kg., 12 moles) were charged into a cooled, evacuated 2-gallon autoclave equipped with a stirrer. The autoclave was pressured to 200 lb./sq. in. with nitrogen and heated at 100° for 15 hours. The reaction mixture was treated as described previously and distillation of the product gave 80.9 g. of N-methyl-2,3-butadienylamine, b.p. 105–107.5° (atm. pressure), and 186 g. of N-methyl-bis-(2,3-butadienyl)-amine as a clear, colorless liquid, b.p. 70–71° (15 mm.), $n^{25}D$ 1.4988. The infrared spectrum showed strong absorption bands at 5.1 and 11.9 μ for an allenic structure and was similar to that of N,N-dimethyl-2,3-butadienylamine.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36; neut. equiv., 135; g. H_2/g., 0.060. Found: C, 80.22; H, 9.95; N, 10.08; neut. equiv., 135; g. H_2/g., 0.064.

N,N-Diethyl-2,3-butadienylamine.—A mixture of diethylamine (141 g., 1.93 moles), water (260 ml.) and vinylacetylene (100 g., 1.92 moles) was charged into a liter reactor, heated at 100° for 15 hours, and then worked up in the same manner as described for the dimethylamine reaction. Distillation of the product gave 57.5 g. of forerun, mostly diethylamine, 29 g. of the diethylamino adduct, b.p. 91–92° (147 mm.), $n^{25}D$ 1.4505, and 29 g. of tar. The infrared spectrum of N,N-diethyl-2,3-butadienylamine showed bands at 5.1 and 11.9 μ, characteristic of a terminal allenic structure.

Anal. Calcd. for $C_8H_{15}N$: C, 76.73; H, 12.08; N, 11.19; g. H_2/g., 0.0322; neut. equiv. 125. Found: C, 76.66; H, 12.15; N, 10.81; g. H_2/g., 0.0371; neut. equiv., 127.

A methiodide, m.p. 109–110° after recrystallization from acetone, was prepared.

N-(2,3-Butadienyl)-morpholine.—In the same manner as described previously for the reaction with dimethylamine, a mixture of vinylacetylene (100 g., 1.92 moles), morpholine (168 g., 1.93 moles) and 260 ml. of water were charged into a liter reactor and heated at 100° for 10 hours. After preliminary purification the product was distilled to give 72 g. of adduct as a clear, colorless liquid, b.p. 70.5–71.5° (9 mm.), $n^{25}D$ 1.4917. The infrared spectrum of this substituted morpholine had bands at 5.1 and 11.8 μ for a terminal allenic structure.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06; neut. equiv., 139; g. H_2/g., 0.029. Found: C, 69.05; H, 9.51; N, 10.04; neut. equiv., 141; g. H_2/g., 0.030.

The methiodide of this amine melted at 105–107° after recrystallization from absolute alcohol.

When the reaction of vinylacetylene with morpholine was repeated in the absence of water, the yield was only 1.9% and the product was impure.

N-*n*-Butyl-2,3-butadienylamine.—Vinylacetylene (100 g., 1.92 moles), *n*-butylamine (141 g., 1.93 moles) and 258 ml. of water were charged into a liter reactor, heated at 100° for 10 hours and treated as described for the dimethylamino compound. Distillation gave 68 g. of unreacted *n*-butylamine and 5.9 g. of adduct, b.p. 89–90° (33 mm.), $n^{25}D$ 1.4582. The infrared spectrum showed bands at 5.1 and 11.9 μ for a terminal allenic structure and a band at 13.4 μ for a secondary amino nitrogen.

Anal. Calcd. for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.19; neut. equiv., 125; g. H_2/g., 0.0322. Found: C, 77.03; H, 12.02; N, 11.41; neut. equiv., 127; g. H_2/g., 0.0319.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Thermal Dimerization of Allene to 1,2-Dimethylenecyclobutane[1]

BY A. T. BLOMQUIST AND JOSEPH A. VERDOL[2]

RECEIVED AUGUST 18, 1955

Allene dimer, 1,2-dimethylenecyclobutane (I), is obtained in *ca.* 50% yield upon passing allene over glass beads heated at 500–510°. This thermal dimer contains no 2-vinyl-1,3-butadiene, but does contain traces of 2-bromopropene, a contaminant of the allene used. I is not cleaved at 500–600° to 2-vinyl-1,3-butadiene in the presence or absence of acetic acid. Two Diels–Alder adducts of allene dimer with maleic anhydride can be obtained. The first, formed at temperatures up to 78°, is the previously described bicyclooctene 1:1 adduct of I. The second, a $\Delta^{4a,8a}$-octahydronaphthalene derivative, derives from the first on heating at 150° with maleic anhydride.

The rather interesting properties of 1,2-dimethylenecyclobutane (I) indicated in a recent study[3] encouraged us to examine a more direct route for its preparation and to study further certain of its properties.

In 1913, Lebedev reported the thermal dimerization of allene to I by heating allene in a sealed glass tube at 140–150° for 3 days.[4] The thermal dimer, obtained in low yield (*ca.* 5%), was contaminated with substantial amounts of inseparable 2-bromopropene or ether depending upon the method used for preparing allene. The assignment of structure I to the dimer was based on its oxidation to succinic acid by permanganate.

For the present study allene was prepared by debromination of 2,3-dibromo-1-propene using zinc dust and ethanol.[5] It proved to be difficult for us to remove the accessory product 2-bromopropene, and even after five careful fractional distillations through a special column designed for low boiling liquids the allene still contained traces of the bromo compound. Infrared analysis of the allene, b.p. −36 to −35°, showed that it contained no methylacetylene.

Repetition of the Lebedev experiment confirmed essentially the original observations. There was obtained about a 5% yield of a product, b.p. 55–60° and $n^{25}D$ 1.4322, whose ultraviolet spectrum indicated the presence of I; absorption maxima at 238 mμ, log ε 3.39, and 246 mμ, log ε 3.47, with a shoulder at 255 mμ. Our best sample of "synthetic" I, b.p. 73–74° and $n^{20}D$ 1.4721, showed the maxima 237 mμ, log ε 3.99, and 246 mμ, log ε 4.01, with a shoulder at 254 mμ.[3] Thus, the liquid product contained about 30% of I. Infrared analysis and sodium fusion tests indicated that the impurity present was probably 2-bromopropene.

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[1] The work reported here was done as part of a research program at the Baker Laboratory of Chemistry, Cornell University, sponsored by the B. F. Goodrich Co.

[2] Abstracted from part of the dissertation presented by Joseph A. Verdol in February, 1955, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. T. Blomquist and J. A. Verdol, THIS JOURNAL, **77**, 1806 (1955).

[4] C. B. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1357 (1913); *C. A.*, **9**, 799 (1915).

[5] C. D. Hurd, R. N. Meinert and L. U. Spence, THIS JOURNAL, **52**, 1143 (1930).

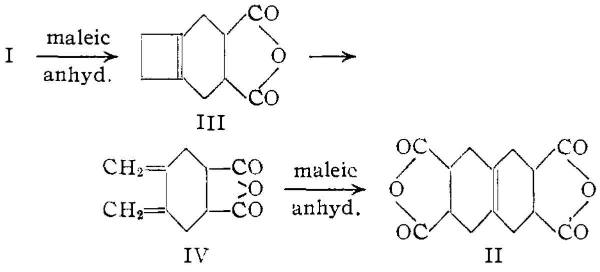
The behavior of allene when passed through a heated tube was then examined.[6] Passage of allene through a Pyrex tube packed with glass beads and heated to 500–510°, with a contact time of about 6 sec., gave *ca.* a 50% yield (2.5–4.8% conversion) of impure I which after one simple distillation gave I (40% yield) having b.p. 73–74° and n^{25}_{D} 1.4652. The infrared spectrum of this I was identical with that of authentic I[3] and its ultraviolet spectrum, with reference to the absorption at 246 mμ, indicated that it comprised at least 96% I. Fractionation through a Podbielniak column afforded I which showed n^{20}_{D} 1.4685 and n^{25}_{D} 1.4662. Sodium fusion tests, using 0.5-g. samples, gave an extremely faint positive test for bromine indicating the presence of a trace of 2-bromopropene. With a packing of carborundum chips in the heated tube the yield of crude I was lower (*ca.* 30%). Infrared examination of allene recovered from the thermal treatment indicated that no isomerization to methylacetylene had occurred.

All samples of the thermal dimer afforded the known simple 1:1 adducts of I with N-phenylmaleimide and maleic anhydride.[3] The yield of adducts varied as expected with the diene content of the dimer sample. The best sample of dimer gave with maleic anhydride an 87% yield of adduct, isolated as the free dicarboxylic acid.[3] Under similar conditions "synthetic" I gave a 91% yield.

In persulfate-initiated polymerization allene dimer behaved like "synthetic" I also. Under conditions which realized an 89% yield of polymer from "synthetic" I the dimer afforded 76% yield of a qualitatively similar tough, rubber-like, soluble polymer.

Pyrolysis of Allene Dimer.—Failure to obtain I in the pyrolysis of 1,2-bis-(acetoxymethyl)-cyclobutane and the realization instead of 2-vinyl-1,3-butadiene,[3] suggested that some cleavage of allene dimer to vinylbutadiene might have occurred as a side reaction in thermal dimerization of allene. It was observed however that compound I, diluted with nitrogen or in the presence of acetic acid, when passed through a Pyrex tube packed with glass beads and heated at 500–600° gave no 2-vinyl-1,3-butadiene as indicated by treating pyrolysates with maleic anhydride. Only the simple 1:1 adduct of I, m.p. 77–78°, was obtained; none of the higher melting, m.p. 240–241°, less soluble adduct of 2-vinyl-1,3-butadiene was isolated. Also, infrared and ultraviolet analysis of all samples of the thermal dimer of allene showed no absorption characteristic of 2-vinyl-1,3-butadiene. Thus it appears that the cyclobutane ring in I is not cleaved under the conditions of thermal dimerization of allene.

Maleic Anhydride Adducts from Allene Dimer.—Of special interest to us was a very recent report by Alder and Ackermann describing the formation of the adduct $\Delta^{4a,8a}$-octahydronaphthalene-2,3,6,7-tetracarboxylic dianhydride (II) when allene was heated in a sealed tube at 175° with maleic anhydride.[7] The formation of II was postulated as arising from (a) dimerization of allene to I, (b) reaction of I with maleic anhydride to form the unisolated intermediate bicyclo[4,2,0]-1(6)-octene-3,4-dicarboxylic anhydride (III), (c) ring opening of the unisolated intermediate to 4,5-dimethylenehexahydrophthalic anhydride (IV), and (d) reaction of IV with maleic anhydride to give the stable adduct II. II was also described as being formed upon refluxing I with maleic anhydride in benzene.



We have confirmed the first of the above observations but find that when I is heated with maleic anhydride in refluxing benzene for 16 hr. only III is produced. III formed in this way is identical with III obtained from "synthetic" I and maleic anhydride.[3]

It has been found further that heating a solution of maleic anhydride in benzene with I *or* III at 150° affords the adduct II. This confirms the postulation that III and probably IV are intermediates in the formation of II. Some III was obtained together with II in the maleic anhydride reaction with I at 150°.

The adduct II, m.p. 245°, strongly depressed the m.p. (*ca.* 20–25°) of the adduct of maleic anhydride and 2-vinyl-1,3-butadiene, m.p. 240–241°.[3] Further, the two dianhydrides give tetramethyl esters differing greatly in m.p.; that from II showed m.p. 133–134° while the one derived from the vinylbutadiene adduct has m.p. 94°.

Experimental Part[9]

Distillation Apparatus for Low Boiling Liquids.—The column for distillation at low temperatures was designed according to the recommendations of Dr. W. T. Miller, E. R. Bergman and J. Fried of this Laboratory. It comprised a vacuum jacketed Vigreux column, 55 cm. in length and 15 mm. in inside diameter, packed with glass helices. The top of the column was welded to a Dry Ice cold finger condenser which permitted total reflux. The condensing liquid was collected in a pool-type well directly beneath the cold finger. A glass tube led from the well to the external take-off arm of the condenser system. The rate of distillation of liquid was controlled by an adjustable brass needle valve ground into the well. A dripper was welded beneath the well from which collected liquid dropped directly on a thermocouple junction (copper–constantan). The thermocouple was in turn connected (externally) to a Dewar maintained at 0°, and finally to a Leeds and Northrup portable potentiometer. Calibration experiments with methylacetylene indicated the thermocouple to be accurate to at least 0.5°.

Preparation of Allene.[5] **Apparatus.**—The reaction vessel comprised a 3-necked flask fitted with water condenser, mechanical stirrer and dropping funnel. A Kjeldahl bulb, attached to the top of the condenser, was connected to a

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[6] Hurd carried out experiments in passing allene through a tube heated to 500° and higher but did not investigate the structure of the resulting products: see C. D. Hurd and R. N. Meinert, This Journal, **52**, 4540 (1930).

[7] K. Alder and O. Ackermann, *Ber.*, **87**, 1567 (1954).

[8] A. T. Blomquist and J. A. Verdol, This Journal, **77**, 81 (1955).

[9] All b.p.'s are uncorrected. All m.p.'s are corrected (block) using Anschütz thermometers.

large Dry Ice cold finger condenser having a receiving flask cooled with Dry Ice–acetone. A Dry Ice trap was also connected in series with the cold finger condenser to avoid loss of allene.

Procedure.—To a stirred, refluxing mixture of 450 g. of zinc dust and 900 ml. of absolute ethanol there was added dropwise 499 g. (2.49 moles) of 2,3-dibromo-1-propene.[10] Formation of allene began immediately and collected in the Dry Ice receiver. There was obtained 112 g. of crude allene which was distilled through the "low temperature" column to give 80.0 g. (80%) of allene showing b.p. −36 to −35°. This distillation left a residue of 23.3 g. of 2-bromopropene, b.p. 45–46°.

The allene was then redistilled four times through the special "low temperature" column. This allene showed b.p. −36 to −35° and contained no methylacetylene as indicated by its infrared spectrum. However, trace amounts of 2-bromopropene were still present.

Thermal Dimerization of Allene. (A) In Sealed Pyrex Tube.—This experiment was carried out essentially as described by Lebedev.[4] A sealed 50-ml. Pyrex bomb containing 10.9 g. (0.27 mole) of allene under nitrogen was heated in a steel high pressure hydrogenation apparatus at 145° for 36 hr. In the hydrogenation bomb an atmosphere of hydrogen of 1500–1800 lb./sq. in. pressure was introduced around the Pyrex bomb before heating was started. After cooling and venting of the hydrogenation bomb, the Pyrex bomb was cooled in a Dry Ice-bath and then unreacted allene permitted to distil into a receiver cooled in Dry Ice. There was recovered 5.5 g. (50%) of unreacted allene. The higher boiling residue was transferred to a distillation flask and separated from a small amount of a solid transparent polymeric material. [The latter was dissolved in benzene and precipitated with ethanol to give 300 mg. of a white, solid, non-elastic polymer which was not investigated.] Upon distillation under nitrogen there was obtained *ca.* 250 mg. of a liquid showing b.p. 55–60° (micro), $n^{25}_{\rm D}$ 1.4322. The ultraviolet spectrum of this material was identical with that of I showing two principal absorption maxima: λ 238 mμ, log ϵ 3.39 and λ 246 mμ, log ϵ 3.47 with a shoulder at λ 255 mμ. Quantitative ultraviolet studies indicated that the material comprised 29% of I.

(B) In Heated Pyrex Tube Packed with Glass Beads.—The apparatus comprised a Pyrex tube, 35 cm. × 25 mm., packed with 25 cm. of glass beads placed in a vertically arranged 30-cm. electrically heated furnace. Allene was introduced at the top of the tube and the exit products were collected in Dry Ice traps. With the tube heated to 500–510° allene was passed through the system at a rate of 50 g. per hr., the contact time being approximately 6 sec. The collected products were first distilled through the column designed for low boiling liquids to recover unchanged allene and leaving a residue of crude allene dimer. The infrared spectrum of recovered allene indicated that it contained no methylacetylene.

In a series of three experiments using 67.4–78.5 g. of allene there was obtained 1.7–3.8 g. (41–61%) of crude dimer. The allene recovered varied from 63.2–72.5 g. The conversion of allene to crude dimer was 2.5–4.8%. Simple distillation *in vacuo* of the combined crude dimer from these experiments (8.6 g.) gave 6.2 g. (41%) of dimer showing b.p. 73–74° (atm.), $n^{25}_{\rm D}$ 1.4652. This sample of dimer gave a very weak positive test for bromine on sodium fusion. Its infrared spectrum was identical in every respect with that of authentic I. In the ultraviolet only the characteristic absorption of I was noted. On the basis of the absorption at 246 mμ the dimer comprised at least 96% I.

Fractional distillation of the above sample through a 28″ Podbielniak column gave the following fractions: (1) 1.1 g., b.p. 73–74°, $n^{20}_{\rm D}$ 1.4671; (2) 2.6 g., b.p. 74°, $n^{20}_{\rm D}$ 1.4681; (3) 1.6 g., b.p. 74°, $n^{20}_{\rm D}$ 1.4685. Sodium fusion tests for bromine using 0.5-g. samples of hydrocarbon gave with fraction 1 a very weak positive result and with fractions 3 a barely perceptible positive test. The ultraviolet analysis of fractions 2 and 3 indicated that they contained about 96–97% I.

Upon reaction of allene dimer with maleic anhydride and N-phenylmaleimide as described earlier for I, the adducts bicyclo[4,2,0]-1(6)-octene-3,4-dicarboxylic anhydride (III), m.p. 77–78°, and bicyclo[4,2,0]-1(6)-octene-3,4-dicarboxy-N-phenylimide, m.p. 113–114°, were obtained. Mixed m.p.'s of these adducts with the corresponding ones derived from I were not depressed.

For a quantitative determination of I content in our best sample of allene dimer ($n^{20}_{\rm D}$ 1.4685) 0.92 g. (0.0115 mole) of the dimer was added to a mixture of 1.17 g. (0.0119 mole) of maleic anhydride, 0.1 g. of 2,5-di-*t*-butylhydroquinone and 15 ml. of benzene in a Pyrex bomb. After sealing and standing at room temp. overnight, the bomb was heated for 6 hr. at 50–60°. The bomb contents were evaporated to dryness *in vacuo* and the residual solid hydrolyzed by refluxing with 10 ml. of water. From the cooled aqueous mixture there was obtained 1.9 g. (87%) of bicyclo[4,2,0]-1(6)-octene-3,4-dicarboxylic acid, m.p. 205–207°, which did not depress the m.p. of an authentic sample of the adduct-acid. Under identical conditions I gave a 91% yield of adduct-acid.

Comparison of allene dimer with I in polymerization was made using the recipe and procedure given earlier.[3] From identical polymerizations carried out for 16 hr. at 50° 1 g. of allene dimer gave 0.76 g. (76% conversion) of polymer and 1 g. of I gave 0.89 g. (89% conversion) of polymer. Both polymers were rubber-like and appeared to be identical in texture and resilience.

Maleic Anhydride Reactions. (A) With Allene Dimer in Refluxing Benzene.—A mixture of 0.5 g. (0.00625 mole) of allene dimer, 1.3 g. (0.013 mole) of maleic anhydride, *ca.* 100 mg. of 2,5-di-*t*-butylhydroquinone and 10 ml. of benzene, after standing at room temperature for a few hours, was refluxed 16 hours. The residue obtained after removing benzene by evaporation was extracted with boiling hexane in which maleic anhydride is only slightly soluble. From the cooled hexane extracts and after recrystallization from hexane there was obtained 0.88 g. (80%) of III having m.p. 77–78°. A mixed m.p. determination of this adduct with the adduct of I and maleic anhydride showed no depression.

(B) With Allene Dimer in Benzene at 150°.—A mixture of 0.5 g. (0.006 mole) of allene dimer, 0.6 g. (0.006 mole) of maleic anhydride, *ca.* 100 mg. of 2,5-di-*t*-butylhydroquinone and 10 ml. of benzene was heated at 150° for 5 hr. in a sealed Pyrex tube. The large white crystals which deposited on the inner walls of the tube were separated, sublimed *in vacuo* and recrystallized from acetic anhydride. There was obtained *ca.* 300 mg. of II as small white needles and having m.p. 245°. This adduct did not depress the m.p. of an authentic sample of II but strongly depressed the m.p. of the maleic anhydride adduct of 2-vinyl-1,3-butadiene. From the mother liquor of the bomb reaction there was isolated a small quantity of III showing m.p. 78°.

(C) With Bicyclo[4,2,0]-1(6)-octene-3,4-dicarboxylic Anhydride (III).—From a mixture of 0.5 g. (0.006 mole) of III, 1.0 g. (0.01 mole) of maleic anhydride, *ca.* 100 mg. of 2,5-di-*t*-butylhydroquinone and 10 ml. of benzene heated at 150° for 12 hr. in a sealed Pyrex tube there was obtained, after purification by vacuum sublimation and recrystallization from acetic anhydride, 0.38 g. of II showing m.p. 245°. This material did not depress the m.p. of an authentic sample of II.

The tetramethyl ester of this adduct, prepared as described subsequently, showed m.p. 133–134° and did not depress the m.p. of authentic II tetramethyl ester.

(D) With Allene in Benzene at 150°.—Using the same apparatus described for the sealed tube thermal dimerization of allene, a mixture of 5 g. (0.125 mole) of allene, 5 g. (0.05 mole) of maleic anhydride and 10 ml. of benzene was heated at 150° for 40 hours. From the cooled tube, after removal of unreacted allene, there was obtained 2.1 g. of crude adduct. After two sublimations *in vacuo* at 200–230°, recrystallization from acetone and finally from acetic anhydride the adduct II showed m.p. 245° (Alder reported m.p. 240–242°).[7] The m.p. of a mixture of this adduct with the maleic anhydride adduct of 2-vinyl-1,3-butadiene (m.p. 241°) showed m.p. *ca.* 215°.

Using an esterification procedure similar to that described by Alder[7] the above adduct was converted to its tetramethyl ester. From 0.5 g. of adduct there was obtained 0.52 g. of the ester, m.p. 133–134° from methanol (Alder reported m.p. 134°).[7]

Pyrolysis of Allene Dimer.—Employing an apparatus identical with that used for the thermal dimerization of allene, a Pyrex tube packed with glass beads, allene dimer was pyrolyzed at 500–600° with nitrogen serving as a diluent. Pyrolysates were collected in Dry Ice traps and added rap-

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(10) The 2,3-dibromo-1-propene was prepared as described in "Organic Syntheses," Col. Vol. I, 2nd Ed., p. 209.

idly to solutions of maleic anhydride in benzene containing 2,5-di-*t*-butylhydroquinone as inhibitor. After standing at room temperature for at least 12 hr. the residues obtained, after evaporating the solutions to dryness, were extracted with boiling hexane to remove the simple 1:1 maleic anhydride–I adduct. The hot hexane-insoluble residues were dissolved in benzene–hexane and examined for higher melting, less soluble maleic anhydride adducts such as that of 2-vinyl-1,3-butadiene. The following results are representative of typical pyrolysis experiments. From 2.5 g. of allene dimer pyrolyzed at 500° there was obtained 1.7 g. of pyrolysate which afforded 0.9 g. of adduct with maleic anhydride, m.p. 77–78°. At 600° 2.5 g. of allene dimer gave 0.9 g. of pyrolysate from which 0.16 g. of adduct m.p. 77–78° was isolated. No adduct corresponding to that of 2-vinyl-1,3-butadiene was isolated in any of the experiments.

Pyrolysis at 500° of 1.0 g. of allene dimer dissolved in 2.0 g. of glacial acetic acid gave 2.1 g. of pyrolysate from which 300 mg. of the adduct having m.p. 77–78° was obtained. In addition, some higher melting material was isolated which showed m.p. 205–207° from benzene. This was characterized as bicyclo[4,2,0]-1(6)-octene-3,4-dicarboxylic acid by a mixed m.p. determination with an authentic specimen of the acid, m.p. 206–207°.[3]

ITHACA, N. Y.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

A Simple Entry to Polycyclopropylated Molecules. Dicyclopropyl Ketone[1]

BY HAROLD HART AND OMER E. CURTIS, JR.

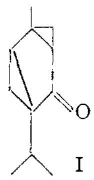
RECEIVED APRIL 22, 1955

Dicyclopropyl ketone has been synthesized from γ-butyrolactone in about 50% over-all yield. The three steps, which include base-catalyzed condensation of the lactone to dibutyrolactone (VIII), conversion with hydrochloric acid to 1,7-dichloro-4-heptanone (VI) and ring closure with base, can be conveniently performed in a few hours, without isolation of the intermediates. The structure of the ketone was demonstrated by Beckmann rearrangement of its oxime to N-cyclopropylcyclopropanecarboxamide, identical with an authentic sample prepared from cyclopropanecarbonyl chloride and cyclopropylamine. Dicyclopropylcarbinol, dicyclopropylmethane and dicyclopropylketazine, a molecule with four cyclopropane rings, are described. The absorption spectra of polycyclopropylated compounds are discussed.

This paper describes a convenient, simple synthesis of dicyclopropyl ketone. Included also are a few of its reactions, and a brief discussion of the influence of the cyclopropane ring on molecular spectra.

Our interest in polycyclopropylated compounds is threefold. Firstly, recent studies on cyclopropylcarbinyl derivatives, particularly by Roberts and his co-workers,[2] have helped to make more explicit our knowledge of carbonium ion structure, and we thought that a study of reactions in which a positive charge might be generated on a carbon with two (or three) cyclopropyl groups attached to it would be significant. Dicyclopropyl ketone might be expected to serve as a good starting point for preparing such compounds.

Secondly, the unsaturated character of the cyclopropane ring is well established. Conjugation of the cyclopropane ring with the ethylenic double bond,[3a–d] carbonyl,[3a,b,e–g] phenyl[3a,g] and pyridyl[3h] groups has been demonstrated. Indeed, the interconversion of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl compounds may be looked upon as a result of the cyclopropane ring conjugating with the unsaturation of a carbonium ion. Recently, the question of whether the cyclopropane ring can conduct a chain of conjugation was raised. Smith and Rogier[4] found 2-phenylbicyclopropyl incapable of transmitting the conjugative effect of the second cyclopropane ring, its spectrum being nearly identical with that of phenylcyclopropane. Eastman,[5] in comparing the spectrum of 1-methyl-4-isopropyltricyclo$[4,1,0^{1,6}0^{2,4}]$heptanon-5 (I) with that of β-dihydroumbellulone (II), found that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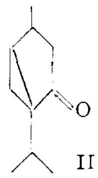
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instead of establishing a chain of conjugation, each cyclopropane ring conjugated separately with the carbonyl. It seemed of interest to examine the spectrum of dicyclopropyl ketone, a flexible model compound of I and spectra of related polycyclopropyl compounds.

Finally, dicyclopropyl ketone, if readily available, would offer an excellent synthetic entry into numerous molecules with two or more cyclopropane rings. Only a small number of simple molecules of this type have been reported. Among them are spiropentane,[6] dicyclopropyl[7] and 2-phenylbicyclopropyl.[4] Dicyclopropyl ketone itself was reported[8] to form in small amounts from the decarboxylation of cyclopropanecarboxylic acid over thoria, but there is some uncertainty whether

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[1] Taken from part of a thesis submitted by Omer E. Curtis, Jr., to Michigan State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1955.

[2] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509, 3542 (1951); C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952); S. Winstein and A. H. Schlesinger, *ibid.*, **70**, 3528 (1948).

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