boxyl carbonyl band at 1695 cm.$^{-1}$ but failed to show any lactone band.

2,2-Bis(3,5-dimethyl-4-hydroxyphenyl)propionic acid. The oil obtained from the reaction of 8.8 g. (0.1 mole) of pyruvic acid and 24.4 g. (0.2 mole) of 2,6-xylenol solidified on standing. The pink solid was dissolved in aqueous sodium bicarbonate. The resulting solution was washed with 50:50 ether–ethyl acetate and acidified with dilute hydrochloric acid. Filtration yielded 11.9 g. (38%) of white solid, m.p. 187–191° dec. Three recrystallizations of a 6-g. sample from 1,2-dichloroethane–acetone yielded 4.5 g. of white needles, m.p. 202–203° dec.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05; neut. equiv., 314. Found: C, 72.50; H, 7.02; neut. equiv., 312.

3-Methyl-3-(2-hydroxy-5-methylphenyl)-5-methylcoumaran-2-one (XVI). A mixture of 86.4 g. (0.80 mole) of *p*-cresol and 17.6 g. (0.20 mole) of pyruvic acid in 150 ml. of glacial acetic acid was saturated with anhydrous hydrogen chloride and the contents of the flask stoppered and allowed to stand at room temperature for several days. At the end of the fifth day, the red solution was again saturated with anhydrous hydrogen chloride. After 9 days, the dark red solution was poured over crushed ice whereupon a light amber oil separated. The oily product was washed several times with water by decantation until the washings were neutral to litmus. The oil was then steam distilled to remove unchanged *p*-cresol. The resulting light tan colored oil thereupon solidified on standing overnight. The solid product was collected and dried *in vacuo* over sulfuric acid. The yield of crude product was 25.0 g. (46.6%) based on pyruvic acid. An analytical sample was obtained by three crystallizations from carbon tetrachloride, m.p. 83–84°, white prisms. Infrared maximum at 1790 cm.$^{-1}$ (5-membered lactone).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.01. Found: C, 76.05; H, 5.84.

Acknowledgment. The authors wish to thank Drs. Howard L. Gerhart and Stewart W. Gloyer, Pittsburgh Plate Glass Co., and Dr. J. Vernon Steinle and the management of S. C. Johnson & Son, Inc., for permission to present this work for publication. Many stimulating discussions with Prof. Charles D. Hurd, Northwestern University, are acknowledged with gratitude.

SPRINGDALE, PA.
RACINE, WIS.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, AND THE CHEMICAL RESEARCH LABORATORIES OF THE GIVAUDAN CORP.]

The Base-Catalyzed Conversion of Ketenes and Ketene Dimers to Ketene Trimers

J. L. E. ERICKSON AND GARRY C. KITCHENS

Received August 16, 1961

Dimethylketene and its dimer, tetramethyl-1,3-cyclobutanedione (IV), were converted by a base-catalyzed process to the trimer, hexamethyl-1,3,5-cyclohexanetrione (VII), which was hydrogenated over copper chromite to yield the *cis* and *trans* isomers of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetriol. Diphenylketene gave the dimer, tetraphenyl-1,3-cyclobutanedione (VIII), and the trimer, hexaphenyl-1,3,5-cyclohexanetrione. The reaction of VIII with phenyllithium resulted in cleavage of the ring.

Ketoketenes dimerize upon standing or when heated to form substituted 1,3-cyclobutanediones. In some cases, depending upon the method employed for the preparation of the ketene, the product actually isolated is the ketene dimer. Thus, the dehydrohalogenation of isobutyryl chloride by the use of a tertiary amine leads to the dimer, tetramethyl-1,3-cyclobutanedione (IV),[1] but there is no evidence of symmetrical trimerization resulting in the formation of hexamethyl-1,3,5-cyclohexanetrione (VII), commonly known as hexamethylphloroglucinol.

The dimerization of ketoketenes is generally classified as a four-center-type reaction,[2] indicating that there are four atoms undergoing covalency change at the same time, and that evidence for the formation of ions or radicals as intermediates is lacking. Our experiments show, however, that ketoketenes, or their dimers may be converted rapidly and almost completely to their trimers in the presence of a basic catalyst such as sodium methoxide, thus suggesting that an ionic process may be involved. In this manner both dimethylketene and its dimer, tetramethyl-1,3-cyclobutanedione (IV), were converted to the dimethylketene trimer, hexamethyl-1,3,5-cyclohexanetrione (VII), a product obtained previously by Herzig and Erthal[3] by methylating phloroglucinol.

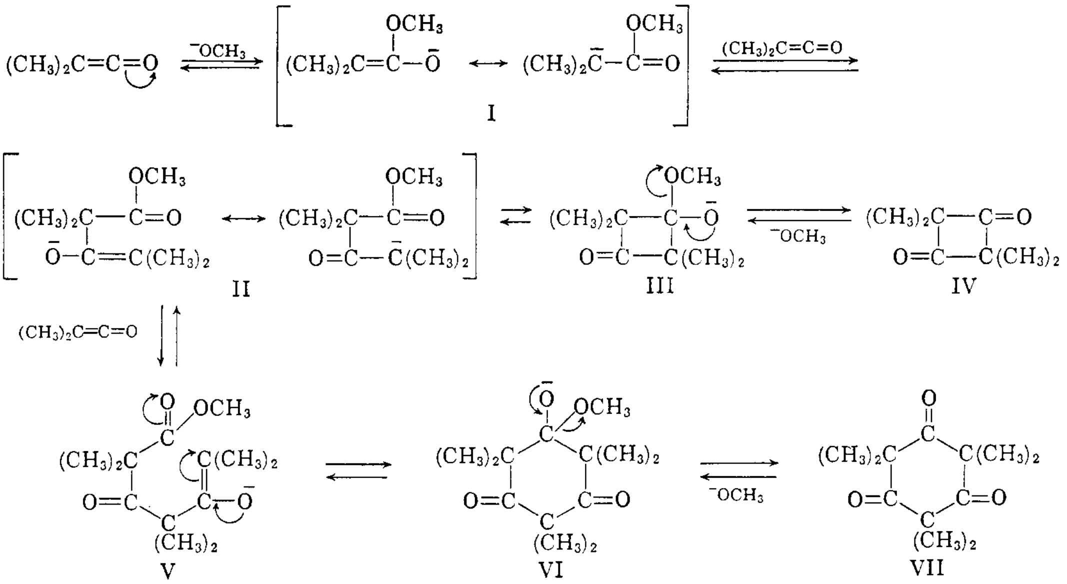
These results suggest a reaction mechanism that employs conventional ideas, and interprets these conversions as base-catalyzed, ionic processes which are reversible, thus accounting for the interconversion of ketene monomers, ketene dimers, and ketene trimers. It can be extended to account for even higher cyclic polymers. The methoxide ion catalyst attacks presumably the relatively positive carbonyl carbon atom of the ketene to form the enolate ion I. The next step in the reaction appears to be one between the ketene and the enolate ion I (similar to aldol addition) to form a second enolate ion II, which may either (a) undergo cycli-

---

(1) E. Wedekind and W. Weisswange, *Ber.*, **39**, 1631 (1906).

(2) J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, 1956, p. 453, *et seq.*

(3) J. Herzig and B. Erthal, *Monatsh.*, **32**, 505 (1911).

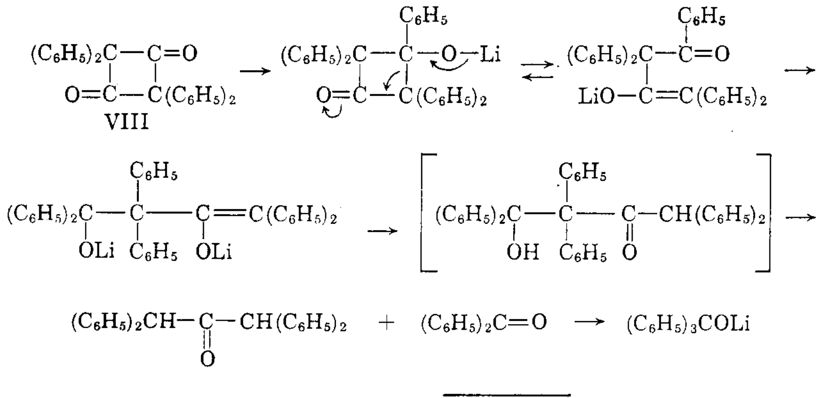


zation to the anion III, which then ejects the catalyst to form the dimer, tetramethyl-1,3-cyclobutanedione (IV), or (b) add another molecule of the ketene to form the enolate ion V, which then undergoes cyclization to the anion VI. The polymerization apparently is terminated when the cyclic anion VI ejects the catalyst and reverts to the stable 6-carbon cyclic trimer, hexamethyl-1,3,5-cyclohexanetrione (VII).

The catalytic hydrogenation of tetramethyl-1,3-cyclobutanedione (IV) to 2,2,4,4-tetramethyl-1,3-cyclobutanediol has already been investigated by Gross,[4] and Miller,[5] and more recently detailed studies have been made by Hasek, Elam, Martin, and Nations.[6] In our investigation of the hydrogenation of hexamethyl-1,3,5-cyclohexanetrione (VII), it was found that the use of a copper chromite catalyst gave excellent yields of the *cis* and *trans* isomers of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetriol, which were separated by fractional crystallization. Raney nickel proved to be relatively ineffective, while reduction of VII with potassium borohydride gave only the higher melting isomer.

Diphenylketene has much less tendency to polymerize, but Staudinger and Goller[7] have shown that diphenylketene–quinoline, upon heating at 170° for eighty hours, yields the dimer in very small yield along with another polymer, presumably the trimer, in much greater amounts. We have found that pure diphenylketene, when heated at 180–200° for six hours, undergoes extensive dimerization and trimerization to yield tetraphenyl-1,3-cyclobutanedione (VIII) and hexaphenyl-1,3,5-cyclohexanetrione, and that these processes may be catalyzed by sodium methoxide.

Unlike tetramethyl-1,3-cyclobutanedione (IV), which has been shown[8] to undergo cleavage of the ring when treated with a number of organic magnesium compounds, tetraphenyl-1,3-cyclobutanedione (VIII) failed to give a noticeable reaction with phenylmagnesium bromide even when heated at 66° for six hours. The reaction of VIII with



---

(4) P. F. Gross, *The Structure of Ketene Dimer*, Ph.D. thesis, Cornell University, 1936.

(5) L. L. Miller, *Structure of Some Derivatives of Dimethylketene*, Ph.D. thesis, Cornell University, 1937.

(6) R. H. Hasek, E. U. Elam, J. C. Martin, and R. G. Nations, *J. Org. Chem.*, **26**, 700 (1961).

(7) H. Staudinger and H. Goller, *Ber.*, **44**, 530 (1911); H. Staudinger, *Die Ketene*, Ferdinand Enke, Stuttgart, 1912, p. 38, *et seq.*

(8) J. L. E. Erickson and G. C. Kitchens, *J. Am. Chem. Soc.*, **68**, 492 (1946).

phenyllithium, however, resulted in cleavage of the ring.

Apparently phenyllithium added to a carbonyl group of VIII to form an unstable lithium salt whose decomposition resulted in cleavage of the ring and the formation of a ketone which did not survive in the presence of an excess of the reagent, but instead added more of the reagent to form a diaddition product, which gave on hydrolysis *sym*-tetraphenylacetone and benzophenone,[8] cleavage products of the β-hydroxy ketone. The interpretation of the course of this reaction is based upon the assumption that the O—Li bond in the lithium salt has sufficient ionic character to permit an oxygen electron pair to initiate or partake in the electron shifts shown, thus resulting in cleavage of the ring in a manner similar to the cleavage of IV by sodium methoxide.

EXPERIMENTAL[9]

2,2,4,4,6,6-Hexamethyl-1,3,5-cyclohexanetrione (VII). *Method A.* Into a flask, equipped with an agitator, thermometer, reflux condenser, and an inlet tube extending to the bottom of the flask, were charged 30 g. of dry toluene and 0.1 g. of solid sodium methoxide. The mixture was agitated and heated at 110° while 10 g. of dimethylketene, prepared[10] by the pyrolysis of dimethylketene dimer, was distilled slowly through the inlet tube into the reaction flask over a period of 0.5 hr. After stirring and heating at 110° for an additional 0.5 hr., the reaction mixture was cooled to 90°, 0.1 g. of sodium methoxide was added, and the agitation continued at 110° for 0.5 hr. The reaction mixture was cooled to 25°, neutralized to phenolphthalein with glacial acetic acid, and filtered to remove a small amount of insoluble material which, after washing with water, melted at 280°. The toluene solution was washed twice with 25-ml. portions of water, and the solvent was removed by distillation under reduced pressure leaving a solid residue of 9.0 g. of product. Recrystallization from 5 ml. of methanol at 0° gave 8.5 g. of VII, m.p. 80–81°. When VII was mixed with hexamethylphloroglucinol, prepared by methylating phloroglucinol according to the method of Herzig and Erthal,[3] the melting point was unchanged.

Method B. 2,2,4,4,6,6-Hexamethyl-1,3,5-cyclohexanetrione (VII) was obtained in high yield by treating tetramethyl-1,3-cyclobutanedione (IV), b.p. 160–161°, m.p. 115–116°, with a catalytic amount of sodium methoxide. To a stirred suspension of 2 g. of solid sodium methoxide and 400 ml. of toluene at 110° was added by means of a solids feeding funnel 200 g. of IV over a period of 0.5 hr. during which time the reflux temperature gradually rose to 118°. The contents of the flask were heated at reflux temperature for 0.5 hr., cooled to 90° while 0.5 g. of sodium methoxide was added, and then refluxed at 118° for an additional 0.5 hr. The reaction mixture was cooled to 25°, neutralized to phenolphthalein by the addition of glacial acetic acid, and then washed four times with 50-ml. portions of water. The toluene was removed by distillation under slight, reduced pressure, and there remained a residue of 196 g. of solid product. Upon recrystallization from 196 ml. of methanol at 0°, there was obtained 174 g. of VII, m.p. 80–81°. The methanol mother liquor, upon concentration to one half its volume and cooling to 0°, gave 12 g. of VII, m.p. 78–80°. The remaining mother liquor was evaporated to remove the methanol, and the residue was distilled to yield 9 g. of VII, b.p. 75–85° (0.5 mm.), m.p. 76–78°. The total yield of VII was 195 g. (97.5%).

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.62; mol. wt., 210.3. Found: C, 68.35; H, 8.24; mol. wt. (benzene), 231.

2,2,4,4,6,6-Hexamethyl-1,3,5-cyclohexanetriol. A mixture of 62 g. of VII, 150 ml. of 1-butanol, and 20 g. of copper chromite was hydrogenated in a rocking autoclave using a stainless steel liner at 170° under 550 p.s.i. of hydrogen for 26 hr. The contents were filtered and the liner and the precipitate were washed with 200 ml. of hot toluene (100°) and then with 200 ml. of warm methanol (60°). The filtrates were combined and cooled to −10°, and 9 g. of crystals, m.p. 243.4–244.4°, was deposited. The mother liquors were distilled under reduced pressure leaving a residue of 55 g which was dissolved in 100 ml. of hot methanol, then cooled to 25° and filtered. There was obtained 12 g. of crystals which were recrystallized from methanol to yield 11 g. of product. The methanol was removed from the mother liquors by distillation and the solid residue was treated with 100 ml. of boiling water, filtered hot, and the solution allowed to crystallize. The crystals obtained were washed with cold water and air dried, and amounted to 15 g., m.p. 243.4–244.4°. The total yield of product was 35 g., m.p. 243.4–244.4°.

Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18; OH, 23.59. Found: C, 66.41; H, 10.91; OH, 23.35.

The aqueous solution was cooled to 5°, and 28 g. of crystals, m.p. 90–93°, were deposited. These crystals were hydrated and lost water above 100°, or when dissolved in 50 ml. of toluene and refluxed, the water was removed by the use of a water separator. The toluene solution was cooled to 5° and yielded 24 g. of a lower melting isomer, m.p. 137–137.5°. Evaporation of the mother liquors gave about 5 g. of impure material containing hydroxy ketones.

Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18; OH, 23.59. Found: C, 66.58; H, 10.84; OH, 22.94.

Reduction of VII *with potassium borohydride.* The reduction of 35 g. of VII in methanol with 8.9 g. of potassium borohydride gave 27 g. of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetriol, m.p. 243.4–244.4°, and 7 g. of impure material containing hydroxy ketones resulting from partial reduction of the cyclic triketone.

Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18; OH, 23.59. Found: C, 66.38; H, 10.94; OH, 23.38.

The dimerization and trimerization of diphenylketene. A modification of the method of Staudinger and Goller,[7] which is perhaps more convenient, was used in the polymerization of this ketene. Pure diphenylketene[11] (50 g.) was heated at 180–200° under an atmosphere of nitrogen for 6 hr., and then allowed to cool and solidify. Digestion with 100 ml. of ether dissolved the greater portion of the trimer, leaving as a residue the very insoluble diphenylketene dimer. One crystallization of the residue from benzene almost completelely separated the two polymers, and yielded 3.3 g. of tetraphenyl-1,3-cyclobutanedione, m.p. 245–247°.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.6; H, 5.2. Found: C, 86.3; H, 5.4.

The ether extract, upon concentration and addition of an equal volume of pentane, gave 19.1 g. of crystals, m.p. 176–177°, and from the benzene and ether–pentane mother liquors there was obtained an additional 8.9 g. of product, making a total of 27 g. (54%) of hexaphenyl-1,3,5-cyclohexanetrione, m.p. 176–177°.

Anal. Calcd. for $C_{42}H_{30}O_3$: C, 86.6; H, 5.2; mol. wt., 582. Found: C, 86.3, 86.4; H, 5.2, 5.4; mol. wt. (benzene), 588.

The polymerization of diphenylketene takes place more rapidly in the presence of a basic catalyst, such as sodium methoxide. A mixture of 10 g. of diphenylketene and 0.1 g. of sodium methoxide was heated at 160° for 2 hr., and then

---

(9) Melting points are uncorrected.

(10) W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 136 (1946).

(11) L. I. Smith and H. H. Hoehn, *Org. Syntheses*, **Coll. Vol. III**, 356 (1955).

allowed to cool. The product was dissolved in hot benzene, then glacial acetic acid was added to neutralize the catalyst, and the benzene solution was washed several times with water. Upon concentration of the benzene solution 0.5 g. of crystals of the dimer, m.p. 245–246°, was obtained. The benzene filtrate was then concentrated, an equal volume of pentane was added, and upon standing there was deposited 6.2 g. of crystals of hexaphenyl-1,3,5-cyclohexanetrione, m.p. 176°.

Tetraphenyl-1,3-cyclobutanedione (VIII). *Cleavage by phenyllithium.* To 100 ml. of an ethereal solution of phenyllithium, prepared from 1.46 g. of lithium and 16.2 g. of bromobenzene, was added in portions 5 g. of VIII. After the reaction had subsided the reaction mixture was refluxed for 1.5 hr., allowed to stand overnight, and then hydrolyzed with iced hydrochloric acid. The ether extract was washed with water, dried, and evaporated almost to dryness leaving 8.5 g. of a residue which gave 2.3 g. of crystals upon the addition of a small quantity of pentane. After recrystallization from alcohol this material was identified as triphenylcarbinol, m.p. 161–163°, mixed m.p. 161.5–163°. Upon the addition of more pentane there was deposited 4.7 g. of a second crop of crystals, which were recrystallized once from an ether-pentane mixture, and twice from alcohol to yield 4.5 g. of material, m.p. 133–134.5°, which was identified as *sym*-tetraphenylacetone. A mixed m.p. with an authentic sample of *sym*-tetraphenylacetone was 132–134°. The solvents from the mother liquors were removed, and the residue was steam distilled to yield a trace of benzophenone, m.p. 47–48°, and a residue which, after recrystallization from alcohol, gave 0.9 g. of triphenylcarbinol. The total yield consisted of 3.2 g. (95%) of triphenylcarbinol, 4.5 g. (96%) of *sym*-tetraphenylacetone, and a trace of benzophenone.

Treatment of VIII *with phenylmagnesium bromide* failed to give an appreciable reaction, and VIII was recovered unchanged. When 1 g. of VIII was added to an ethereal solution of phenylmagnesium bromide, prepared from 0.95 g. of magnesium and 6.12 g. of bromobenzene, and the solution was refluxed for 1.5 hr. and then hydrolyzed, 0.8 g. of VIII was recovered. In another experiment, using the same quantities of materials, the ether was partially replaced by benzene, and the solution was refluxed at 66° for 6 hr. Upon working up the product, 0.6 g. of VIII, m.p. 245–247°, was recovered.

BATON ROUGE, LA.
DELAWANNA, N. J.

[CONTRIBUTION FROM THE PFISTER CHEMICAL WORKS, INC.]

The Action of Perchloryl Fluoride on Acylamidomalonates

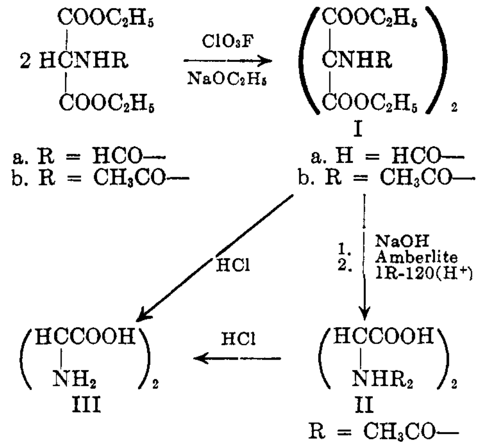
HERMAN GERSHON AND ALFRED SCALA

Received August 10, 1961

Acylamidomalonates were oxidatively dimerized by perchloryl fluoride in the presence of strong base. These dimers were hydrolyzed to diaminosuccinic acid.

It was reported by Inman, Oesterling, and Tyczkowski[1] that compounds containing active methylene groups could, in the presence of strong base, be fluorinated by perchloryl fluoride. Since, in our work on amino acid synthesis, extensive use of the aminomalonates is made, it was desired to ascertain the effect of perchloryl fluoride on this group of reagents which possesses active methylene groups.

SCHEME I



Ethyl formamidomalonate and ethyl acetamidomalonate, respectively, were subjected to the action of perchloryl fluoride in the presence of sodium ethoxide. The reaction products were identified by hydrolysis to diacetamidosuccinic acid and to diaminosuccinic acid according to scheme I. Product Ia was obtained in 39.5% yield and melted at 141–142°; product Ib was obtained in 54% yield and melted at 151.5–152.5°. On saponification of Ib by sodium hydroxide at 35° overnight, followed by passage through a column of Amberlite IR-120(H+), carbon dioxide evolution on the column was observed. Compound II, 2,3-diacetamidosuccinic acid, was obtained in 14.8% yield and melted at 237–238° dec., lit.[2] m.p. 235° dec. On hydrolysis of Ia with concentrated hydrochloric acid under reflux for two hours, compound III, 2,3-diaminosuccinic acid, was obtained in 6.8% yield, and it decomposed at 310–315°. Although no stereochemical studies were made, the diaminosuccinic acid obtained was undoubtedly in the meso form. The decomposition point of (+)-2,3-diaminosuccinic acid was reported by Hochstein[3] to be 240–290°. The *dl*-form, according to

---

[1] C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 6533 (1958).

[2] Beilstein, **IV**, p. 487.

[3] F. A. Hochstein, *J. Org. Chem.*, **24**, 679 (1959).