apparently derived from the combination of catechol with four moles of ethylene.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.71; H, 9.95.

The infrared and ultraviolet spectra of this fraction, however, showed that it was a mixture; —OH 2.9 μ (nonphenolic), >C=O 5.8, 6.0 μ, C=C 6.1 μ (shoulder), λ_{max} 303, 239 mμ, ε 80, 5800.

Characterization of products from phenol and propylene. The product from the reaction of 80 g. of phenol (two runs) with propylene at 275° and 3000 atm. was dissolved in pentane and extracted with several portions of Claisen's alkali. The product (22 g.) obtained by distillation of the dried pentane solution appeared to consist of aromatic ether and nonaromatic hydrocarbon on the basis of its infrared spectrum. Distillation of the phenols obtained by acidification and extraction of the Claisen's alkali solution afforded (a) 11 g., b.p. 110–120° (17 mm.), n_D^{25} 1.5153; (b) 103 g. (65% conversion) of crude 2,6-diisopropylphenol, b.p. 120–126° (17 mm.) together with fractions b.p. 55–67° (0.2 mm.), n_D^{25} 1.5124–1.5063; and (c) a residue of 5 g. The analysis and the ultraviolet spectrum of a constant boiling fraction obtained in the above distillation were consistent with the values for 2,6-diisopropylphenol, 38 g., b.p. 126° (17 mm.), n_D^{25} 1.5111, λ_{max} 278, 271 mμ, ε 1890, 1870. Since the last cut obtained in the distillation had a very similar ultraviolet spectrum (λ_{max} 278, 271 mμ, ε 1744, 1707), it appears that the crude 2,6-diisopropylphenol was contaminated with a small amount of hydrocarbon.

Characterization of the products from phenol and isobutylene. The product from the reaction of phenol (120 g., three runs) and isobutylene at 275° and 3000 atm. for 14 hr., was dissolved in pentane and extracted with three 200-ml. portions of Claisen's alkali. After the pentane was removed from the dried solution, the residue (105 g.) was distilled to obtain 68 g. (28% conversion) of 2,6-di-*t*-butylphenol, b.p. 136–143° (21 mm.), n_D^{25} 1.4989–1.5001. The refractive index and infrared spectra of the lower (n_D^{25} 1.4719) and higher boiling fractions (n_D^{25} 1.48–1.46) indicated that these materials were largely hydrocarbons. The crude 2,6-di-*t*-butylphenol was redistilled in a 36″ column to obtain 51 ml. of pure 2,6-di-*t*-butylphenol, b.p. 133° (20 mm.), m.p. 34–37°, λ_{max} 278, 271 mμ, ε 1750, 1730.

Acidification and extraction of the Claisen's alkali solution afforded 55 g. (29% conversion) of 2-*t*-butylphenol, b.p. 96–107° (16 mm.), n_D^{25} 1.5211. Redistillation gave 37 g. of pure 2-*t*-butylphenol, b.p. 101–103.5° (13 mm.), n_D^{25} 1.5212, λ_{max} 278, 271 mμ, ε 2070, 2025, having the correct analysis.

WILMINGTON, DEL.

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

Some Applications of Isopropylidene Malonate and Its Derivatives to the Synthesis of Cyclic Compounds

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Diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate and its 3-methyl and 3-phenyl derivatives have been prepared by treating the sodium salts of diisopropylidene methylenedimalonate, diisopropylidene ethylidenedimalonate, and diisopropylidene benzylidenedimalonate, respectively, with iodine or bromine. By alkylation of the sodium salt of isopropylidene malonate in dimethylformamide at room temperature, isopropylidene 1,1-cyclohexanedicarboxylate and isopropylidene 1,1-cyclopentanedicarboxylate have been prepared.

Methylations of isopropylidene malonate (I) have yielded principally the dimethylmalonate derivative. The reactions have been carried out by treating the isolated silver salt, in ether suspension, with methyl iodide,[3] or, better, by treating isopropylidene malonate with silver oxide and methyl iodide in acetonitrile.[4] It has now been found that benzylation of this malonic acid derivative likewise has a strong tendency to proceed to the dialkylation product. Alkylation with benzyl chloride in methanol, ethanol or dimethylformamide (DMF) gave only isopropylidene dibenzylmalonate, as did also a reaction of the sodium salt of isopropylidene malonate with benzyldimethylphenylammonium chloride. Isopropylidene benzylmalonate was obtained by hydrogenation of the benzalmalonate.[5]

These observations suggested that the alkylation of isopropylidene malonate with methylene iodide be examined. The various products that might be expected from reaction between these reagents are diisopropylidene methylenedimalonate (IIa),[5] the cyclobutane derivative (IV) and isopropylidene methylenemalonate (V). When the reaction was carried out in acetonitrile with approximately equimolar quantities of the dihalide, the malonate and silver oxide, a product was obtained which proved to be none of these. The infrared spectrum of the substance was identical with that of a compound obtained earlier from diisopropylidene ethylenetetracarboxylate (VI)[6] and diazomethane, and the identity of the two samples was confirmed by a mixed melting point determination. Mild hydrolysis converted the compound to 1,1,2,2-cyclopropanetetracarboxylic acid. Thus the reaction product must be diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate (IIIa).

The cyclopropane derivative (IIIa) was probably

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[1] Sun Oil Co. Fellow, 1959–1960.

[2] Phillips Petroleum Co. Fellow, 1956–1957.

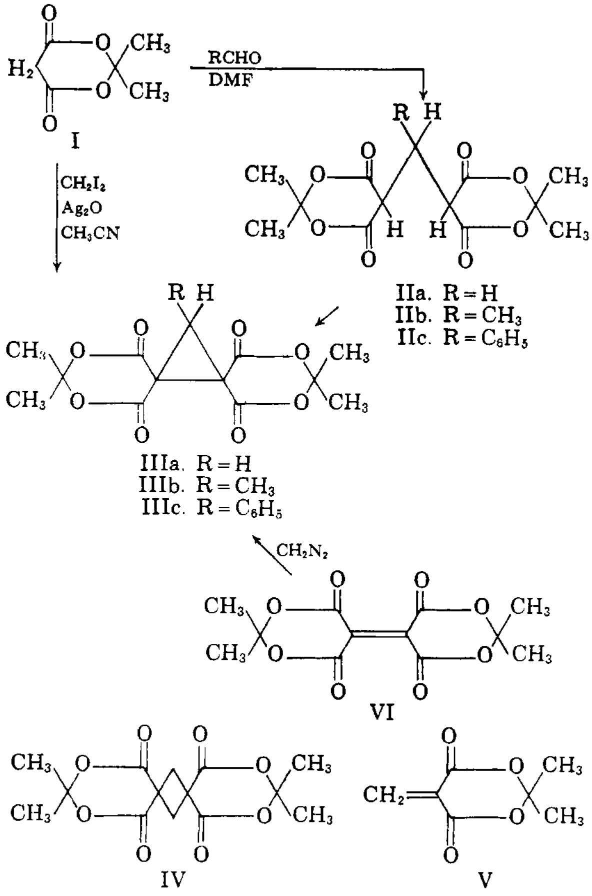
[3] E. Ott, *Ann.*, **401**, 159 (1913).

[4] D. Davidson and S. A. Bernhard, *J. Am. Chem. Soc.*, **70**, 3426 (1948).

[5] J. A. Hedge, C. W. Kruse, and H. R. Snyder, *J. Org. Chem.*, in press.

[6] H. R. Snyder and C. W. Kruse, *J. Am. Chem. Soc.*, **80**, 1942 (1958).

formed from diisopropylidene methylenedimalonate (IIa) through iodination and cyclization by silver oxide, the iodination occurring as the result of the formation of free iodine or its equivalent in the reaction mixture. Cyclization of IIa by treatment with dilute aqueous sodium hydroxide or sodium bicarbonate and solid iodine gave IIIa in yields of about 80%. Stirring a solution of IIa in acetonitrile with silver oxide did not bring about any reaction.

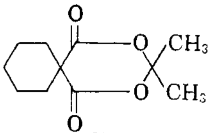


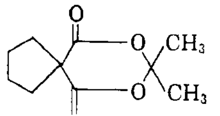
Cyclopropane derivatives were also prepared from diisopropylidene ethylidenedimalonate (IIb),[5] the condensation product of acetaldehyde and isopropylidene malonate, and from diisopropylidene benzylidenedimalonate (IIc),[5] the benzaldehyde condensation product. These cyclizations were most successful (yields 69% and 48%, respectively) when the sodium salts were prepared in methanol and treated with bromine. No exhaustive study of the effects of various reaction conditions on the yields was made, but cyclization of the former in dimethylformamide-aqueous sodium bicarbonate with solid iodine and of the latter in dimethylformamide by treatment with sodium methoxide and then with iodine occurred in yields of only about 15%. Dibenzylidene methylenedimalonate[5] was cyclized with dilute sodium hydroxide and solid iodine to form the dibenzylidene analog of IIa in 69% yield.

An attempt to prepare IV by the alkylation of IIa with methylene iodide in dimethylformamide containing sodium methoxide resulted only in the formation of a gel from which the sodium salt of IIa eventually precipitated.

Attempts to alkylate isopropylidene malonate in ethanolic sodium ethoxide solution resulted in the precipitation of the monosodium salt of isopropylidene malonate, which had been previously characterized by Meldrum.[7] Because of the insolubility of the sodium salt in ethanol, further alkylations were carried out in dimethylformamide, in which the sodium salt was more soluble.

When equimolar amounts of 1,5-dibromopentane and the monosodium salt of isopropylidene malonate (prepared from equimolar amounts of isopropylidene malonate and ethanolic sodium ethoxide) were allowed to react in dimethylformamide at room temperature, isopropylidene 1,1-cyclohexanedicarboxylate (VII) was obtained in 21% yield. The yield was doubled (41%) when a 2:1 ratio of monosodium salt to dihalide was employed. From this it was evident that a second mole of the monosodium salt or some other base was necessary if acceptable yields were to be obtained. However, when powdered sodium methoxide was added to supply the second mole of base, the expected product (VII) was obtained in a lower yield (11%) and, in addition, a small yield (6%) of 1,1-cyclohexanedicarboxylic acid was obtained. Evidently a portion of the methoxide had attacked the desired product (VII) to give 1,1-cyclohexanedicarboxylic acid, the methyl half-ester being a probable intermediate according to the work of Scheuer and Cohen.[8] Dimethylacetamide was found to be an equally suitable solvent for the preparation of VII.


VII


VIII

The reaction of two moles of monosodium salt and one mole of 1,4-dibromobutane in dimethylformamide at room temperature afforded isopropylidene 1,1-cyclopentanedicarboxylate (VII) in 33% yield. 1,1-Cyclopentanedicarboxylic acid was formed in one experiment when dilute hydrochloric acid was added at the end of the reaction period and the mixture was allowed to stand at room temperature overnight. The benzylidene analog of VII, benzylidene 1,1-cyclopentanedicarboxylate, was prepared in low yield from equimolar amounts of benzylidene malonate, sodium methoxide and 1,4-dibromobutane. Attempts to prepare isopropylidene 1,1-cyclobutanedicarboxylate by similar methods were unsuccessful.

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(7) A. N. Meldrum, *J. Chem. Soc.*, 598 (1908).

(8) P. J. Scheuer and S. G. Cohen, *J. Am. Chem. Soc.*, **80**, 4933 (1958).

EXPERIMENTAL[9,10,11]

Isopropylidene malonate was prepared according to the procedure of Davidson and Bernhard[4] and benzylidene malonate according to the procedure of Michael and Weiner.[12]

Isopropylidene dibenzylmalonate. A. *With methanol as solvent.* To 10 ml. of methanol in which 0.15 g. (6.5 mg.-atoms) of sodium had been dissolved were added 0.94 g. (6.5 mmoles) of isopropylidene malonate and 0.82 g. (6.5 mmoles) of benzyl chloride. Large crystals, which deposited during a 2-day period at room temperature, were collected and washed with methanol to yield 0.2 g. (19%) of isopropylidene dibenzylmalonate, m.p. 230–232°. An analytical sample, m.p. 231–232°, was prepared by recrystallization from ethanol.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.06; H, 6.47.

B. *With ethanol as solvent.* A sodium ethoxide solution was prepared from 2.2 g. (0.096 g.-atom) of sodium and 100 ml. of absolute ethanol. Isopropylidene malonate, 6.9 g. (0.048 mole), was added to one-half of the sodium ethoxide solution and the mixture was heated to reflux. The remaining sodium ethoxide solution and 12.0 g. (0.096 mole) of benzyl chloride were added to the refluxing mixture over a 30-min. period. After the stirred reaction mixture was refluxed for 5 hr., the ethanol was evaporated *in vacuo* and the pasty residue was dissolved in water and extracted with 100 ml. of chloroform. The chloroform layer was concentrated *in vacuo* to a small volume and diluted with methanol to cause precipitation. Filtration afforded 2.5 g. (16%) of isopropylidene dibenzylmalonate, m.p. 227–230°.

C. *With dimethylformamide and sodium methoxide.* A mixture of 7.2 g. (0.05 mole) of isopropylidene malonate, 12.6 g. (0.1 mole) of benzyl chloride and 5.4 g. (0.1 mole) of sodium methoxide in 100 ml. of dimethylformamide was stirred at room temperature for 50 hr. The solid which had formed throughout the reaction period was collected and washed with water and a small amount of acetone to yield 4.7 g. of product. The filtrate from the reaction mixture was diluted with water and extracted with chloroform. The chloroform layer was concentrated *in vacuo* and diluted with methanol to yield 0.9 g. of product. The total yield of isopropylidene dibenzylmalonate was 5.6 g. (35%).

D. *With dimethylformamide and the monosodium salt of isopropylidene malonate.* A solution of 0.83 g. (5 mmoles) of the monosodium salt of isopropylidene malonate (prepared as described in a later portion of this experimental section) and 0.63 g. (5 mmoles) of benzyl chloride in 60 ml. of dimethylformamide was left at room temperature for 6 days. A trace of insoluble material was removed by filtration, and 125 ml. of cold water was added to the filtrate to cause the precipitation of 0.45 g. of crude isopropylidene dibenzylmalonate, m.p. 190–230°. Recrystallization from acetone afforded 0.34 g. (42%) of nearly pure product, m.p. 232–233°.

E. *By alkylation with benzyldimethylphenylammonium chloride.* A solution of 1.0 g. (4 mmoles) of benzyldimethylphenylammonium chloride,[13] 0.58 g. (4 mmoles) of isopropylidene malonate and 0.34 g. (4 mmoles) of sodium bicarbonate in a minimum amount of water was concentrated *in vacuo* at 80°. The bath temperature was raised to 110–120° and a small amount of material, probably dimethylaniline, distilled at 75–80° (11 mm.). The residue was triturated first with methanol and then with water to yield 0.3 g. (46%) of reasonably pure product, m.p. 229–231°.

Isopropylidene benzylmalonate. The hydrogenation of 0.236 g. (1.01 mmoles) of isopropylidene benzalmalonate[5] in methanol over platinum at room temperature and atmospheric pressure afforded a nearly theoretical yield of isopropylidene benzylmalonate, m.p. 80–81°. The melting point was not changed by recrystallization from high-boiling petroleum ether.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.82; H, 6.15.

Diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate (IIIa). A. *With silver oxide and acetonitrile.* To a magnetically stirred suspension of 6.5 g. (28 mmoles) of silver oxide and 6.7 g. (25 mmoles) of methylene iodide in 15 ml. of acetonitrile at 0° was added dropwise over a 10-min. period 3.6 g. (25 mmoles) of isopropylidene malonate in 12 ml. of acetonitrile. After the addition had been completed, stirring was continued at room temperature for 2 hr. At the end of this period the grey solids were removed by filtration and washed well with acetonitrile. The acetonitrile solution was concentrated *in vacuo* (bath temperature 45°) to a red oil. The addition of 30 ml. of cold water caused a mixture of oil and crystals to separate. The water-acetonitrile layer was decanted, and acetone was added to the oil and solid mixture. The solid remained undissolved. Upon filtration and washing with acetone, 0.35 g. of gray solid, m.p. 226–228° dec. with sublimation above 200°, was obtained. The combined acetone washes were concentrated to a red oil which yielded three successive crops (0.15 g.). These crops were obtained by adding acetone or ether to the concentrated red oil to cause precipitation, filtering, concentrating the filtrate and repeating the process. The total yield of diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate (IIIa) was 0.50 g. (13%). The crude product was purified by dissolving in acetonitrile, filtering to remove any insoluble impurities and adding twice the volume of ether. Two such recrystallizations from acetonitrile-ether gave the analytical sample, m.p. 226–227° dec.

Anal. Calcd. for $C_{13}H_{14}O_8$: C, 52.35; H, 4.73. Found: C, 52.47; H, 4.80.

After a third recrystallization from acetonitrile alone, an even purer sample, m.p. 223.5–224° dec. in a capillary tube, was obtained. (*Anal.* Found: C, 52.35; H, 4.75.)

A mixed melting point of this pure material and the product (see part D) of the reaction of diazomethane with diisopropylidene ethylenetetracarboxylate (VI)[6] showed no depression (m.p. 225–227° dec.).

B. *With sodium hydroxide and iodine.* To a solution of 0.6 g. (2 mmoles) of diisopropylidene methylenedimalonate (IIa)[5] in 2 ml. (4 mmoles) of 2*N* sodium hydroxide solution and 23 ml. of water was added rapidly while stirring 1.04 g. (4 mmoles) of solid iodine. Stirring was continued at room temperature, and a white precipitate slowly formed over a 45-min. period. The precipitate was filtered, any remaining iodine crystals were mechanically separated and the filter cake was washed well with water to yield 0.47 g. (79%) of diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate (IIIa), m.p. 226–227° dec.

C. *With sodium bicarbonate and iodine.* To a solution of 0.3 g. (1 mmole) of diisopropylidene methylenedimalonate (IIa)[5] in approximately 4 ml. of 5% sodium bicarbonate solution and 12 ml. of water at room temperature was added 0.25 g. (1 mmole) of solid iodine. A white precipitate formed slowly. Filtration and washing with cold water gave 0.23 g. (77%) of product (IIIa), m.p. 225–227° dec.

D. *With diazomethane.* A suspension of a few milligrams of diisopropylidene ethylenetetracarboxylate (VI)[6] in 10 ml. of ethereal diazomethane solution was allowed to stand at room temperature. After about 24 hr. the yellow color had vanished and compound IIIa, m.p. 226–227° dec., was col-

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(9) All melting points were taken on a Kofler micro hot stage, unless otherwise specified.

(10) The infrared spectra were determined by P. E. McMahon and his associates. The spectra were obtained from a Perkin-Elmer Model 21 double beam recording spectrophotometer equipped with sodium chloride optics.

(11) The microanalyses were performed by J. Nemeth, Mrs. Ruby Ju, Miss Claire Higham, Mrs. A. S. Bay, and Miss Jane Liu.

(12) A. Michael and N. Weiner, *J. Am. Chem. Soc.*, 58, 680 (1936).

(13) W. Michler and A. Gradmann, *Ber.*, 10, 2078 (1877).

lected by filtration. Infrared spectra of this product and the product from part A were identical.

1,1,2,2-Cyclopropanetetracarboxylic acid. A. *By acid hydrolysis.* A mixture of 0.150 g. (0.5 mmole) of diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate (IIIa) and 2.5 ml. of concentrated hydrochloric acid in 17.5 ml. of water was heated for 19 hr. on a steam bath. A small amount of undissolved material was removed by filtration. The filtrate was concentrated *in vacuo* to dryness to give the crude product, m.p. 175–185° dec. The crude product was stirred in 75 ml. of ether, filtered to remove any undissolved impurity, and the solution was concentrated to dryness to yield 0.069 g. (63%) of crude product, m.p. 180–187° dec.

B. *By basic hydrolysis.* To a hot solution of 0.3 g. of potassium hydroxide in 0.5 ml. of water was added in small portions with stirring 0.198 g. (0.67 mmole) of diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate (IIIa). Stirring was continued until each portion had dissolved. The addition required about 30 min. The solution was allowed to cool and crystals formed. Water (5 ml.) was added to dissolve the crystals, and the solution was filtered to remove a small amount of remaining black solid. Acetic acid was added until the solution reached *p*H 6, and the solution was concentrated to dryness. Triturating the white solids in ether did not dissolve any material. This showed that the product was still present as the potassium salt. Anhydrous hydrobromic acid was bubbled into the ether suspension, and a fine white precipitate (potassium bromide) formed. The precipitate was collected and washed well with ether. Upon evaporation of the ether filtrate 0.101 g. (69%) of crude, pale yellow solid, m.p. 198–203° dec., was obtained. An acetone-carbon tetrachloride solution of the crude product was treated with Darco and allowed to evaporate. Evaporation yielded yellow needles, m.p. 210–214° dec., which were broken up, filtered and ether washed. A solution of this material in 4 ml. of concentrated hydrochloric acid was allowed to evaporate slowly to form large, colorless crystals, m.p. 217–218° dec. (lit., m.p. 218–220° dec.,[14] 210–212° dec.[15])

Anal. Calcd. for $C_7H_6O_8$: C, 38.54; H, 2.77. Found: C, 38.49; H, 3.02.

Diisopropylidene 3-methyl-1,1,2,2-cyclopropanetetracarboxylate (IIIb). A. *With sodium bicarbonate and iodine.* To a solution of 1.57 g. (5 mmoles) of diisopropylidene ethylidenedimalonate (IIb)[5] in 17 ml. of 5% sodium bicarbonate solution, 3 ml. of water and 10 ml. of dimethylformamide was added 1.27 g. (5 mmoles) of solid iodine. After 12 hr. at room temperature, a small amount of acetonitrile was added, and the mixture was heated on a steam bath for 15 min., cooled and filtered to yield 0.2 g. (13%) of white powdery product (IIIb), m.p. 216–217° dec. Recrystallization from acetonitrile, followed by recrystallization from acetone, gave the analytical sample, m.p. 208–210.5° dec. in a capillary tube.

Anal. Calcd. for $C_{14}H_{16}O_8$: C, 53.84; H, 5.16. Found: C, 53.58; H, 5.09.

B. *With sodium methoxide and bromine.* A sodium methoxide solution was prepared from 0.41 g. (17.8 mg.-atoms) of sodium and 25 ml. of commercial absolute methanol. To this sodium methoxide solution was added 2.79 g. (8.9 mmoles) of diisopropylidene ethylidenedimalonate (IIb).[5] A cloudy solution resulted. Bromine, 1.42 g. (8.9 mmoles), was added fairly rapidly to the cloudy solution. Heat was evolved and immediate precipitation resulted. The mixture was cooled for 5 min., filtered and washed with cold water to give 1.85 g. of powdery white product (IIIb), m.p. 208–209.5° dec. A second crop (0.05 g.) formed in the methanol-water filtrate. The total yield was 1.90 g. (69%).

Diisopropylidene 3-phenyl-1,1,2,2-cyclopropanetetracarboxylate (IIIc). A. *With sodium methoxide and bromine.* A sodium methoxide solution was prepared from 0.35 g. (15 mg.-atoms) of sodium and 25 ml. of commercial methanol. Diisopropylidene benzylidenedimalonate (IIc),[5] 2.82 g. (7.5 mmoles), was added to the sodium methoxide solution, not quite all dissolving. To this suspension was added 1.2 g. (7.5 mmoles) of bromine. A precipitate began to form within 15 min. at room temperature. After 20 min., 1.1 g. of crude product, m.p. 160–163° dec., was collected and washed with methanol. Addition of water to the methanol filtrate gave 0.25 g. of second-crop material. The total yield of crude product was 1.35 g. (48%). Treatment of the crude product with 5% potassium carbonate solution, followed by an acetone-water recrystallization, gave 1.2 g. (43%) of nearly pure product (IIIc), m.p. 185–187° dec. A second acetone-water recrystallization gave the analytically pure sample, m.p. 181–182.5° dec. in a capillary tube.

Anal. Calcd. for $C_{19}H_{18}O_8$: C, 60.96; H, 4.85. Found: C, 61.02; H, 4.75.

B. *With sodium methoxide and iodine.* To a solution of 1.88 g. (5 mmoles) of diisopropylidene benzylidenedimalonate (IIc)[5] in 60 ml. of dimethylformamide was added 0.54 g. (10 mmoles) of powdered sodium methoxide. Iodine, 1.27 g. (5 mmoles), was added to the clear, slightly yellow solution to give a red solution. After 5 hr. at room temperature, the mixture was poured into 300 ml. of ice water, but no precipitate resulted. Extraction of the dimethylformamide-water solution with ethyl acetate, followed by the addition of water to the concentrated ethyl acetate layer, gave 0.26 g. (14%) of crude product, m.p. 147–170° dec. The crude product was triturated in 5% potassium carbonate solution and recrystallized from acetone-ethanol-water to give white crystalline product (IIIc), m.p. 181–183° dec.

Dibenzylidene 1,1,2,2-cyclopropanetetracarboxylate. To a solution of 0.5 g. (1.26 mmoles) of dibenzylidene methylenedimalonate[5] in 1.25 ml. (2.5 mmoles) of 2*N* sodium hydroxide and 8 ml. of water was added 0.32 g. (1.26 mmoles) of solid iodine. The solution was agitated for a few minutes and left in an ice bath for 1 hr. Acetone was added to the mixture, and some gummy white precipitate, mixed with unchanged iodine, was collected. A second crop formed in the acetone-water filtrate. Filtration gave 0.23 g. of second crop material, m.p. 210–220° dec. The impure first crop was dissolved in acetone, carbon tetrachloride was added to remove the unchanged iodine, and water was added to give a fluffy white precipitate. The precipitate was collected and dried to yield 0.11 g. of product, m.p. 218–220° dec. The total yield of crude product was 0.34 g. (69%).

The crude material was stirred in 5% sodium bicarbonate solution, filtered and washed with water. Acidification of the filtrate gave a trace of crude dibenzylidene methylenedimalonate, m.p. 191–193° dec. Further purification was accomplished by dissolving the product in acetone and adding water to give, upon filtration and drying, 0.28 g. of dibenzylidene 1,1,2,2-cyclopropanetetracarboxylate, m.p. 222–225° dec.

The partially purified product was dissolved in acetonitrile and a small amount of petroleum ether (b.p. 30–60°) was added A trace of precipitate formed and was collected to give a white solid, m.p. 193–195° dec., which was soluble in 5% sodium bicarbonate solution. Apparently this material was dibenzylidene methylenedimalonate which had not been completely removed by the trituration in sodium bicarbonate solution. Evaporation of the petroleum ether and addition of water to the acetonitrile solution afforded, upon filtration and drying, the analytically pure material, m.p. 220–224.5° dec.

Anal. Calcd. for $C_{21}H_{14}O_8$: C, 63.96; H, 3.58. Found: C, 64.18; H, 3.53.

Unsuccessful attempts to prepare diisopropylidene 1,1,3,3-cyclobutanetetracarboxylate (IV). A. *From diisopropylidene methylenedimalonate and methylene iodide.* To a solution of 1.5 g. (5 mmoles) of diisopropylidene methylenedimalonate

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(14) T. W. D. Gregory and W. H. Perkin, Jr., *J. Chem. Soc.*, 780 (1903).

(15) J. J. Lennon and W. H. Perkin, Jr., *J. Chem. Soc.*, 1513 (1928).

(IIa) in 40 ml. of dimethylformamide was added 0.54 g. (10 mmoles) of powdered sodium methoxide. The sodium methoxide did not dissolve completely, and additional solids appeared to form. To this mixture was added 1.4 g. (5.2 mmoles) of methylene iodide in 20 ml. of dimethylformamide. Solids continued to form. After 15 min., the mixture had started to gel, and more dimethylformamide (20 ml.) was added. After 2 hr., 30 ml. of dimethylformamide was added to the now solid gel and the mixture was warmed, but the gel became only slightly less viscous. After 1 day, the gel was less viscous. After 3 days, a white powder was removed by filtration. Dissolving a portion of this powder in water and acidifying gave crude diisopropylidene methylenedimalonate (IIa), m.p. 133–137° dec. The sodium salt was recombined with the dimethylformamide filtrate, more methylene iodide (1.4 g.) was added, and the mixture was heated at 80°for 70 min. The mixture was cooled and a small amount of sodium salt was collected and washed with acetone. An infrared spectrum of this fraction in Nujol was identical to a spectrum of the sodium salt taken before the mixture was heated. Both spectra were different from the spectrum of the monosodium salt of isopropylidene malonate in Nujol. Water was added to the dimethylformamide filtrate and the solution was extracted with ethyl acetate; however, evaporation of the ethyl acetate layer gave no solid product.

B. *From isopropylidene malonate and methylene iodide.* A sodium ethoxide solution was prepared from 2.3 g. (0.1 g.-atom) of sodium and 150 ml. of absolute ethanol. Solid isopropylidene malonate, 7.2 g. (0.05 mole), was added to the sodium ethoxide solution. The needles of isopropylidene malonate changed to white powder as the sodium salt formed. To this suspension was added 13.4 g. (0.05 mole) of methylene iodide. No heat of reaction was observed. After the mixture had stood at room temperature for about 16 hr., 4.0 g. of unchanged monosodium salt was removed by filtration. Further work-up yielded only more of the sodium salt of isopropylidene malonate.

C. *From diisopropylidene methylenedimalonate, methylene iodide and silver oxide.* A mixture of 1.5 g. (5 mmoles) of diisopropylidene methylenedimalonate (IIa),[5] 1.34 g. (5 mmoles) of methylene iodide and 1.16 g. (5 mmoles) of silver oxide in 60 ml. of acetonitrile was stirred magnetically at 0° for 5 hr. After standing in the refrigerator for 14 hr., the reaction mixture was filtered and the filtrate was concentrated to a small volume. The addition of water caused the formation of a precipitate which was filtered and dried to give 0.69 g. (46%) of diisopropylidene methylenedimalonate, m.p. 142–146° dec.

D. *From diisopropylidene methylenedimalonate and formaldehyde.* To a solution of 1.5 g. (5 mmoles) of diisopropylidene methylenedimalonate (IIa) and 0.41 g. (5 mmoles) of 37% aqueous formaldehyde in 35 ml. of dimethylformamide was added 0.95 g. (5 mmoles) of powdered *p*-toluenesulfonic acid. After standing at room temperature for 52 hr., the clear solution was poured into cold water; but only a clear solution resulted. No solid material was obtained from an ether extraction of the clear solution.

Monosodium salt of isopropylidene malonate. A sodium ethoxide solution was prepared from 3.85 g. (0.167 g.-atom) of sodium and 120 ml. of commercial absolute ethanol in a dried flask with a drying tube. A warm solution of 24.1 g. (0.167 mole) of dry isopropylidene malonate (dried in a desiccator over phosphorus pentoxide) in 200 ml. of absolute ethanol was added fairly rapidly to the sodium ethoxide solution. Monosodium salt began to precipitate immediately. The mixture was cooled for 20 min., filtered and washed with absolute ethanol and absolute ether to give 18.7 g. of monosodium salt. The filtrate was concentrated *in vacuo* to near dryness. The resulting precipitate, upon filtration, gave a second crop (7.8 g.) of monosodium salt. The total yield was 26.5 g. (95%). The solubility of the sodium salt in ethanol is approximately 2.4 g. per 100 ml. at 25°.

Isopropylidene 1,1-cyclohexanedicarboxylate (VII). A. *From equimolar amounts of monosodium salt and dihalide.* A mixture of 3.32 g. (20 mmoles) of the monosodium salt of isopropylidene malonate and 4.6 g. (20 mmoles) of 1,5-dibromopentane in 35 ml. of dimethylformamide was left at room temperature for 84 hr. All of the sodium salt dissolved within about 14 hr., and the color of the solution changed from colorless to yellow. At the end of the 84-hr. period the addition of water to the yellow solution caused precipitation. The mixture was cooled for 1 hr., filtered and pressed dry to give 0.9 g. (21%) of crude isopropylidene 1,1-cyclohexanedicarboxylate (VII), m.p. 114–118.5° with sublimation above 80°. The pure material, m.p. 119–119.5°, was obtained by dissolving the product in methanol and adding a small amount of water.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.21; H, 7.58.

B. *From a 2:1 ratio of monosodium salt and dihalide.* Conditions and amounts of the reactants for this reaction were the same as in part A except that only 2.3 g. (10 mmoles) of 1,5-dibromopentane was used. Work-up as in part A gave 1.1 g. of a mixture of VII and, probably, isopropylidene malonate. Trituration of this mixture in 5% sodium bicarbonate solution afforded 0.87 g. (41%) of crude VII.

C. *From equimolar amounts of monosodium salt, dihalide and sodium methoxide.* Conditions and amounts of the reactants for this reaction were the same as in part A except that 1.08 g. (20 mmoles) of powdered sodium methoxide was added after 25 hr. of the reaction. At the end of the 84-hr. period about 0.6 g. of light yellow powder was removed by filtration. This powder was dissolved in 3 ml. of water and the solution was acidified to yield 0.2 g. (6%) of 1,1-cyclohexanedicarboxylic acid, m.p. 177–178° dec. (lit., m.p. 176° dec.,[16] m.p. 179.5° dec.[17]). Work-up of the dimethylformamide filtrate as in part A yielded 0.09 g. of VII. Ether extraction of the dimethylformamide-water solution gave 0.37 g. of VII upon evaporation of the ether layer. The total yield of VII was 0.46 g. (11%).

D. *With dimethylacetamide as solvent.* Conditions and amounts of the reactants were the same as in part A except that dimethylacetamide was used instead of dimethylformamide as solvent. Work-up as in part A yielded 0.85 g. of VII. Extraction of the dimethylacetamide-water layer with ether and evaporation of the ether layer gave an additional 0.30 g. of VII. The total yield of VII was 1.15 g. (27%).

Isopropylidene 1,1-cyclopentanedicarboxylate (VIII). A mixture of 3.32 g. (20 mmoles) of the monosodium salt of isopropylidene malonate and 2.16 g. (10 mmoles) of 1,4-dibromobutane in 35 ml. of dimethylformamide was left at room temperature for 48 hr. The addition of cold water caused cloudiness but no precipitation. The dimethylformamide-water layer was extracted three times with ether, and the ether extract (undried) was allowed to evaporate slowly to a small volume of yellow oil (mostly dimethylformamide). The addition of a small amount of water caused the slow formation (1 or 2 days) of a precipitate which was filtered, washed with water and pressed dry. A second crop was obtained from the oil and water filtrate after 1 day. The total yield of crude isopropylidene 1,1-cyclopentanedicarboxylate (VIII), m.p. 75–84°, was 0.66 g. (33%). Recrystallization from ethanol-water gave a purer product, m.p. 85–87° with sublimation above 70°. A second recrystallization from ethanol-water, followed by a recrystallization from acetone-water, gave the analytically pure material, m.p. 86–87.5°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.81; H, 7.16.

1,1-Cyclopentanedicarboxylic acid. A mixture of 1.80 g. (10.8 mmole) of the monosodium salt of isopropylidene malonate and 2.34 g. (10.8 mmole) of 1,4-dibromobutane in 20 ml. of dimethylformamide was heated on a steam bath for 50 min. and left at room temperature for 4 days. At the

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(16) W. A. Wightman, *J. Chem. Soc.*, 2541 (1926).

(17) A. I. Vogel, *J. Chem. Soc.*, 1487 (1929).

end of this period 60 ml. of water and 15 ml. of dilute hydrochloric acid were added. A cloudy solution resulted but no crystalline precipitate formed. After standing overnight, the now clear solution was extracted first with chloroform and then ether. Evaporation of the ether layer gave about 0.01 g. of long needles, which melted with decomposition at 173–182° with sublimation above 120°. The chloroform layer was evaporated to a red oil. Extraction of this red oil with ether gave, upon evaporation, a mixture of oil and crystals. This mixture was filtered and washed with a small amount of chloroform to give 0.25 g. of 1,1-cyclopentanedicarboxylic acid, m.p. 185–192° dec. (lit., m.p. 184–185° dec.,[18] m.p. 190° dec.[17]). The total yield of the diacid was 0.26 g. (15%).

Benzylidene 1,1-cyclopentanedicarboxylate. To a solution of 1.4 g. (7.3 mmoles) of benzylidene malonate and 1.57 g. (7.3 mmoles) of 1,4-dibromobutane in 50 ml. of dimethylformamide was added 0.39 g. (7.3 mmoles) of powdered sodium methoxide. After 53 hr. at room temperature, the clear yellow solution was poured into cold water. Precipitation resulted. Filtration gave 0.1 g. (6%) of benzylidene 1,1-cyclopentanedicarboxylate, m.p. 176–178° with sublimation above 120°. The product was insoluble in 5% sodium bicarbonate solution. Recrystallization from acetone-water and then from ethyl acetate gave the pure product, m.p. 177–178° in a capillary tube.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.96; H, 5.71.

Unsuccessful attempts to prepare isopropylidene 1,1-cyclobutanedicarboxylate. A. *With sodium methoxide in dimethylformamide.* To a mixture of 7.2 g. (0.05 mole) of isopropylidene malonate and 5.4 g. (0.10 mole) of sodium methoxide in 60 ml. of dimethylformamide at room temperature was added 10.1 g. (0.05 mole) of 1,3-dibromopropane. Heat was evolved and the mixture was cooled. After stirring for 11 hr., the mixture was allowed to stand for 48 hr. The addition of water caused no precipitation. Evaporation of ether and chloroform extracts gave no solid products. Concentration of the remaining water layer gave only the monosodium salt of isopropylidene malonate.

B. *With sodium ethoxide and ethanol.* A sodium ethoxide solution was prepared from 0.9 g. (40 mg.-atoms) of sodium and 80 ml. of absolute ethanol. To this sodium ethoxide solution at room temperature were added 2.9 g. (20 mmoles) of isopropylidene malonate and 4.0 g. (20 mmoles) of 1,3-dibromopropane in 80 ml. of absolute ethanol. No reaction was observed. Concentration of the ethanol gave only monosodium salt.

C. *With sodium ethoxide and refluxing ethanol.* The amounts of the reactants were the same as in part B. The 1,3-dibromopropane was added to the refluxing mixture and heating was continued for 5 hr. Work-up of the reaction mixture gave only malonic acid.

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(18) E. Haworth and W. H. Perkin, Jr., *J. Chem. Soc.*, 86 (1894).

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Epoxy Ketones. V.[1] Stereochemistry of 2-Benzal-4,4-dimethyl-1-tetralone Oxide. Diol Synthesis

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The boron trifluoride rearrangement of 2-benzal-4,4-dimethyl-1-tetralone oxide (I) gives 6-phenyl-9,9-dimethylbenzocycloheptane-5,7-dione which was isolated in a diketo and mixed enol form. The structures of the products resulting from the reaction of hydrogen chloride and methanol-sulfuric acid solutions with I have been shown to be 2-hydroxy-2-(α-chlorobenzyl)-4,4-dimethyl-1-tetralone (VII) and 2-hydroxy-2-(α-methoxybenzyl)-4,4-dimethyl-1-tetralone (XI), respectively, by diagnostic chemical methods. The spiro-epoxy ketone I has been converted to various hydroxy ketones, epoxy alcohols and 1,2-diols through various hydrogenations or reaction with a Grignard reagent. A study of the infrared spectra, hydrogen bonding and the stereostructure of these hydroxy tetralin derivatives was investigated and tentative assignments of conformations and configurations have been made.

In a previously reported study[3] proton-donor, acid catalyzed reactions of 2-benzal-1-tetralone oxides were found to lead to cleavage of the epoxide ring and 2-hydroxy-1-tetralones were postulated as products, mainly on the basis of absorption spectra studies. As is discussed in detail later this has definitely now been shown to be the case.

When the spiroepoxy ketone, 2-benzal-4, 4-dimethyl-1-tetralone oxide[4] (I), was treated with the Lewis acid, boron trifluoride (see Chart 1), under the conditions described by House and Wasson for rearranging 2-benzalcyclohexanone-1 oxide,[5] an 85% yield of a product was obtained which has the analytical and spectral characteristics of the expected seven membered ring 1,3-diketone, 6-phenyl-9,9-dimethylbenzocycloheptane-5,7-dione (II). This product had none of the characteristics to be expected for the isomeric 1,2-diketone, 7-phenyl-9,9-dimethylbenzoheptane-5,6-dione. The diketo form II is readily converted to an enolic isomer IIA-C on recrystallization from acidified methanol. The enol structures IIA and IIB would be favored over IIC which does not allow for conjugation between the carbonyl oxygen and the hydroxyl

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(1) *a.* For paper IV in this series see, N. H. Cromwell, F. H. Schumacher, and J. L. Adelfang, *J. Am. Chem. Soc.* **83**, 974 (1961); *b.* Presented in part at the American Chemical Society Meeting, September 1960, New York, N. Y.

(2) Abstracted from the Ph.D. thesis of R. E. Bambury, University of Nebraska, January 1960.

(3) N. H. Cromwell, R. E. Bambury, and R. P. Barkley, *J. Am. Chem. Soc.*, **81**, 4294 (1959).

(4) A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).

(5) H. O. House and R. L. Wasson, *J. Am. Chem. Soc.* **78**, 4394 (1956).