.5°, identified as the nitrone from nicotinamide-1-benzylochloride by the identity of the infrared spectrum with that of an authentic sample. In another run, 2,4-dinitrophenylhydrazine reagent was added directly to the reaction solution after 10 min. of reflux to give benzaldehyde 2,4-dinitrophenylhydrazone (89%), identified by mixed melting point with an authentic sample. In another run, the ethanol was removed from the reaction mixture, and the residue was extracted with 20 ml. of warm water. The extract was washed with ether, treated with charcoal, and evaporated to dryness, leaving nicotinamide, which was identified as the picrate (0.696 g., 42%) by mixed melting point with an authentic sample.

A solution of nitrosobenzene (0.503 g.) and 1-benzyl-1,4-dihydronicotinamide (1.01 g.) in 20 ml. absolute ethanol was refluxed for 1 hr. The alcohol was evaporated and the residue was extracted with 20 ml. of water. The extract was washed with two 20-ml. portions of ether, treated with charcoal, and evaporated to dryness. The residue was taken up in 5 ml. of ethanol. Addition of alcohol saturated with picric acid gave no precipitate of nicotinamide picrate. The residue remaining from the water extraction was dissolved in 10 ml. of ethanol and distilled with 5 ml. of phosphoric acid and 5 ml. of water. Addition of 2,4-dinitrophenylhydrazine reagent to the distillate gave benzaldehyde 2,4-dinitrophenylhydrazone (3%), identified by mixed melting point (235°) with an authentic sample. In other runs, hydrazobenzene, phenylhydroxylamine and aniline were identified by paper chromatography.

Reaction of nicotinamide-1-benzylochloride and p-nitrosodimethylaniline. Nicotinamide-1-benzylochloride (2.51 g., 0.0101 mole), *p*-nitrosodimethylaniline (1.51 g., 0.0101 mole) and piperidine (1 ml., 0.01 mole) in 50 ml. of ethanol were refluxed for 25 min. Enough water was added to bring the total volume to 100 ml. A brown solid (0.961 g., 40%) precipitated on chilling. Two recrystallizations from 50% acetone gave yellow crystals (0.145 g.), m.p. 137–139°. An analytical sample of this nitrone melted at 141–143°.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.82, 75.10; H, 6.73, 6.81; N, 11.63, 11.73.

Reduction of phenylhydroxylamine. Phenylhydroxylamine (0.500 g.) and 1-benzyl-1,4-dihydronicotinamide (1.00 g.) were heated at 139° under nitrogen for 30 min. The reaction mixture was extracted with 30 ml. of 1:5 sulfuric acid. The extract was washed with two 15-ml. portions of ether, made basic with 10% sodium hydroxide, saturated with sodium chloride, and extracted with two 20-ml. portions of ether. Evaporation of the ether left aniline (14%) identified as phenylthiourea by mixed melting point (155°) with an authentic sample. In another run, 1% benzaldehyde was identified as its 2,4-dinitrophenylhydrazone.

In a blank run, phenylhydroxylamine (0.632 g.) was heated at 139° under nitrogen for 63 min. Aniline was identified as the phenylthiourea (0.120 g., 9%) by mixed melting point (155.5°) with an authentic sample.

Reduction of azoxybenzene. Azoxybenzene (0.927 g.) and 1-benzyl-1,4-dihydronicotinamide (1.01 g.) were heated under nitrogen at 139° for 43 min. Benzaldehyde (1%) was isolated when the reaction mixture was hydrolyzed. In another run with twice the above quantities, the reaction mixture was extracted with 30 ml. of 1:5 sulfuric acid. The extract was washed with three 15-ml. portions of ether, made basic with sodium hydroxide solution, saturated with salt, and extracted with two 20-ml. portions of ether. Evaporation of the ether left aniline, identified as diphenylthiourea (0.384 g., 18%) by mixed melting point with an authentic sample. The infrared spectra of the samples were identical. Paper chromatography indicated a trace of hydrazobenzene.

Reduction of azobenzene. Azobenzene (0.431 g.) and 1-benzyl-1,4-dihydronicotinamide (0.502 g.) were heated at 139° under nitrogen for 1 hr. Paper chromatography showed the presence of hydrazobenzene. Distillation of the acidified reaction mixture gave benzaldehyde identified as its 2,4-dinitrophenylhydrazone (0.022 g., 3%).

PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

The Chemistry of Dimethylketene Dimer. IV. The Polyester and β-Lactone Dimer of Dimethylketene[1]

ROBERT H. HASEK, R. DONALD CLARK, EDWARD U. ELAM, AND JAMES C. MARTIN

Received June 28, 1961

The polymerization of dimethylketene catalyzed by sodium methoxide yields a polyester which decomposes on heating to the β-lactone dimer of dimethylketene. Mechanisms for formation and pyrolysis of the polyester are offered. The β-lactone dimer can also be prepared by the aluminum chloride-catalyzed dimerization of dimethylketene or rearrangement of the normal dimer, tetramethyl-1,3-cyclobutanedione.

In the last paper of a series of publications on ketenes, Staudinger described the polymeric products obtained by treatment of monomeric dimethylketene with catalytic amounts of triethylamine.[2] These polymers had properties of both polyketones (I) and polyacetals (II); ozonization gave some acetone, but degradation by acids and bases also gave isobutyric acid, dimethylmalonic acid, and diisopropyl ketone. Thermal decomposition regenerated 50–60% of the monomeric dimethylketene. Staudinger suggested that the polymer

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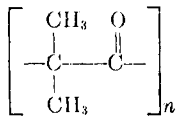
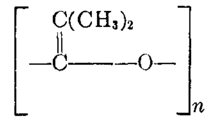
[1] Paper III: R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 4340 (1961).

[2] H. Staudinger, F. Felix, P. Meyer, H. Harder, and E. Stirnemann, *Helv. Chim. Acta*, **8**, 322 (1925).

structures contained random arrangements of units I and II.[3]

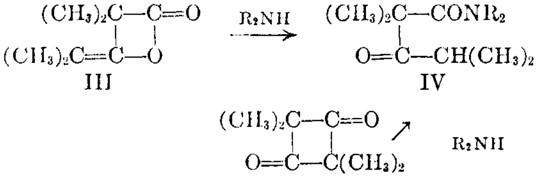

$[-C(CH_3)_2-C(=O)-]_n$

I


$[-C(=C(CH_3)_2)-O-]_n$

II

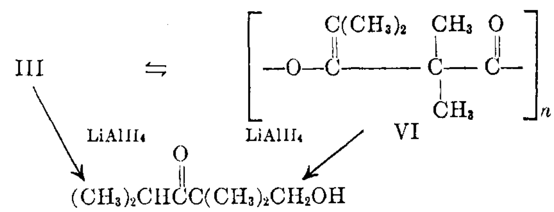
In our current study of dimethylketene, we obtained a polymeric material when dimethylketene was passed into a suspension of sodium methoxide in ether. This polymer differed from those described by Staudinger. Thermal decomposition gave only a small amount of dimethylketene; the major product was a liquid dimer of dimethylketene. The infrared and NMR spectra of this dimer were consistent with an unsaturated β-lactone structure (III), homologous with the accepted structure of diketene. The significant features of the infrared spectrum were a doublet at 5.4–5.5 μ (carbonyl) and a strong band at 5.75 μ(olefinic). The NMR spectrum (40 mc.) contained two single, sharp peaks of equal intensities at 56 and 66 c.p.s. (1.4 and 1.65 ppm.) below the internal reference, tetramethylsilane.



V

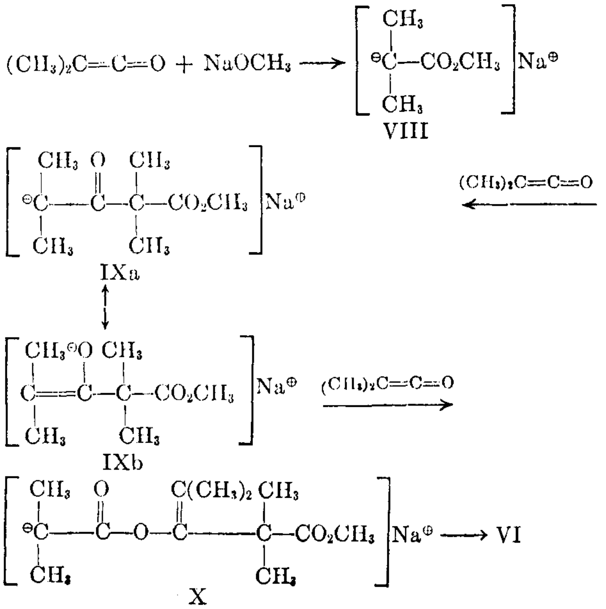
The structure of the liquid dimer was confirmed by preparation of derivatives identical with those previously made from tetramethyl-1,3-cyclobutanedione (V), the normal solid dimer of dimethylketene. III reacted rapidly with ammonia and amines to form 2,2,4-trimethyl-3-oxovaleramides (IV), including derivatives of aromatic and secondary aliphatic amines which are formed very sluggishly from V.[1] In this respect, the β-lactone dimer III was more like the lower homolog, diketene. It had a sharp odor and a lachrymatory action, which are totally absent in the camphoraceous solid dimer V.

Treatment of the liquid dimer with sodium methoxide in refluxing benzene produced a polymer which was essentially the same as that obtained directly from monomeric dimethylketene. Both polymers had identical infrared and NMR spectra and were decomposed thermally to the liquid dimer. It was apparent that these polymers were polyesters (VI) of the hydroxy acid (enol form of the keto acid) derived from the β-lactone dimer. This conclusion was confirmed by data reported by Natta and co-workers, who obtained a polymer of structure VI by polymerization of dimethylketene at −60° in the presence of triethylaluminum;[4] their published infrared spectrum was apparently identical with ours.[5] The polymer structure was deduced by Natta from formation of acetone by ozonolysis and of 1-hydroxy-2,2,4-trimethyl-3-pentanone (VII) by reduction with lithium aluminum hydride. We obtained the latter product by reduction of the β-lactone dimer of dimethylketene with lithium aluminum hydride. This result corresponds to the reduction of the β-lactone dimer of ethylketene to 1-hydroxy-2-methyl-3-pentanone.[6]



VII

The formation of the polyester VI from monomeric dimethylketene requires (a) a regular, but alternating, addition across the olefinic bond and carbonyl group of successive dimethylketene molecules, or (b) the initial formation of a dimeric intermediate. In the first mechanism, (a), the sequence of alternating modes of addition is logical if it is assumed that an ester anion undergoes *C*-acylation, but a β-keto ester anion is *O*-acylated. Thus, addition of sodium methoxide to dimethylketene produces the sodium derivative of methyl



X

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(3) H. Staudinger, *Die Hochmolekularen Organische Verbindungen*, Julius Springer, Berlin, 1932, p. 146.

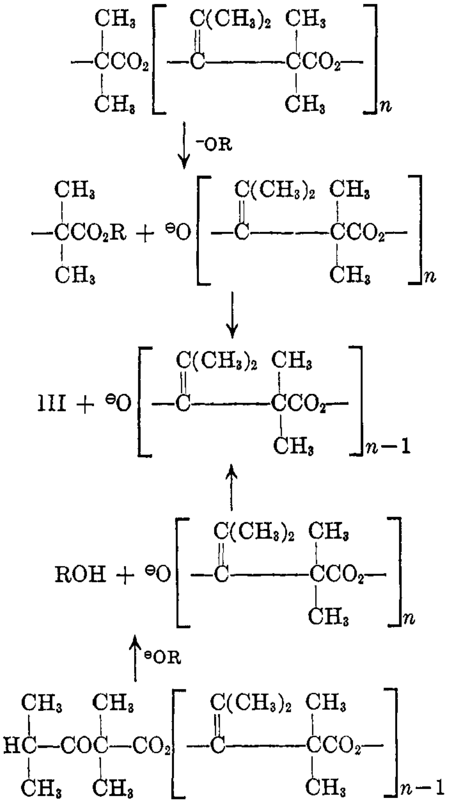
(4) (a) G. Natta, G. Mazzanti, G. Pregaglia, M. Binaghi, and M. Peraldo, *J. Am. Chem. Soc.*, **82**, 4743 (1960); (b) G. Natta, G. Mazzanti, G. Pregaglia, and M. Binaghi, *Makromol. Chem.*, **44–46**, 537 (1961).

(5) Preparation of a polyester from diketene was reported recently by A. Kawasaki, J. Furukawa, T. Salgusa, M. Mise, and T. Tsuruta, *Makromol. Chem.*, **42**, 25 (1960). The assignment of structure was based primarily on studies of infrared spectra.

(6) R. L. Wear, *J. Am. Chem. Soc.*, **73**, 2390 (1951).

isobutyrate (VIII), which is *C*-acylated by dimethylketene to the sodium enolate of methyl isobutyrylisobutyrate (IXa and IXb). The latter undergoes *O*-acylation to produce the sodium derivative of an isobutyrate ester (X), and the sequence of *C*- and *O*-acylations is repeated.

The thermal decomposition of VI presumably involves a straightforward ester interchange, initiated by cleavage of an ester group in the polymer chain, or by formation of an anion of a terminal keto ester group. The latter effect was noted with higher esters of 2,2,4-trimethyl-3-oxovaleric acid, which normally are quite stable but which decompose when heated with basic catalysts to form, among other products, appreciable quantities of the β-lactone dimer III.

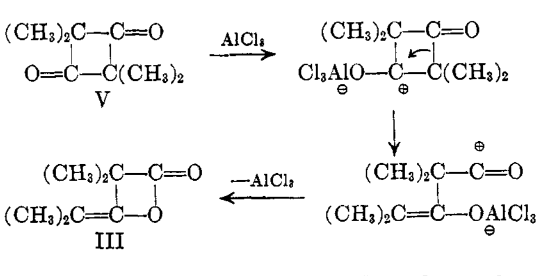


The alternate mode, (b), of formation of a polyester from dimethylketene assumes the initial formation of a dimeric intermediate. All evidence indicates that this mechanism is untenable. Traces of dimethylketene were regenerated by pyrolysis of the monomer-derived polymer, but not from the polymer prepared from the dimer. This difference in behavior indicates that the dimethylketene polymer contained slight irregularities in the polyester structure, presumably arising from random *C*- or *O*-acylation of the growing chain. From the reported pyrolysis of vinyl isobutyrate to acetaldehyde (and, by inference, to dimethylketene)[7] and from our failures to obtain dimethylketene by pyrolysis of β-polyketones or β-keto esters, we believe that sequences of structure II are necessary for thermal cleavage to monomeric dimethylketene. This poly(ketene acetal) structure, produced by exclusive *O*-acylation, must be the predominant feature of Staudinger's triethylamine-catalyzed polymers.

Relative rates of polymerization also indicate that the polyester VI is formed directly from dimethylketene; under comparable conditions, the polyester was produced much more rapidly from the ketene than from its lactone dimer. The driving force in the polymerization depends on the reactivity of the monomer as an acylating reagent, and in this respect, dimethylketene is a more powerful reagent than the β-lactone dimer. The normal dimer (V) is decidedly less reactive and does not form a polymer. An equimolar mixture of the dimers, heated with sodium methoxide in refluxing ether, gave a 96% yield of polyester, based on III; 92% of V was recovered.

Because of its greater reactivity, the β-lactone dimer is a more useful reagent in acylation reactions than the normal dimer of dimethylketene. Its superiority in the acylation of weak or sterically hindered amines has already been cited. It should be noted, however, that the lactone dimer is by no means as reactive as the well known homolog, diketene, and catalysis by acids or bases usually is necessary to produce reasonable reaction rates in esterification reactions. There is a very practical advantage in the liquid form of the β-lactone dimer, which eliminates many difficulties in handling, particularly in removal of unconverted dimer during the distillation of reaction mixtures. The volatile solid dimer is quite troublesome in this respect.

In view of its useful properties, a good synthetic method for the β-lactone dimer was desirable. This was achieved by a convenient preparation from the commercially available solid dimer, which rearranged spontaneously to III when heated with a trace of aluminum chloride. The β-lactone dimer was obtained in high yield with surprisingly little formation of polymeric byproducts.



Alternately, III was prepared by direct dimerization of dimethylketene in the presence of aluminum chloride. The dimerization took place rapidly at temperatures much lower than those required to isomerize the solid dimer V; the normal dimer,

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[7] R. J. P. Allen, R. L. Forman, and P. D. Ritchie, *J. Chem. Soc.*, 2721 (1955).

therefore, is not an intermediate in the direct preparation of III from dimethylketene.

EXPERIMENTAL

Polymerization of dimethylketene and pyrolysis of the polymer. A stream of dimethylketene[8] (approximately 400 g.) was passed into a stirred suspension of 5 g. of sodium methoxide in 1500 ml. of ether for 2 hr. The mixture began to reflux vigorously a few minutes after addition of dimethylketene was started, and a white powdery solid separated. The mixture was stirred at room temperature overnight and then filtered. The crude polymer (252 g.) was washed thoroughly with water and dried in air; the residue weighed 223 g. and melted sharply at 175°.

Anal. Calcd. for $(C_4H_6O)_x$: C, 68.5; H, 8.6. Found: C, 68.9; H, 8.8; mol. wt. (ebullioscopic in benzene), 2640.

The ethereal filtrate was evaporated on the steam bath to 146 g. of liquid, nonvolatile residue, which was distilled to give 11.2 g. boiling at 70–108° (100 mm.) (contained a small amount of crystalline solid, probably V); 105 g. boiling at 108–150° (100 mm.); and 12 g. of residue. In addition to these fractions, a deep yellow liquid (dimethylketene) collected in the cold trap, particularly during the latter part of the distillation. This was destroyed by adding methanol to the trap. Part of the 108–150° (100 mm.) fraction may have been present as such before distillation; however, much of it evidently was formed by pyrolysis during the distillation, as the temperature in the distilling flask rose from 130° to over 200° during removal of this fraction. Redistillation of this fraction gave 61 g. of crude 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (III), b.p. 107–113° (100 mm.); gas chromatographic analysis indicated the material contained 80% III.

A 100-g. sample of the solid polymer was subjected to distillation at 100 mm. through a short distillation column. The polymer melted to a viscous liquid and decomposed smoothly at about 280°. Distillate (81 g.) was collected to a head temperature of 150° (100 mm.). Toward the end of the distillation, the head temperature fell sharply, and a few drops of deep yellow liquid (dimethylketene) distilled into the cold trap. The crude pyrolysate was redistilled through the same column to give 5.6 g. of forerun and 63.0 g. of III, b.p. 105–110° (100 mm.). This sample of III was 97% pure, by gas chromatographic analysis.

Pure III was obtained by distillation through a 1 × 84-in. column packed with Podbielniak Helipak packing. A fraction, b.p. 110–111° (101 mm.), n_D^{20} 1.4382, was analyzed.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.5; H, 8.6; mol. wt., 140. Found: C, 68.4; H, 8.5; mol. wt. (cryoscopic in benzene), 120, 127.

The NMR spectrum was determined with a Varian Associates Model V-4300B, high-resolution NMR instrument (40 mc.) equipped with a flux stabilizer. The chemical shift positions were determined relative to tetramethylsilane as an internal standard.

The infrared spectrum, recorded on a Baird Associates infrared recording spectrophotometer, showed major bands at 5.35, 5.50, 5.75, 8.80, 9.00, 10.90, and 12.65 μ.

Polymerization of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (III) *and pyrolysis of the polymer.* One hundred grams of III was added gradually to a stirred, refluxing suspension of 5 g. of sodium methoxide in 500 ml. of anhydrous ether under a nitrogen atmosphere. There was no apparent reaction at first, but after 45 min., polymer separated rapidly and the reaction mixture became semisolid. The total reaction time was approximately 1 hr. The crude polymer (97 g.) was filtered and then washed repeatedly with water in a Waring Blendor until the washings were no longer alkaline. The washed polymer weighed 84.5 g. (84.5% yield), melted at 198–200°, had a molecular weight (ebullioscopic in toluene) of 11,900, and exhibited an inherent viscosity (0.25% solution in 60:40 phenoltetrachloroethane mixture at 25°) of 0.37. The infrared spectrum of this material was identical with that of the polymer prepared directly from dimethylketene and sodium methoxide.

A sample was purified for analysis by dissolving it in hot dimethylformamide, filtering the solution, and precipitating the polymer in methanol.

Anal. Calcd. for $(C_4H_6O)_x$: C, 68.5; H, 8.6. Found: C, 68.2; H, 8.7.

Fifty grams of the polymer was pyrolyzed by distillation at 100 mm. The molten polymer began to decompose at about 250°; the temperature at the distilling head remained fairly constant at 105–110°. No significant amount of material condensed in the cold trap, and no dimethylketene (yellow color) was noted. The distillate, n_D^{20} 1.4362, weighed 39 g. (80% yield). Analysis by gas chromatography indicated that the pyrolysate contained 96% III and 4% diisopropyl ketone. The identification of the major component as III was confirmed by its infrared spectrum.

Diethylene glycol bis(2,2,4-trimethyl-3-oxovalerate). Two grams of sodium was dissolved in 800 g. (7.5 moles) of diethylene glycol. The solution was stirred and heated in an open beaker to 60–70°, and 2100 g. of tetramethyl-1,3-cyclobutanedione (V, 15 moles) was added gradually. The reaction mixture was cooled occasionally to keep the temperature below 110°. After about half of the V had been added, the reaction slowed, and a solution of 1 g. of sodium in diethylene glycol was added. The reaction again became exothermic and remained so until addition of the V was complete. The mixture was stirred at 80–100° for 10–15 min., acidified with 20 ml. of concd. hydrochloric acid, and washed with water. Unconverted V was removed by heating the mixture to 200° and passing a stream of nitrogen through it for 3 hr. The residue was distilled to give 1507 g. (52%) of diethylene glycol bis(2,2,4-trimethyl-3-oxovalerate), b.p. 200–205° (3 mm.) n_D^{24} 1.4492.

Anal. Calcd. for $C_{20}H_{34}O_7$: sapon. equiv., 193. Found: sapon. equiv., 193.

Pyrolysis of diethylene glycol bis(2,2,4-trimethyl-3-oxovalerate). A mixture of 125 g. of diethylene glycol bis(2,2,4-trimethyl-3-oxovalerate) and 5 g. of sodium acetate was distilled at 5 mm. through a 15-in. column packed with Penn State protruded packing. Removal of undecomposed ester was prevented by an automatic still head and temperature controller, which placed the column on total reflux if the head temperature exceeded 125°. The temperature in the distilling flask rose to 205°, then fell slowly to 185°, and, as the decomposition progressed, rose again to 195°. The distillation was continued until the distilling flask was dry. The distillate weighed 101 g. (81% of the charge). This material contained, by gas chromatographic analysis (area percent), 0.8% of unidentified material, 29.9% of III, 6.8% of hexamethyl-1,3,5-cyclohexanetrione, and 62.5% of diethylene glycol diisobutyrate. Peaks were identified by calibration with known compounds. No diethylene glycol bis(2,2,4-trimethyl-3-oxovalerate) was present. Redistillation gave 28 g. of III, b.p. 85° (40 mm.); 8 g., b.p. 85–160° (40 mm.), which partly crystallized on cooling; 13 g., b.p. 160–178° (40 mm.); and 42 g. of diethylene glycol diisobutyrate, b.p. 178–180° (40 mm.), n_D^{20} 1.4282.

The identity of the 85° (40 mm.) fraction as III was confirmed by its infrared spectrum.

Anal. Calcd. for $C_8H_{12}O_2$: sapon. equiv., 140. Found: sapon. equiv., 143.

The solid which separated from the 85–160° (40 mm.) fraction, after being filtered and washed with hexane, melted at 78–82°. It was identified as hexamethyl-1,3,5-

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[8] Attention is drawn to the formation of sensitive, explosive peroxides if dimethylketene is contacted with air (H. Staudinger, *Die Ketene*, F. Enke, Stuttgart, Germany, 1912, p. 141). All operations involving monomeric dimethylketene were carried out under nitrogen.

cyclohexanetrione by comparison (melting point of a mixture and infrared spectrum) with an authentic sample.[9]

The diethylene glycol diisobutyrate fraction was characterized by its infrared spectrum, which showed the expected ester carbonyl and ether absorptions.

Anal. Calcd. for $C_{12}H_{22}O_5$: C, 58.5; H, 9.0; sapon. equiv., 123. Found: C, 58.7; H, 9.3; sapon. equiv., 123.

Derivatives of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (III). *A. Reduction by lithium aluminum hydride.* A solution of 140 g. (1.0 mole) of III in 300 ml. of ether was added slowly to a stirred slurry of 30 g. (0.79 mole) of lithium aluminum hydride in 1000 ml. of ether. The temperature of the exothermic reaction was kept below 30° by an ice bath. After the addition was complete, the solution was refluxed for 30 min. The solution was cooled and 100 ml. of methanol was added slowly, followed by 100 ml. of 10% sulfuric acid solution. The ether layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Distillation of this solution through a 10-in. packed column gave 102 g. (82%) of 1-hydroxy-2,2,4-trimethyl-3-pentanone (VII) b.p. 108–110° (30 mm.), n_{D}^{20}1.4382.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.2. Found: C, 66.6; H, 11.2.

The infrared spectrum of VII showed bands at 2.9 μ (—OH) and 5.9 μ with a shoulder at 5.8 μ (>C═O). The *p*-nitrobenzoate melted at 83–84° (lit. m.p. 82–83°).[10]

Anal. Calcd. for $C_{15}H_{19}NO_5$: N, 4.8. Found: N, 4.8.

B. Reaction with aniline. Aniline (93 g., 1.0 mole) was mixed with 140 g. (1.0 mole) of III. The flask was stoppered loosely, heated on the steam bath for 3 hr., and allowed to stand overnight. The solid reaction mixture was recrystallized twice from diisopropyl ether to give 202 g. (87%) of 2,2,4-trimethyl-3-oxovaleranilide, m.p. 94–95°.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.1; H, 8.2; N, 6.0; mol. wt., 233. Found: C, 72.0; H, 8.1; N, 5.9; mol. wt. (ebullioscopic in benzene), 235.

In attempts to prepare this derivative from aniline and tetramethyl-1,3-cyclobutanedione (V), Staudinger obtained a product, m.p 95–96°, but elemental analyses did not agree with the theoretical values.[11]

C. Reaction with piperidine. Piperidine (65 g., 0.76 mole) was mixed with 110 g. (0.79 mole) of III. After the rapid, exothermic reaction subsided, the mixture was distilled through a 1.8 × 51-cm. column packed with stainless steel protruded packing. The yield of 1-(2,2,4-trimethyl-3-oxovaleryl)piperidine, b.p. 146.5–147.5° (7.0–7.4 mm.), n_{D}^{20} 1.4830, was 123 g. (70%). The product was identical with the corresponding derivative of tetramethyl-1,3-cyclobutanedione (V).[1]

D. Reaction with 2-chloroethanol. 2-Chloroethanol (241.5 g., 3.0 moles) was mixed with 421 g. (3.0 moles) of III and 5.0 g. of *p*-toluenesulfonic acid, and the mixture was heated to 90° over a period of 25 min. An exothermic reaction proceeded without further external heating to 157° during 40 min. Heating was then resumed, and the temperature was maintained at 160–165° for 2 hr. The product was distilled through a 1.8 × 51-cm. column packed with stainless steel protruded packing. The yield of 2-chloroethyl 2,2,4-trimethyl-3-oxovalerate, b.p. 123° (10 mm.), n_{D}^{20} 1.4463, was 583 g. (88%).

Anal. Calcd. for $C_{10}H_{17}ClO_3$: C, 54.4; H, 7.8; Cl, 16.1; mol. wt., 221. Found: C, 54.1; H, 7.7; Cl, 16.1; mol. wt., 223.

E. Reaction with p-tert-butylbenzenethiol. A mixture of 25 g. (0.15 mole) of *p-tert*-butylbenzenethiol, 21 g. (0.15 mole) of III, 0.3 g. of sodium, and 100 ml. of toluene was refluxed with stirring for 8 hr. The cooled reaction solution was washed with dilute sodium hydroxide solution and water and dried over anhydrous magnesium sulfate. Evaporation of this solution on a steam bath gave 44.5 g. (96%) of *p-tert*-butylphenyl 2,2,4-trimethyl-3-oxothiovalerate, m.p. 54–57°. A sample, m.p. 58–59°, prepared by recrystallization from hexane, was identical with material prepared from *p-tert*-butylbenzenethiol and tetramethyl-1,3-cyclobutanedione.[12]

Isomerization of tetramethyl-1,3-cyclobutanedione (V) *to 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone* (III). In a 3-l. flask equipped with a reflux condenser, 1000 g. of tetramethyl-1,3-cyclobutanedione was heated until molten (115–120°), and 1 g. of anhydrous aluminum chloride was added. As the exothermic reaction took place, the temperature rose to 153°, and the mixture refluxed at a moderate rate. When the reaction subsided, external heat was applied to maintain reflux for 30 min. The reaction mixture was distilled rapidly through a short Vigreux column at atmospheric pressure to give 868 g. (87%) of crude III, b.p. 165–175°. By gas chromatographic analysis, the product was 94% pure, with V as the principal impurity. Fractionation of an aliquot gave pure III, b.p. 119.5–120° (150 mm.), n_{D}^{20} 1.4380.

Dimerization of dimethylketene to 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (III). Dimethylketene (70 g.) was added to a stirred solution of 3 g. of aluminum chloride in 82 g. of III under a nitrogen atmosphere. The reaction was quite exothermic; the temperature was kept at 40–70° by an ice bath. The reaction appeared to be complete in a few minutes, but stirring was continued for an additional hour. Examination of the solution by gas chromatography showed primarily one component. Distillation through a 6-in. Vigreux column gave 133 g. (72%) of III, b.p. 83–85° (40 mm.), n_{D}^{20} 1.4381.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.5; H, 8.6; sapon. equiv., 140. Found: C, 68.4; H, 8.7; sapon. equiv., 140.

The dimerization was also carried out in a similar manner with chloroform as the solvent.

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