Anal. Calcd. for $C_7H_{10}O_4$: C, 53.16; H, 6.37; neut. equiv., 79.07. Found: C, 52.82; H, 6.15; neut. equiv., 79.6, 79.6.

Acknowledgments.—We are indebted to Dr. B. C. Pratt who suggested the alkaline rearrangement of 3-methylenecyclobutane-1,2-dicarboxylic acid and to Dr. J. L. Anderson for many helpful suggestions and discussions.

Wilmington 98, Del.

[Contribution No. 512 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co.]

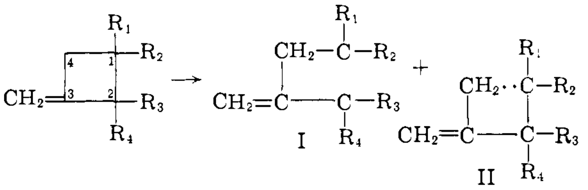
Chemistry of Cyclobutanes. IV. Thermal Cleavage of Methylenecyclobutanes

By J. J. Drysdale, H. B. Stevenson and W. H. Sharkey

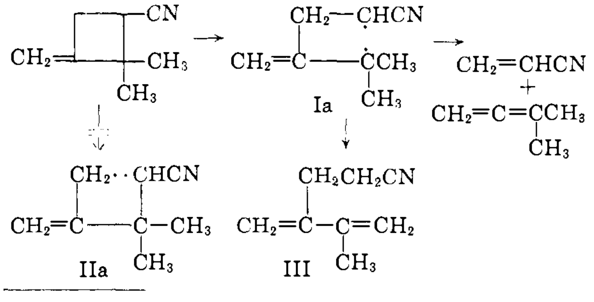
Received March 25, 1959

Syntheses for substituted 1,3-dienes, 1,4-dienes and allenic esters have been discovered in the thermal rearrangement of substituted methylenecyclobutanes. 2-(2-Cyanoethyl)-3-methyl-1,3-butadiene, 2-cyano-4-methyl-1,4-pentadiene and methyl 2,3-butadienoate have been obtained from 2,2-dimethyl-3-methylenecyclobutanecarbonitrile, 1-methyl-3-methylenecyclobutanecarbonitrile and dimethyl 3-methylenecyclobutane-1,2-dicarboxylate, respectively.

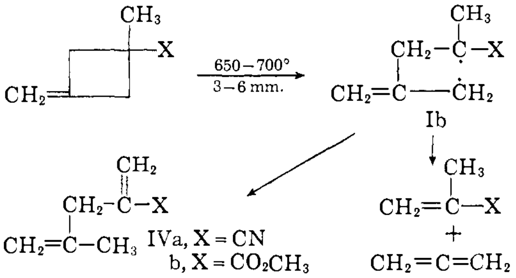
Following the discovery of the cycloaddition of allenes to appropriately substituted olefins to form 3-alkylidenecyclobutanes,[1] it became of interest to examine the thermal rearrangement of these cyclobutanes. Since the weakest points in a methylenecyclobutane are the allylic bonds, thermal cleavage would be expected to involve either or both of the transient diradicals I and II. We have found that cleavage is highly selective and that formation of I is favored when the R groups are methyl, cyano or methoxycarbonyl.



Pyrolysis of 2,2-dimethyl-3-methylenecyclobutanecarbonitrile at 650° and 1–2 mm. showed that rearrangement of this compound occurs exclusively *via* a diradical Ia formed by scission of the bond between the 1- and 2-positions. Products isolated were 2-(2-cyanoethyl)-3-methyl-1,3-butadiene (III) which was formed in 30% yield, 1,1-dimethylallene and acrylonitrile. These compounds are believed to be derived from the transient diradical by hydrogen transfer and cleavage, respectively. Allene and 3-methylcrotononitrile were not isolated, which indicates that ring cleavage to give the diradical IIa does not occur.



1,4-Dienes are produced by pyrolysis of 1-alkyl-3-methylenecyclobutanes. For example, 1-methyl-3-methylenecyclobutanecarbonitrile gave 2-cyano-4-methyl-1,4-pentadiene (IVa) in 47% yield. The remainder of the cyclobutane was cleaved to allene and methacrylonitrile. Under similar conditions, 2-methoxycarbonyl-4-methyl-1,4-pentadiene (IVb) was prepared in 38% yield from methyl 1-methyl-3-methylenecyclobutanecarboxylate. In these cases rearrangement involves cleavage of the allyl bond between the 1- and 2-carbon atoms of the ring to give a diradical Ib, followed by transfer of a hydrogen atom from a methyl group to the carbon at the 2-position of the ring or by cleavage to allene and the methacrylic derivative.

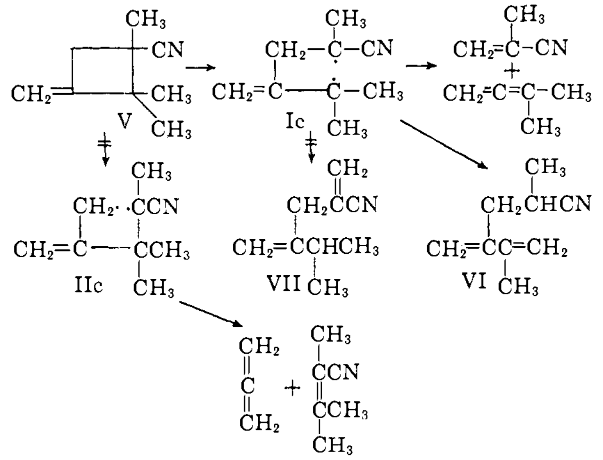


A methylenecyclobutane containing methyl groups on both the 1- and 2-carbon atoms might be expected to give both 1,3- and 1,4-dienes. Thermal rearrangement of a cyclobutane of this type, 1,2,2-trimethyl-3-methylenecyclobutanecarbonitrile (V), gave 2-(2-cyanopropyl)-3-methyl-1,3-butadiene (VI) in 20% yield, but efforts to isolate a 1,4-diene, such as VII, were not successful. The remainder of the cyclobutane was cleaved to 1,1-dimethylallene and methacrylonitrile. These data indicate that ring scission occurs between the 1- and 2-carbon atoms to form Ic, which then reacts further to give the products isolated. Although no effort was made to collect allene, 2,3-dimethylcrotononitrile was not detected in the pyrolysis product. Accordingly, it is unlikely that 1–4 cleavage to give IIc occurs to any appreciable extent.

The structure of VI was determined by infrared and nuclear magnetic resonance. Conjugated

---

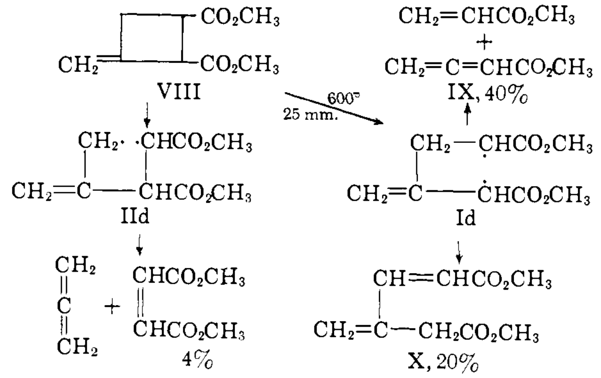
[1] H. N. Cripps, J. K. Williams and W. H. Sharkey, This Journal, **80**, 757 (1958); **81**, 2723 (1959).



C=C and non-conjugated nitrile were shown by infrared absorption at 6.27 and 4.45 μ, respectively. The proton magnetic resonance spectrum consisted of peaks for methyl plus tertiary hydrogen, vinyl hydrogen and methylene hydrogen in a ratio of 7:4:2.

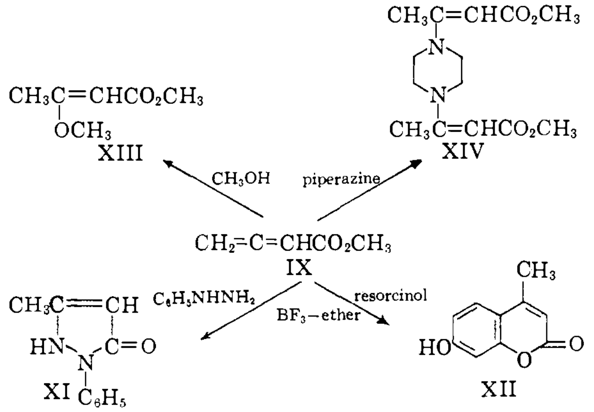
1,3- and 1,4-dienes also have been prepared directly from allenes and acrylonitriles. Passage of 1,1-dimethylallene and acrylonitrile at atmospheric pressure through a tube heated to 600° gave III in 8% conversion. Under similar conditions, allene and methacrylonitrile gave IVa in 10% conversion. In both cases yields based on the acrylonitrile consumed were at least 50%.

An interesting special case is that of dimethyl 3-methylenecyclobutane-1,2-dicarboxylate (VIII). Direct pyrolysis of this compound gives methyl 2,3-butadienoate (IX) and methyl acrylate.

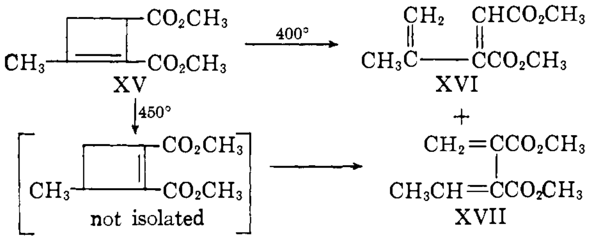


Dimethyl 3-methylene-2,3-dihydromuconate (X) is also formed in appreciable yield together with small amounts of dimethyl fumarate and dimethyl maleate.

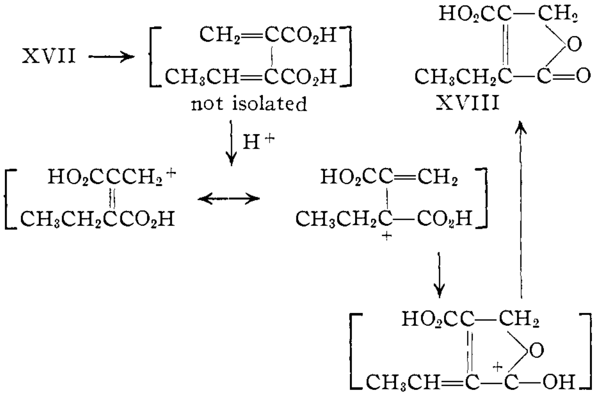
Brief investigation of the chemistry of methyl 2,3-butadienoate indicated that it can be considered an anhydro form of acetoacetic ester. For example, reaction with phenylhydrazine gave the same product, 3-methyl-1-phenylpyrazolone (XI), as obtained from acetoacetic ester. With resorcinol in the presence of boron trifluoride etherate, 4-methyl-7-hydroxycoumarin (XII) was formed. In addition, substituted crotonic esters XIII and XIV were obtained by reaction with methanol and piperazine, respectively.



If dimethyl 3-methylenecyclobutane-1,2-dicarboxylate is rearranged to a cyclobutenedicarboxylic ester[2] before pyrolysis, it can be used as a precursor of new 1,3-butadienes. The cyclobutene obtained, dimethyl 3-methyl-2-cyclobutene-1,2-dicarboxylate (XV), is rearranged readily at 400–450° and 25 mm. to the butadienes XVI and XVII. At 400°



XVI was the main product, and at 450° XVI and XVII were obtained in roughly a 2:1 ratio. The presence of XVII indicates that at high temperature the double bond rearranges to some extent to the 1,2-position to form the cyclobutene shown in brackets above. Acid hydrolysis of XVII gave a lactone, XVIII,[3] that appears to have been formed by the route



Experimental[4]

2-(2-Cyanoethyl)-3-methyl-1,3-butadiene (III).—2,2-Dimethyl-3-methylenecyclobutanecarbonitrile[1] (50 g.) was pyrolyzed in a 25-mm. Vycor tube 75 cm. long mounted vertically with an 8-mm. Vycor tube, open only to the

---

[2] H. N. Cripps, J. K. Williams, V. Tullio and W. H. Sharkey, THIS JOURNAL, **81**, 4904(1959).

[3] Dr. J. H. Werntz of this Laboratory has also prepared XVIII by heating 3-methylenecyclobutane-1,2-dicarboxylic acid at 150° in the presence of palladium-on-charcoal.

[4] All melting points and boiling points are uncorrected.

outside, running up the center for a thermocouple well. The pyrolysis tube was packed with chips of 6-mm. Vycor tubing for a length of 50 cm., the bottom 30 cm. of which was heated with an electric furnace. An addition funnel was connected to the top and a trap to the bottom. The trap was cooled with liquid nitrogen and the system evacuated to 1–2 mm. Pyrolysis was carried out at 650° over a period of 30 minutes. Distillation of the liquid pyrolysate gave 1,1-dimethylallene, acrylonitrile and 2-(2-cyanoethyl)-3-methyl-1,3-butadiene, b.p. 125–126° (80 mm.), n^{25}D 1.4800–1.4810. The yield of the diene was 15 g. (30%). Infrared analysis showed conjugated C=C (6.24 μ) and non-conjugated nitrile (4.47 μ). Proton nuclear magnetic resonance[5] analysis showed methyl, two types of methylene and vinyl protons in a ratio of 3:2:2:4.

Anal. Calcd. for $C_8H_{11}N$: C, 79.28; H, 9.15. Found: C, 79.85; H, 8.93.

The 1,3-diene reacted exothermically with maleic anhydride to give a Diels–Alder adduct which was recrystallized from benzene and cyclohexane, m.p. 95–96°.

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98. Found: C, 65.91; H, 6.06.

2-(2-Cyanoethyl)-3-methyl-1,3-butadiene from 1,1-Dimethylallene and Acrylonitrile.—A mixture of 100 g. of acrylonitrile and 50 g. of 1,1-dimethylallene was passed through the reaction tube described above over a period of 2.5 hours, and during this time the tube was maintained at 600° and atmospheric pressure. The product was collected in a trap chilled with a mixture of solid carbon dioxide and acetone. Distillation gave 7 g. (8% conversion) of a crude product, b.p. 124–128° (80 mm.), n^{27}D 1.4780. Maleic anhydride (5 g.) was added to this crude product, and the resulting Diels–Alder adduct was recrystallized from benzene–cyclohexane. Infrared absorption of the recrystallized product, m.p. 95–97°, showed that it was identical with the Diels-Alder adduct prepared from 2-(2-cyanoethyl)-3-methyl-1,3-butadiene.

2-(2-Cyanopropyl)-3-methyl-1,3-butadiene (VI).—1,2,2-Trimethyl-3-methylenecyclobutanecarbonitrile[1] (35 g.) was added over a period of 20 minutes to the reaction tube maintained at 650° and 3 mm. Distillation of the liquid pyrolysate gave 1,1-dimethylallene, methacrylonitrile and 7 g. (20%) of 2-(2-cyanopropyl)-3-methyl-1,3-butadiene, b.p. 98° (22 mm.), n^{25}D 1.4680. Infrared analysis showed conjugated C=C (6.27 μ) and non-conjugated nitrile (4.49 μ). Proton nuclear magnetic resonance analysis showed methyl, methylene, vinyl and tertiary protons in the appropriate ratio.

Anal. Calcd. for $C_9H_{13}N$: C, 79.93; H, 9.69. Found: C, 79.83; H, 9.86.

2-Cyano-4-methyl-1,4-pentadiene (IVa).—1-Methyl-3-methylenecyclobutanecarbonitrile[1] (43 g.) was added to the reaction tube maintained at 700° and 3 mm. during a period of 30 minutes. At the end of the addition, the trap was removed from the pyrolysis system and the allene allowed to evaporate. Distillation of the remaining liquid gave methacrylonitrile and 20 g. (47%) of 2-cyano-4-methyl-1,4-pentadiene (XVIII), b.p. 65° (30 mm.), n^{25}D 1.4446. Infrared analysis showed conjugated nitrile (4.55 μ), conjugated C=C (6.17 μ) and non-conjugated C=C (6.06 μ). Proton nuclear magnetic resonance analysis showed methyl, methylene and vinyl protons in the appropriate ratio.

Anal. Calcd. for C_7H_9N: C, 78.46; H, 8.46. Found: C, 78.48; H, 8.62.

2-Cyano-4-methyl-1,4-pentadiene from Allene and Methacrylonitrile.—Methacrylonitrile (80 g.) was added at a rate of 1 g. per minute to the reaction tube maintained at 600° and atmospheric pressure. Allene was simultaneously introduced into the reaction zone at a rate of 8.5 l. per hour. The effluent reaction mixture was collected in a trap chilled by solid carbon dioxide and acetone. Distillation of the reaction mixture gave recovered starting materials and 5.5 g. (10% conversion) of 2-cyano-4-methyl-1,4-pentadiene (IVa), b.p. 66–68° (30 mm.), n^{25}D 1.4496–1.4470. Infrared and nuclear magnetic resonance analyses showed that it was identical with IVa prepared from 1-methyl-3-methylenecyclobutanecarbonitrile.

2-Methoxycarbonyl-4-methyl-1,4-pentadiene (IVb).—Methyl 1-methyl-3-methylenecyclobutanecarboxylate[1] (40 g.) was added to the reaction tube maintained at 650° and 4–6 mm. over a period of 30 minutes. Distillation of the liquid pyrolysate gave 18.5 g. of material boiling at 160°. Proton nuclear magnetic resonance analysis indicated that this material was a mixture of recovered starting cyclobutane and 2-methoxycarbonyl-4-methyl-1,4-pentadiene. This mixture (18.5 g.) was repyrolyzed at 700° and 2–4 mm. to give, after distillation, 15 g. (38%) of 2-methoxycarbonyl-4-methyl-1,4-pentadiene, b.p. 160–161°. Infrared analysis showed conjugated ester carbonyl (5.78 μ), conjugated C=C (6.12 μ) and non-conjugated C=C (6.05 μ). Proton nuclear magnetic resonance analysis showed methyl, methoxyl, methylene and vinyl protons in the appropriate ratio.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.56. Found: C, 68.44; H, 8.83.

Methyl 2,3-Butadienoate (IX).—Dimethyl 3-methylenecyclobutane-1,2-dicarboxylate[2] (VIII) (164 g., 0.89 mole) was added over a period of 2.8 hours at 25 mm. pressure to a vertical 1-inch Vycor tube packed with quartz rings for 14 inches of its length and maintained at 600°. The pyrolysate, which was caught in a trap at −78°, was distilled through a 30-inch spinning band column. After collecting 42 g. (55%) of methyl acrylate, n^{25}D 1.4012, b.p. 34–37° (154 mm.), there was obtained 36.6 g. (42%) of methyl 2,3-butadienoate, b.p. 59–60° (52 mm.), 48–49° (26 mm.), m.p. −23°, n^{25}D 1.4635. Infrared analysis showed =CH (shoulder at 3.25 μ), saturated CH (3.25, 3.4, 3.51 μ), C=C=C (5.1, 5.15 μ), ester C=O (5.75 μ).

Anal. Calcd. for $C_5H_6O_2$: C, 61.21; H, 6.17. Found: C, 61.55; H, 6.41.

In addition, there was recovered 5 g. (4%) of a mixture of dimethyl fumarate and dimethyl maleate, 18 g. (11%) of starting material and 33 g. (20%) of dimethyl 3-methylene-2,3-dihydromuconate, b.p. 150–151° (25 mm.), n^{25}D 1.4778.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.74; H, 6.57; sapon. no., 610. Found: C, 58.64; H, 6.36; sapon. no., 610.

Infrared analysis showed saturated CH (3.39, 3.51 μ), ester C=O (5.75 μ), C=C (5.95 μ), CH_2=C (11.65 μ). Ultraviolet analysis showed —C=C—C=O (240, 217 mμ).

Dimethyl 3-methylene-2,3-dihydromuconate (18.4 g.) was refluxed 3 hours with 16.8 g. of potassium hydroxide in 54 ml. of water and 25 ml. of methanol; the mixture was acidified to *p*H 1 with sulfuric acid and the resulting solution was evaporated to dryness. The solid was extracted with ethyl acetate to give 11.5 g. of 3-methylene-2,3-dihydromuconic acid, m.p. 163–164°, after one recrystallization from ethyl acetate. Infrared analysis showed acid–OH (3.79, 3.92 μ), C=O (shoulder at 5.85, 5.90 μ), C=C (6.0 μ), CH_2=C (11.4 μ).

Anal. Calcd. for $C_7H_8O_4$: C, 53.84; H, 5.16; neut. equiv., 78.1. Found: C, 53.70; H, 5.21; neut. equiv., 78.2.

Reactions of Methyl 2,3-Butadienoate.—A solution of 2 g. of methyl 2,3-butadienoate and 2.2 g. of resorcinol in 10 ml. of benzene containing 3 drops of boronfluoride ethearate was refluxed 16 hours. The solid obtained on cooling was recrystallized three times from aqueous methanol to give silky needles of 7-hydroxy-4-methylcoumarin (β-methylumbelliferone) (XII), m.p. 186–187°.

Methyl 2,3-butadienoate (10 g.) and 11 g. of phenylhydrazine in 40 ml. of benzene were refluxed 7 hours, cooled to induce crystallization and the solid was recrystallized successively from benzene and aqueous methanol to give 3-methyl-1-phenyl-5-pyrazolone (XI), m.p. 127.5–129°.

Methyl 2,3-butadienoate (19.6 g.) was refluxed 5 hours in 40 ml. of methanol containing 0.3 g. of potassium acetate. Distillation gave 20 g. (77%) of methyl β-methoxycrotonate (XIII), b.p. 89–91° (50 mm.), n^{25}D 1.4539. Infrared analysis showed saturated CH (3.39, 3.51 μ), C=O (5.80 μ), C=C (6.1 μ); ether C–O–C (8.75 μ).

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.98; H, 7.94.

Methyl 2,3-butadienoate (19.6 g.) was mixed with 33 g. of cyclopentadiene in 60 ml. of ether. After 16 hours at room temperature, ether and cyclopentadiene were removed. The residue amounted to 4.3 g. of unreacted methyl 2,3-

---

(5) N.m.r. spectra were obtained using a Varian High Resolution Spectrometer and associated magnet system operating at 40 mc. and 9500 gauss. Resonance shifts were measured by a side-band technique relative to water at zero. Positive shifts are to the low field side and negative to the high field side.

butadienoate and 19 g. (77%) of methyl 2-methylenebicyclo[2.2.1]hept-5-ene-3-carboxylate, b.p. 102–103° (25 mm.), $n^{26}\text{D}$ 1.4900 (literature[6] values are b.p. 100–105° (10 mm.), $n^{14.5}\text{D}$ 1.4950). Infrared analysis showed =CH (3.20 μ), saturated CH (3.35, 3.45 μ), C=O (5.75 μ); exocyclic C=C (5.99 μ), ring C=C (6.35 μ), CH_2=C (11.3 μ).

Methyl 2,3-butadienoate (8.8 g.) and piperazine (8 g.) in 40 ml. of benzene were refluxed 64 hours. Replacement of the benzene by water gave a yellow solid which was recrystallized from methanol. There was obtained 7.2 g. (57%) of rhombic crystals of dimethyl N,N'-diethylene-β-aminocrotonate (XIV), m.p. 167–168.5°.

Anal. Calcd. for $C_{14}H_{22}O_4N_2$: C, 59.56; H, 7.86; N, 9.92. Found: C, 59.84; H, 8.13; N, 10.03.

Dimethyl 3-Methyl-1,3-butadiene-1,2-dicarboxylate (XVI).—Dimethyl 3-methyl-2-cyclobutene-1,2-dicarboxylate (XV) (110 g., 0.6 mole) was added over 2.25 hours at 28 mm. pressure at 400° to the packed Vycor tube used in making IX. The pyrolysate as collected at −78° was a vitreous solid which became a slush on warming to 0°. Removal of the mother liquor and recrystallization of the residue three times from ether gave 38.5 g. (35% conversion, 87% yield) of dimethyl 3-methyl-1,3-butadiene-1,2-dicarboxylate, m.p. 42.5–43°. Infrared analysis showed =CH (3.30 μ), saturated CH (3.36 μ), C=O (5.72, 5.77 μ), conjugated C=C (6.15 μ).

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.74; H, 6.57. Found: C, 59.11; H, 6.71.

Reactions of Dimethyl 3-Methyl-1,3-butadiene-1,2-dicarboxylate.—A solution of 2 g. of dimethyl 3-methyl-1,3-butadiene-1,2-dicarboxylate and 2 g. of maleic anhydride in 15 ml. of benzene containing 0.05 g. of hydroquinone was refluxed under nitrogen for 30 hours. Water (1 ml.) was added and refluxing was continued for 2 hours. Evaporation of the solution gave a white solid which on recrystallization from water gave 1.6 g. of dimethyl 1-methyl-4,5-dicarboxy-1-cyclohexene-2,3-dicarboxylate, m.p. 165–170°.

Anal. Calcd. for $C_{13}H_{16}O_8$: C, 52.00; H, 5.37; acid no., 374. Found: C, 52.17; H, 5.68; acid no., 374.

A solution of 3.64 g. of dimethyl 3-methyl-1,3-butadiene-1,2-dicarboxylate and 2.2 g. of *p*-benzoquinone in 10 ml. of benzene was allowed to stand 6 days at 25°. The precipitate of fine needles was filtered off and recrystallized three times from methanol to give 4.1 g. of dimethyl 7-methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone-5,6-dicarboxylate, m.p. 121–123°.

Anal. Calcd. for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 62.04; H, 5.73.

Warming 1 g. of the above naphthoquinone in 2 ml. of methanol containing 0.05 g. of sodium hydroxide for 5 minutes at 45° caused isomerization to dimethyl 7-methyl-5,8-dihydro-1,4-naphthohydroquinone-5,6-dicarboxylate, m.p. 162–163° after recrystallization from chloroform. Crystals of this naphthohydroquinone changed from white to brown on exposure to air.

Anal. Calcd. for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.39; H, 5.40.

Dimethyl 1,3-Pentadiene-2,3-dicarboxylate (XVII).—Dimethyl 3-methyl-2-cycylobutene-1,2-dicarboxylate (XV) (160 g.) was pyrolyzed at 450° instead of at 400° through the Vycor tube used for synthesizing XVI. The mother liquor remaining after crystallization of dimethyl 3-methyl-1,3-butadiene-1,2-dicarboxylate (XVI) was fractionated to obtain 16 g. (10% conversion) of dimethyl 1,3-pentadiene-2,3-dicarboxylate (XVII), b.p. 107° (16 mm.), m.p. −1°, $n^{25}\text{D}$ 1.4631.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.74; H, 6.57. Found: C, 58.67; H, 6.77.

Infrared analysis showed =CH (3.24 μ), saturated CH (3.39, 3.51 μ), C=O (5.77 μ), conjugated C=C (6.13 μ), CH_2=C (11.1 μ), RCH=C (12.64 μ).

A solution of 3.7 g. of dimethyl 1,3-pentadiene-2,3-dicarboxylate (XVII) and 2.5 g. of maleic anhydride in 25 ml. of benzene was refluxed for 147 hours, then cooled to give crystals. These were dissolved in boiling water, and the solution was refluxed 5 hours. Cooling gave 4 g. of dimethyl 3-methyl-4,5-dicarboxy-1-cyclohexene-1,2-dicarboxylate, m.p. 185–191°.

Anal. Calcd. for $C_{13}H_{16}O_8$: C, 52.00; H, 5.37; Found: C, 51.99; H, 5.32.

A mixture of 2 g. of dimethyl 1,3-pentadiene-2,3-dicarboxylate (XVII), 3 ml. of methanol, 0.1 g. of *p*-toluenesulfonic acid and 10 ml. of water was refluxed for 236 hours. The resulting solution was evaporated on the steam-bath and the residue was recrystallized from a benzene–ethyl acetate mixture to give white plates of 3-ethyl-1-oxa-3-cyclopentene-2-one-4-carboxylic acid (XVIII), m.p. 153–154.5°. This was shown to be identical by infrared spectroscopy and mixed melting point with the lactone acid prepared[3] by heating 3-methylenecyclobutane-1,2-dicarboxylic acid with 10% palladium-on-charcoal at 150° for 2 hours.

Anal. Calcd. for $C_7H_8O_4$: C, 53.84; H, 5.16; neut. equiv., 156. Found: C, 53.98; H, 5.6; neut. equiv., 155.

Infrared analysis showed saturated CH (3.35, 3.48 μ), acid —OH (3.82, 3.96 μ), lactone C=O (5.73 μ) acid C=O (5.85 μ), C=C (6.02 μ).

Four n.m.r. peaks (5% solution in deuteriochloroform) were obtained. These were in the ratio 1:2:2:3 and are assigned as follows: COOH, +202 c.p.s., —OCH_2—C, −3 c.p.s.; CH_2—C=, −63 c.p.s.; CH_3, −113 c.p.s. These resonance positions are slightly different from those usually encountered for the several types of protons, but these differences are reasonable because of the ability of solvents to shift resonances.

WILMINGTON 98, DEL.

---

(6) E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4073 (1956).