were removed under vacuum below 50°. Claisen-distillation of the residue gave 28 g. of glycidaldehyde oxime acetate, b.p. 60–65° (1 mm.), $n^{20}D$ 1.4647. The yield was 44% over-all based on glycidaldehyde.

Anal. Calcd. for $C_5H_7NO_3$: C, 46.5; H, 5.5; N, 10.8; sapon. equiv., 129; oxirane oxygen, 12.4. Found: C, 46.5; H, 5.5; N, 10.8; sapon. equiv.,[19] 131; oxirane oxygen, 11.2.[20]

Glycidonitrile.—A 32.8-g. (0.25 mole) sample of oxime acetate was charged to a 100-ml. distillation kettle and attached to a 0.7 × 50 cm. glass spiral-packed column. The pressure was held at 50 mm. while heating with an oil-bath. Deacetylation started when the bath temperature reached 115–120°, but in order to obtain a satisfactory distillation rate it was necessary to hold the bath at 140–145°. Takeoff was adjusted to maintain a maximum head temperature of 70°. After 2.5 hr., 24.8 g. of a mixture of acetic acid and glycidonitrile had been collected and the rate of takeoff was very slow; by lowering the pressure to 1 mm. only 0.4 g. more material distilled as a separate fraction. The distillation residue was 5.0 g.

Careful distillation of the mixture of acid and nitrile through the same column afforded 7.3 g. (42% yield) of glycidonitrile, b.p. 47.5–48° (20 mm.), $n^{20}D$ 1.4094. Infrared analysis showed nitrile absorption at 4.43 μ and epoxide absorption at 8.05 and 11.98 μ.

Anal. Calcd. for C_3H_3NO: C, 52.2; H, 4.4; N, 20.3; oxirane oxygen, 23.2. Found: C, 52.2; H, 4.5; N, 20.0; oxirane oxygen, 22.1.[16]

The epoxy nitrile was also isolated by dissolving 69 g. of the mixture of acetic acid and glycidonitrile in 300 ml. of ether and washing out the acetic acid with a concentrated sodium bicarbonate solution. Distillation of the dried ether solution gave 21 g. of glycidonitrile with the above b.p.

Glyceraldehyde from Glycidaldehyde.—A freshly flashed aqueous solution containing 0.25 mole of glycidaldehyde in 200-ml. total volume was treated with 2 ml. of formic acid and allowed to stand at room temperature. The disappearance of epoxide was followed by titration[16] and after 2 weeks only 1% remained. The solution was concentrated under vacuum at <40° to a viscous residue and then triturated with 5 ml. of ethanol. After completion of the crystallization process (2–3 days), the solid mass was crushed and dried to a constant weight of 21.4 g. (95% yield), m.p. 125–130°. After trituration with warm acetone there remained 18.9 g. (84% yield) of glyceraldehyde dimer, m.p. 136–137°; a mixed m.p. with an authentic sample (Nutritional Biochemical Corp.) was not depressed.

Anal. Calcd. for $C_6H_{12}O_6$: C, 40.0; H, 6.7. Found: C, 39.8; H, 6.8.

α-Methylglycidaldehyde from Methacrolein.—To a 1-liter, 5-neck flask equipped as above were charged 300 ml. of water and 1.05 mole of 30% hydrogen peroxide. The mixture was stirred at 35–40° and 70 g. (1.0 mole) of methacrolein was added over 15 minutes at a *p*H of 8–8.5; the latter was maintained by the addition of 1 *N* sodium hydroxide. After an additional hour at the same temperature and *p*H, iodometric titration indicated the consumption of 0.96 mole of hydrogen peroxide; acidic by-product amounted to 0.08 mole as determined by alkali consumption. The yield of epoxide was 0.82 mole by titration for oxirane oxygen.[16]

The crude mixture was flashed as above, using an extra 100 ml. of water after the volume had been reduced to 50–100 ml. Recovery of volatile epoxide (α-methylglycidaldehyde) amounted to 0.79 mole in a total volume of 600 ml.

For the recovery of anhydrous epoxy aldehyde, the solution was saturated with 400 g. of ammonium sulfate and extracted with five 200-ml. portions of ether. Titration of the aqueous salt solution indicated the presence of 0.21 mole of epoxide, so the mixture was warmed to 35° and extracted with two more 200-ml. portions of ether. The combined ether extracts, containing 0.71 mole of epoxide by titration, were dried for 1 hour over 100 g. of anhydrous magnesium sulfate and finally over 100 g. of Drierite for 1 hour. The filtered solution was distilled through a 10-tray Oldershaw column to give a concentrate of 260 ml. This was further concentrated using a 0.7 × 50 cm. glass spiral-packed column until the kettle temperature reached 80°. Distillation under vacuum then afforded 55 g. (64% yield based on methacrolein) of α-methylglycidaldehyde, b.p. 52–53° (80 mm.). There was no pre-cut and virtually no residue.

Anal. Calcd. for $C_4H_6O_2$: C, 55.8; H, 7.0; oxirane oxygen, 18.6. Found: C, 55.5; H, 7.1; oxirane oxygen, 18.1.[16]

The 2,4-dinitrophenylhydrazone derivative was prepared exactly as described above, m.p. 137–138°.

Anal. Calcd. for $C_{10}H_{10}N_4O_5$: N, 21.0. Found: N, 21.1.

EMERYVILLE, CALIF.

---

[19] Sample allowed to stand for 0.5 hr. at room temperature with excess 0.1 *N* sodium hydroxide; back titration made with 0.1 *N* hydrochloric acid.

[20] Hydrochloric acid–dioxane method; see ref. 16, p. 135.

[CONTRIBUTION NO. 510 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Chemistry of Cyclobutanes. II. Cyclobutenes from 3-Methylenecyclobutane-1,2-dicarboxylic Anhydride

BY H. N. CRIPPS, J. K. WILLIAMS, V. TULLIO AND W. H. SHARKEY

RECEIVED MARCH 25, 1959

The adduct from allene and maleic anhydride, 3-methylenecyclobutane-1,2-dicarboxylic anhydride, has proved to be a versatile intermediate to a variety of functionally substituted cyclobutenes. Upon treatment with alkali, this anhydride is converted to 3-methyl-2-cyclobutene-1,2-dicarboxylic acid. Other functionally substituted cyclobutenes with ester, amide, nitrile, amine and hydroxyl groups have been obtained from this acid. The stereochemistry of the saturated dicarboxylic acids obtained by hydrogenation of 3-methyl-2-cyclobutene-1,2-dicarboxylic acid has been established.

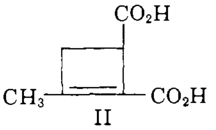
The discovery of a convenient synthesis of substituted methylenecyclobutanes[1] has made compounds of this type readily accessible for the first time. Among these is 3-methylenecyclobutane-1,2-dicarboxylic anhydride (I) a compound that, because of its multiple functionality, appeared ideally suited as an intermediate to a variety of new four-membered ring compounds (Fig. 1). Our interest in I was greatly increased when it was found that treatment with excess alkali followed by acidification gave 3-methyl-2-cyclobutene-1,2-dicarboxylic acid (II) in 84% yield.

The structure of II was assigned on the basis of spectral data. Its infrared spectrum showed absorption at 5.85 μ for an unconjugated carboxyl group, at 5.92 μ for a conjugated carboxyl group, a shoulder at about 6.05 μ for the double bond and a band at 7.29 μ for the methyl group. The ultraviolet spectrum in ethanol had a maximum at 220 mμ (ϵ 8580) consistent with an α,β-conjugated

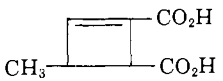
---

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

acid structure. The two acids consistent with the spectral data are 3-methyl-2-cyclobutene-1,2-dicarboxylic acid (II) and 4-methyl-2-cyclobutene-1,2-dicarboxylic acid (III). The product was identified as II by examination of its proton magnetic resonance in deuterium oxide which had four peaks in approximately the correct intensities for structure II.[2] A peak at 0 c.p.s. of relative intensity 2 appeared for the HOD and H_2O formed by exchange with the carboxyl hydrogens. The other peaks appeared at −38 c.p.s. of relative intensity 1 for the hydrogen on the number one carbon atom, at −80 c.p.s. of relative intensity 2 for the ring hydrogens on the number four carbon atom, and at −104 c.p.s. of relative intensity 3 for the methyl group attached to the number three carbon atom. The absence of any proton resonance for hydrogen attached to a doubly bonded carbon atom ruled out 4-methyl-2-cyclobutene-1,2-dicarboxylic acid (III) as a possible structure for this compound.



II



III

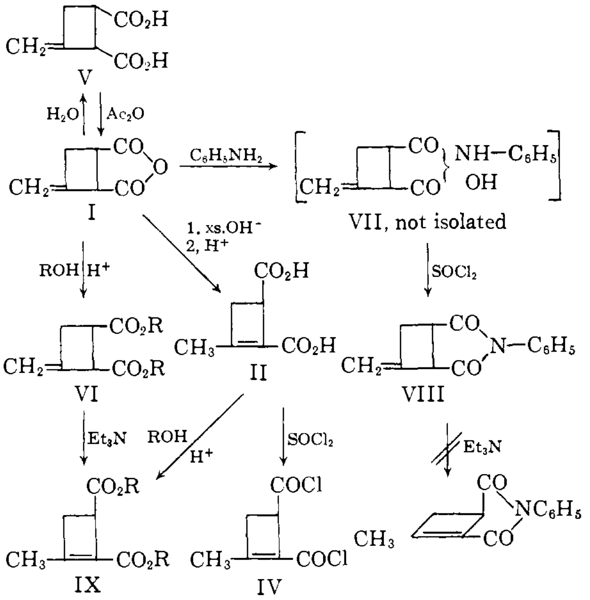


Fig. 1.—Reactions of 3-methylenecyclobutane-1,2-dicarboxylic anhydride.

Reaction of II with thionyl chloride gave a diacid chloride in 97% yield that was shown by spectral studies to be 3-methyl-2-cyclobutene-1,2-dicarbonyl chloride (IV). The infrared spectrum of IV had bands at 5.65 μ for the unconjugated carbonyl, at 5.70 μ for the conjugated carbonyl group, at 6.09 μ for the conjugated double bond, and at 7.29 μ for the methyl group. The proton magnetic resonance spectrum of IV was completely consistent with the assigned structure. Resonance was observed at −32 c.p.s. of relative intensity 1 for the hydrogen on the number one carbon atom, at −85 c.p.s. of relative intensity 2 for the hydrogens at the number four carbon atom and at −108 c.p.s. of relative intensity 3 for the methyl group attached to the number three carbon atom.

Derivatives of I in which the double bond did not rearrange were obtained easily under acidic conditions. For example, treatment of I with water gave 3-methylenecyclobutane-*cis*-1,2-dicarboxylic acid (V) which was reconverted to I with acetic anhydride. Acid-catalyzed esterification of I with methyl or ethyl alcohol gave the unrearranged esters VI. Isomeric amic acids VII were formed in good yield by reaction of I with a molar equivalent of aniline. The imide VIII was formed when the amic acid VII was heated at reflux with thionyl chloride.

Under basic conditions, the exocyclic double bond of derivatives of I undergoes rearrangement to give cyclobutenes. Thus, treatment of VI (R = ethyl) with triethylamine gave the rearranged ester IX (R = ethyl) that was also prepared by the acid-catalyzed esterification of II. As expected, because of steric considerations, no rearrangement occurred when the imide VIII was treated with triethylamine.

The functional groups of 3-methyl-2-cyclobutene-1,2-dicarboxylic acid (II) and its derivatives undergo conventional chemical transformations (see Fig. 2). Thus, ethanol reacted with IX (R = ethyl) in the presence of sodium ethoxide to give the adduct X (R = ethyl). Reduction of IX (R = methyl) with lithium aluminum hydride gave the glycol XI.

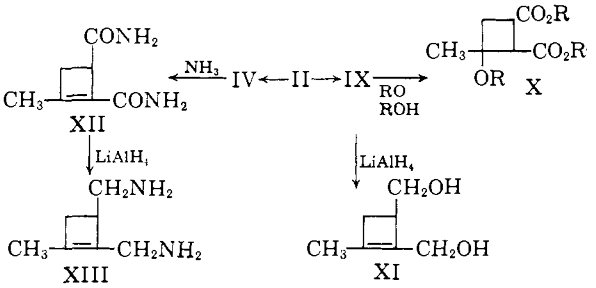


Fig. 2.—Reactions of 3-methyl-2-cyclobutene-1,2-dicarboxylic acid and its derivatives.

Reaction of the acid chloride IV with ammonia gave the 3-methyl-2-cyclobutene-1,2-dicarboxamide (XII) which was reduced by lithium aluminum hydride to 3-methyl-2-cyclobutene-1,2-bis-(methylamine) (XIII). Exposure of derivatives of II to temperatures above about 125° causes isomerization to substituted 1,3-butadienes.[3] Consequently, care must be exercised when these compounds are manipulated. Studies of the thermal rearrangement of cyclobutanes will be reported in a subsequent paper.

3-Methyl-2-cyclobutene-1,2-dicarboxylic acid (II) upon hydrogenation over palladium-on-carbon

---

(2) We are indebted to Dr. W. D. Phillips of this Laboratory who determined and interpreted the n.m.r. spectra. N.m.r. spectra were obtained by means of a high-resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of H_2O. Negative frequency displacements indicate resonances occurring at higher fields relative to the reference.

(3) (a) R. Willstätter and W. V. Schmaedel, *Ber.*, **38B**, 1994 (1905); (b) J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949); (c) E. Vogel, *Angew. Chem.*, **66**, 640 (1954); **68**, 189 (1956); (d) W. Cooper and W. D. Walters, THIS JOURNAL, **80**, 4220 (1958).

gave a mixture of two isomeric saturated dicarboxylic acids (Fig. 3). If *cis* addition of hydrogen to the double bond is assumed,[4] then the structures of these isomeric acids must be XIV and XV. Separation of XIV and XV was accomplished by treating the isomeric mixture with thionyl chloride.

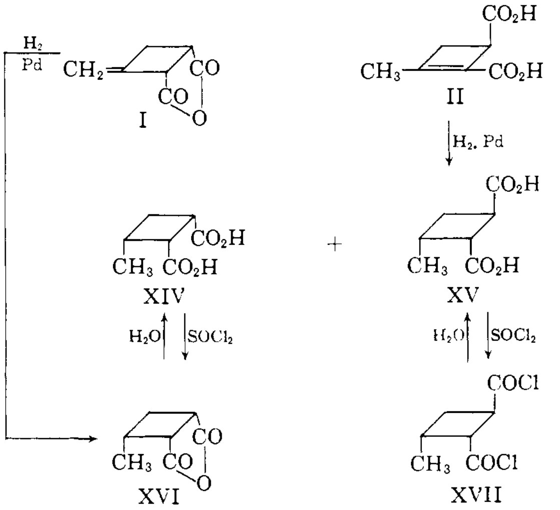


Fig. 3.—Saturated acids derived from 3-methylenecyclobutane-1,2-dicarboxylic anhydride.

The anhydride XVI and the acid chloride XVII were separated easily by distillation. Hydrogenation of I also gave an anhydride which was shown to be identical to XVI by comparison of infrared spectra.[5] Hydrolysis of the anhydride XVI gave a pure sample of *cis,cis*-3-methylcyclobutane-1,2-dicarboxylic acid (XIV) m.p. 122.5–123.5°.[6] Hydrolysis of the acid chloride XVII gave *trans,cis*-3-methylcyclobutane-1,2-dicarboxylic acid (XV), m.p. 140–141°.

Experimental[7]

3-Methyl-2-cyclobutene-1,2-dicarboxylic Acid (II).—A solution of 400 g. (10 moles) of sodium hydroxide in 1600 ml. of distilled water was stirred and maintained at 10–15° while 552 g. (4 moles) of 3-methylenecyclobutane-1,2-dicarboxylic anhydride was added over a 3.5-hour period.[8] The solution was stirred for 1.5 hours at 10° and allowed to stand at room temperature for 6 days. The solution was acidified with 1 liter of concentrated hydrochloric acid. The precipitated 3-methyl-2-cyclobutene-1,2-dicarboxylic acid was washed with 300 ml. of water. The air-dried acid weighed 565 g. (90.7%) and melted at 182–185°. Recrystallization of 15 g. of the crude acid from 35 ml. of water gave 13 g. of II, m.p. 189–190.5°.

Anal. Calcd. for $C_7H_8O_4$: C, 53.84; H, 5.16; neut. equiv., 78.06; quant. hydrog., 0.0128 g. H_2/g. Found: C, 53.92; H, 5.14; neut. equiv., 77.2; quant. hydrog., 0.0124 g. H_2/g.

3-Methyl-2-cyclobutene-1,2-dicarbonyl Chloride (IV).—A mixture of 644 g. of 3-methyl-2-cyclobutene-1,2-dicarboxylic acid and 2 kg. of thionyl chloride was heated under reflux for 4 hours. Thionyl chloride was removed by distillation under reduced pressure and the oil that remained was distilled through a 12-inch Vigreux column. The yield of acid chloride, b.p. 95–105° at 1.5–2.2 mm., was 770 g. (97%). The anilide melted at 185–186° after recrystallization from benzene.

Anal. Calcd. for $C_{19}H_{18}O_2N_2$: C, 74.79; H, 5.92; N, 9.15. Found: C, 74.40; H, 5.98; N, 8.93.

3-Methylenecyclobutane-1,2-dicarboxylic Acid (V).—3-Methylenecyclobutane-1,2-dicarboxylic anhydride (150 g., 1.09 moles) was added to 75 ml. of distilled water at 80°. After several minutes the clear solution that was obtained was poured into a crystallizing dish. The hard white solid that formed when the mixture cooled was freed of liquid, and then dried in a vacuum oven at 45°. The product weighed 120 g. (90.5%) and melted at 121–126°. Two recrystallizations from benzene gave 3-methylenecyclobutane-1,2-dicarboxylic acid melting at 131–131.5°. The infrared spectrum of this acid has absorption at 5.84 μ for the carboxyl group and at 11.14 μ for the exocyclic double bond.

Anal. Calcd. for $C_7H_8O_4$: neut. equiv., 78.06. Found: neut. equiv., 78.8, 78.6.

A mixture of 78 g. (0.5 mole) of 3-methylenecyclobutane-1,2-dicarboxylic acid and 200 ml. of acetic anhydride was heated under reflux for one hour and then distilled at atmospheric pressure through a one-foot Vigreux column to remove the unreacted acetic anhydride and acetic acid. The remaining oil was distilled under reduced pressure to give 65 g. (94%) of 3-methylenecyclobutane-1,2-dicarboxylic anhydride (I), b.p. 148° (16 mm.), $n^{25}\mathrm{D}$ 1.4943–1.4953. The infrared spectrum of this product was identical with that of a sample of I obtained from allene and maleic anhydride.[1]

Diethyl 3-Methylenecyclobutane-1,2-dicarboxylate (VI).—A suspension of 50 ml. of ethanol-washed Amberlite IR 120 (acid form) ion exchange resin was heated under reflux for 72 hours with a solution of 200 g. (1.45 moles) of 3-methylenecyclobutane-1,2-dicarboxylic anhydride in 600 ml. of absolute ethanol. The mixture was filtered and distilled to give 225 g. (73.2%) of diethyl 3-methylenecyclobutane-1,2-dicarboxylate that boiled at 161° (48 mm.), $n^{25}\mathrm{D}$ 1.4533–1.4540. The infrared spectrum of this ester showed bands at 5.75 μ for ester carbonyl and 5.95 and 11.25 μ for the exocyclic methylene group.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.59; sapon. equiv., 106.1. Found: C, 62.14; H, 7.49; sapon. equiv., 106.9.

N-Phenyl-3-methylenecyclobutane-1,2-dicarboximide (VIII).—A solution of 90 g. of aniline in 50 ml. of methylene chloride was added dropwise to a solution of 138 g. of 3-methylenecyclobutane-1,2-dicarboxylic anhydride in 300 ml. of methylene chloride while the temperature was maintained below 20°. The reaction mixture was diluted to one liter with methylene chloride and a solution of 87 ml. of thionyl chloride in 100 ml. of methylene chloride was added over the course of 1 hour. The reaction mixture was stirred for 0.5 hour at room temperature and then heated under reflux for 1.5 hours. After removal of the volatile materials by distillation on a steam-bath, the liquid residue was diluted with 100 ml. of absolute ethanol and allowed to cool to 0°. The tan needles that precipitated were collected and recrystallized twice from ethanol to give 142 g. (69%) of VIII as light tan needles, m.p. 86–86.5°.

Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.29; H, 5.30; N, 6.55.

Diethyl 3-Methyl-2-cyclobutene-1,2-dicarboxylate (IX, R = Ethyl). **A. From II.**—A mixture of 234 g. (1.5 moles) of II, 5 g. of sulfuric acid, 1 liter of absolute ethanol and 400 ml. of benzene was heated in a flask surmounted by a 30-inch packed column. The benzene–water–ethanol azeotrope (b.p. 64–65°) was removed over the course of 22 hours. The cooled reaction mixture was treated with 5.35 g. of sodium carbonate and stirred for 20 hours at room temperature. The reaction mixture was filtered to remove inorganic salts and distilled through a spinning band column. The diethyl 3-methyl-2-cyclobutene-1,2-dicarboxylate (IX), $n^{25}\mathrm{D}$ 1.4591, boiled at 72–73° (2 mm.) and weighed 290 g. (91%). The infrared spectrum showed absorption at 5.75 μ for the unconjugated ester carbonyl group, at 5.80 μ for the conjugated ester carbonyl group, at 5.97 μ for the conjugated double bond and at 7.27 μ for the methyl group.

---

(4) K. N. Campbell and B. K. Campbell, *Chem. Revs.*, **31**, 77 (1942).

(5) The hydrogenation of I would be expected to give an all *cis* product since absorption of the molecule on the catalyst surface would be hindered on the side of the ring bearing the bulky anhydride group; R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, This Journal, **64**, 1985 (1942).

(6) K. Alder and O. Ackermann, *Ber.*, **90**, 1697 (1957), report a melting point of 113–114° for a 3-methylcyclobutane-1,2-dicarboxylic acid of unspecified stereochemical configuration.

(7) All melting points and boiling points are uncorrected.

(8) B. C. Pratt, U. S. Patent 2,848,478, August 19, 1958

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.26; H, 7.60. Found: C, 61.65; H, 7.50.

B. From VI.—A mixture of 21.2 g. of diethyl 3-methylenecyclobutane-1,2-dicarboxylate (VI) and 100 ml. of triethylamine was heated under reflux for 17 hours. Distillation of the reaction mixture gave 15 g. (71%) of IX that was identified by comparison of its infrared spectrum with that of the authentic material prepared by esterification of II.

Dimethyl 3-Methyl-2-cyclobutene-1,2-dicarboxylate (IX, R = Methyl).—3-Methyl-2-cyclobutene-1,2-dicarboxylic acid (II) (121 g.), methanol (247 g.) and sulfuric acid (19.2 ml.) were heated under reflux for 4 hours. The reaction mixture was diluted with water and the aqueous solution was extracted with ether. After removal of ether, the residue was distilled to obtain 94 g. of dimethyl 3-methyl-2-cyclobutene-1,2-dicarboxylate, b.p. 75–77° (0.4 mm.), $n^{25}\text{D}$ 1.4648.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.69; H, 6.55.

Diethyl 3-Ethoxy-3-methylcyclobutane-1,2-dicarboxylate (X).—Diethyl 3-methyl-2-cyclobutene-1,2-dicarboxylate (21.2 g., 0.1 mole) was added to 100 ml. of absolute ethanol in which 1 g. of sodium had been dissolved. After heating under reflux for 40 hours, 25 ml. of methyl iodide was added to destroy sodium ethoxide. Refluxing was continued for 1.5 hours. The volatile materials were removed under reduced pressure and the residue distilled through a 24-inch packed column. Three fractions were collected: I, b.p. 139–147° (18 mm.), 2.5 g., $n^{25}\text{D}$ 1.4407; II, b.p. 147.5–157° (18 mm.), 10.0 g., $n^{25}\text{D}$ 1.4402; III, b.p. 157° (18 mm.), 4.0 g., $n^{25}\text{D}$ 1.4404. The wide boiling range is due to the presence of stereoisomers. The infrared spectrum of fraction II showed a band at 5.75 μ (ester C═O) but had no absorption in the 3.25 μ region (no unsaturated C—H) and none in the 6 or 11.25 μ regions (no C═C or $C{=}CH_2$).

Anal. Calcd. for $C_{13}H_{22}O_5$: C, 60.45; H, 8.59. Found for fraction II: C, 60.98; H, 8.77.

3-Methyl-2-cyclobutene-1,2-bis-(methanol) (XI).—A solution of 21 g. of dimethyl 3-methyl-2-cyclobutene-1,2-dicarboxylate in 100 ml. of ether was added with stirring to 6.2 g. of lithium aluminum hydride in 125 ml. of ether. The reaction mixture was stirred for 0.5 hour and 12 g. of ethyl acetate was added to decompose the excess lithium aluminum hydride. Water (100 ml.) then was added followed by 80 ml. of 25% sulfuric acid. The ether layer was separated and combined with two ether extracts of the water layer. The ether solution was dried with magnesium sulfate and the ether was removed by distillation. The product XI weighed 8.5 g. (58%), b.p. 95–98° (0.3 mm.), $n^{25}\text{D}$ 1.4855. The infrared spectrum of the glycol showed absorption for hydroxyl at 3.04 μ and for endocyclic C═C at 5.95 μ.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.55; H, 9.54.

3-Methyl-2-cyclobutene-1,2-dicarboxamide (XII).—Three liters of concentrated ammonium hydroxide was placed in a five-liter creased flask and cooled in an ice-bath while 770 g. of 3-methyl-2-cyclobutene-1,2-dicarbonyl chloride (IV) was added over a period of 1.5 hours at a temperature of 15–30°. After the addition of the acid chloride was complete, the reaction mixture was stirred for 15 minutes. The white crystalline amide was collected by filtration and washed with water until the washings were colorless. The product then was dried in a vacuum oven at 60°. The amide weighed 549 g. (86.5%) and melted at 226.5° dec. The melting point of the amide was not raised by recrystallization from water.

Anal. Calcd. for $C_7H_{10}O_2N_2$: N, 18.17. Found: N, 18.25.

3-Methyl-2-cyclobutene-1,2-bis-(methylamine) (XIII).—To a slurry of 15 g. of lithium aluminum hydride in 500 ml. of tetrahydrofuran was added 15 g. of finely powdered amide XIII in portions over the course of 0.25 hour. The mixture was stirred under reflux for 90 hours. The complex was decomposed by the addition of 70 ml. of 33% sodium hydroxide solution. The mixture was stirred for 1.25 hours and then the upper, tetrahydrofuran phase was decanted. The lower layer was stirred with 150 ml. of tetrahydrofuran. The combined tetrahydrofuran solutions were dried over potassium hydroxide and freed of tetrahydrofuran by distillation. The oil that remained (13 g.) was purified by distillation. There was obtained 2.6 g. of 3-methyl-2-cyclobutene-1,2-bis-(methylamine) (XIII), b.p. 57° (1.6 mm.).

Anal. Calcd. for $C_7H_{14}N_2$: N, 22.20; neut. equiv., 63.1. Found: N, 22.38; neut. equiv., 64.1.

The dibenzoyl derivative of XIII melted at 142–143.5° after two recrystallizations from a mixture of ethanol and methylcyclohexane.

Anal. Calcd. for $C_{21}H_{22}N_2O_2$: N, 8.38. Found: N, 8.57, 8.30.

The infrared spectrum of XIII contained bands at 3.00, 3.08 and 6.23 μ for primary amine and at 5.95 μ for endocyclic C═C.

Hydrogenation of 3-Methyl-2-cyclobutene-1,2-dicarboxylic Acid. Preparation of XVI and XVII.—A solution of 84 g. (0.49 mole) of II in 375 ml. of ethanol containing 0.6 g. of 10% palladium-on-charcoal catalyst was hydrogenated for 1.5 hours at room temperature at 30–40 lb./sq. in. The theoretical amount of hydrogen was absorbed. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was a thick gum that did not crystallize. The crude product (76.6 g.) was heated under reflux for 15 hours with 250 ml. of thionyl chloride. After removal of unreacted thionyl chloride, the residue was distilled through a one-foot Vigreux column. Two constant boiling fractions were obtained: A, 22.4 g. (23%), b.p. 75° (2.7 mm.), $n^{25}\text{D}$ 1.4811; and B, 41.9 g. (62%), b.p. 105° (2.7 mm.), $n^{25}\text{D}$ 1.4742. Fraction A was the diacid chloride XVII.

Anal. Calcd. for $C_7H_8Cl_2O_2$: Cl, 36.36; neut. equiv., 48.8. Found: Cl, 36.22; neut. equiv., 49.6.

The bis-anilide of XVII melted at 248.5–249° after recrystallization from aqueous methanol.

Anal. Calcd. for $C_{19}H_{20}N_2O_2$: N, 9.09. Found: N, 9.09, 9.04.

Fraction B was the anhydride XVI. The infrared spectrum of fraction B, XVI, showed the characteristic anhydride doublet at 5.41 and 5.63 μ. Hydrogenation of I in acetic anhydride gave a compound identical to XVI as judged by comparison of infrared spectra.

Anal. Calcd. for $C_7H_8O_3$: neut. equiv., 70.0. Found: neut. equiv., 70.8, 71.0.

***cis,cis*-3-Methylcyclobutane-1,2-dicarboxylic Acid (XIV).**—A mixture of 7.0 g. of anhydride XVI and 5 ml. of water was heated on a steam-bath until a homogeneous solution was obtained. Benzene (100 ml.) was added and the mixture concentrated by boiling to remove excess water by azeotropic distillation. When the volume was approximately 25 ml., the clear solution was cooled slowly to room temperature. The resultant white crystalline acid (5.2 g.) XIV melted at 118–120°. The crude acid was dissolved in 5 ml. of boiling ethyl acetate and rapidly stirred as 45 ml. of boiling cyclohexane was added slowly. Acid XIV rapidly crystallized as the solution cooled to room temperature. After two such crystallizations, the acid XIV melted at 122.5–123.5°. The melting point was not changed by further crystallization or by sublimation.

Anal. Calcd. for $C_7H_{10}O_4$: C, 53.16; H, 6.37; neut. equiv., 79.07. Found: C, 53.22; H, 6.34; neut. equiv., 79.1, 78.8.

Acid XIV (3.7 g., m.p. 122.5–123°) was recovered unchanged in essentially quantitative yield when shaken in ethanol (25 ml.) with 0.2 g. of 10% palladium-on-carbon for 1.5 hours under a hydrogen pressure of 40 lb./sq. in. Therefore, no detectable rearrangement occurs during hydrogenation.

A mixture of acid XIV (4.1 g., m.p. 121.5–122°) and 25 ml. of thionyl chloride was stirred at room temperature for one hour and then heated under reflux for 20 hours. All volatile products were removed by distillation at about 15 mm. at room temperature. The residue (3.7 g., 100%) was a pale yellow oil that had an infrared spectrum identical with the previously described anhydride XVI. Distillation through a 3-inch Vigreux column gave pure anhydride (3.1 g., 84%) that boiled at 107° (3 mm.), $n^{25}\text{D}$ 1.4740, neut. equiv., 70, 69.6 (calcd. 70). Thus acid XIV does not undergo isomerization when treated with thionyl chloride.

***trans,cis*-3-Methylcyclobutane-1,2-dicarboxylic Acid (XV).**—Hydrolysis of XVII with water gave dibasic acid XV that melted at 136.8–138° after recrystallization from a mixture of ethyl acetate and carbon tetrachloride. Sublimation gave pure XV that melted at 140–141°.

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.]

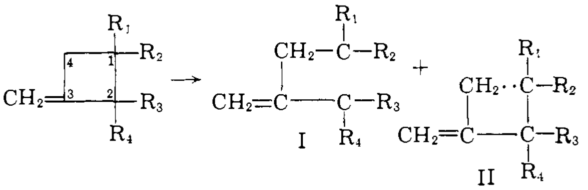
Chemistry of Cyclobutanes. IV. Thermal Cleavage of Methylenecyclobutanes

BY J. J. DRYSDALE, H. B. STEVENSON AND W. H. SHARKEY

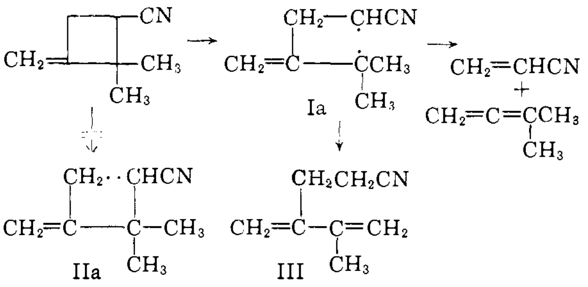
RECEIVED MARCH 25, 1959

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.

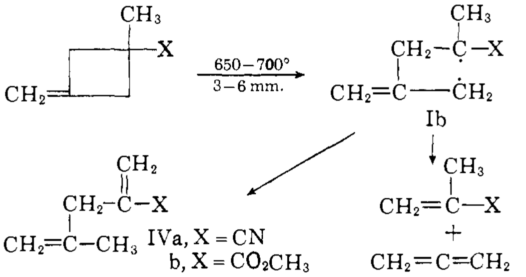
Following the discovery of the cycloaddition of allenes to appropriately substituted olefins to form 3-alkylidenecyclobutanes,[1] it became of interest to examine the thermal rearrangement of these cyclobutanes. Since the weakest points in a methylenecyclobutane are the allylic bonds, thermal cleavage 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).