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Synthetic Studies in the Field of Fluorinated Cyclopropanes

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The synthesis of 1-trifluoromethylcyclopropane, 1-methyl-1-trifluoromethylcyclopropane, 1-trifluoromethyl-1,2,2-trifluorocyclopropane and ethyl (2-methyl-2-trifluoromethyl)-cyclopropanecarboxylate has been achieved by the addition of diazo compounds to fluorinated olefins. The cyclic structure of the products has been confirmed by infrared analysis. This method appears to have general application. The mechanism of the reaction is discussed. The Freund reaction resulted in the synthesis of 1-trifluoromethylcyclopropane and 1,1-difluorocyclopropane, although in very poor yield.

The work described in this paper originated from the need of obtaining several fluorinated cyclopropanes. Previous reports on open-chain fluoroalkanes^{2,3} led us to believe that the presence of fluorine atoms might reduce the flammability of cyclopropane without affecting its anesthetic activity. Although the idea is not new,⁴ no fluorinated cyclopropane had been synthesized and the structure definitely established, to our knowledge, as of early 1952, when the work reported in this paper was completed.

Some fluorinated cyclopropanes were mentioned by Park and co-workers,⁵ but no evidence for their cyclic structure was presented. Benning⁶ reported the synthesis of hexafluorocyclopropane, but subsequently this compound was shown to be perfluoropropylene.⁷⁻⁹ In the last few years, however, hexafluorocyclopropane has been prepared by Atkinson¹⁰ and by Haszeldine¹¹ and other fluorinated cyclopropanes have recently been reported.¹²

Among the several methods described in the literature for the synthesis of substituted cyclopropanes,¹³ we investigated mainly: (1) the addition of a diazo compound to olefins, a method which usually gives an intermediate pyrazoline, but occasionally the corresponding cyclopropane in one step,¹⁴ (2) the Freund reaction, where an active metal such as zinc, sodium or magnesium acts on a 1,3-dihalo compound and (3) the Perkin reaction, where a compound containing an active methylene group reacts with a 1,2-dihalo compound.

The first method was the only satisfactory one and appears to be of general application except in the case of olefins containing other halogen atoms in addition to fluorine atoms. Reaction of 1,1,1-

trifluoropropene (I), 2-methyl-3,3,3-trifluoropropene (IV) and 1,1,1,4,4,4-hexafluoro-2-butene¹⁵ (IX) with diazomethane gave, respectively, the corresponding 5-trifluoromethyl-2-pyrazoline (II), 5-methyl-5-trifluoromethyl-2-pyrazoline (V) and 4,5-bis-trifluoromethyl-3-pyrazoline (X) in good yield. The pyrazolines II and V were pyrolyzed with loss of nitrogen to the corresponding 1-trifluoromethylcyclopropane (III) and 1-methyl-1-trifluoromethylcyclopropane (VI).

The reaction of compounds I and IV with diazomethane had to be activated by ultraviolet light; no reaction occurred after several hours without irradiation. Although several reactions of diazomethane have been described in the literature^{16,17} in which ultraviolet light was used as an activator, it was surprising to find that it catalyzed the pyrazoline synthesis, since this reaction is known to occur by an ionic mechanism.¹⁴ The explanation probably lies in the fact that fluorinated olefins are more reactive under free radical than under polar conditions. It has already been suggested¹⁴ that, in a free radical mechanism of addition, the reactive intermediates are the uncoupled forms of both diazomethane and the olefin.

The accumulation of fluorine atoms in hexafluoro-2-butene (IX) appears to promote the reaction, since this substance, which is known to be sluggish to both nucleophilic and electrophilic reagents,¹⁸ reacted very rapidly with diazomethane and did not even require ultraviolet light.

It is believed that the structure of the pyrazolines II, V and X is as indicated, since it is well known¹⁹ that the product obtained by the addition of an unsymmetrical reagent to a fluorinated olefin under both free radical and polar conditions always contains the negative portion as far away as possible from the fluorine atoms.

Obviously the pyrazolines may exist in several tautomeric forms. Compounds II and V are probably Δ^2 -pyrazolines, since infrared analysis indicated a carbon-to-nitrogen double bond. Compound X would seem to be a Δ^3 -pyrazoline, since the imino band was very intense, and the spectrum indicated a carbon-to-carbon double bond.

The olefin IV reacted with diazoacetic ester at

(1) Ortho Pharmaceutical Corporation, Raritan, N. J., to whom inquiries regarding this paper should be addressed.

(2) B. H. Robbins, *J. Pharmacol. Exp. Therap.*, **86**, 197 (1946).

(3) E. T. McBee, H. B. Hass, R. M. Thomas, W. J. Toland, Jr., and A. Truchano, *THIS JOURNAL*, **69**, 944 (1947).

(4) A. L. Henne, M. W. Renoll and H. M. Leicester, *ibid.*, **61**, 938 (1939).

(5) J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius and R. C. McHarness, *Ind. Eng. Chem.*, **39**, 354 (1947).

(6) A. F. Benning, F. B. Downing and J. D. Park, U. S. Patent 2,394,581 (1946).

(7) E. G. Young and W. S. Murray, *THIS JOURNAL*, **70**, 2814 (1948).

(8) W. F. Edgell, *ibid.*, **70**, 2816 (1948).

(9) F. A. M. Buck and R. L. Livingston, *ibid.*, **70**, 2817 (1948).

(10) B. Atkinson, *J. Chem. Soc.*, 2684 (1952).

(11) R. N. Haszeldine, *ibid.*, 3761 (1953).

(12) P. Tarrant, A. M. Lovelace and M. R. Lilyquist, *THIS JOURNAL*, **77**, 2783 (1955).

(13) H. Gilman, "Organic Chemistry, an Advanced Treatise," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, Ch. 2.

(14) "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, New York, N. Y., 1948, pp. 551-558.

(15) A. L. Henne and W. G. Finnegan, *THIS JOURNAL*, **71**, 298 (1949).

(16) H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942).

(17) W. H. Urry and J. R. Eiszner, *THIS JOURNAL*, **73**, 2977 (1951).

(18) A. L. Henne, J. V. Schmitz and W. G. Finnegan, *ibid.*, **72**, 4195 (1950).

(19) A. L. Henne and M. Nager, Abstracts of Papers of the 119th Meeting of the American Chemical Society, April, 1951, p. 79M.

110–130° to give a very low yield of ethyl (2-methyl-2-trifluoromethyl)-cyclopropanecarboxylate (XI).

Reactions of diazomethane with compound VII, 1,1,1,2,3,3-hexafluoropropene, yielded no pyrazoline, but compound VIII, 1-trifluoromethyl-1,2,2-trifluorocyclopropane, was immediately formed. The reaction of 1,1-difluoroethylene with diazomethane, in the presence of ultraviolet light, appeared to take a parallel course, but substantiating evidence for the formation of 1,1-difluorocyclopropane (XII) is lacking at this time, since this work was prematurely discontinued. These reactions of diazomethane with olefins containing fluorine atoms directly attached to the carbon atoms of the double bond probably occur through the CH_2 : \ddagger diradical, resulting from the dissociation of diazomethane, although the possibility exists that the corresponding pyrazoline was formed and decomposed prior to its isolation.

The main feature in the infrared spectra²⁰ of compounds III, VI, VIII and XI was a major band between 9.9 and 11 μ , which was considered characteristic of a fluorinated cyclopropane structure, the actual position depending on the substituents. This conclusion is in substantial agreement with the recent reports of other investigators.^{11,12,21}

The Freund reaction was applied to the synthesis of compounds III and XII, from the dibromides $\text{CF}_2\text{CHBrCH}_2\text{CH}_2\text{Br}$ (XIII) and $\text{CF}_2\text{BrCH}_2\text{CH}_2\text{Br}$ (XIV). The preparation of compound XIII from ethyl γ,γ,γ -trifluoroacetoacetate is described in detail in the Experimental part. It involved the replacement of a hydroxyl group adjacent to a trifluoromethyl group by a bromine atom. Except for the reports by Swarts,^{22,23} this reaction has only led to failures^{24,25} until the present work and some very recent reports.^{26,27}

Compounds III and XII were obtained in such a poor yield that their purification was impossible, and infrared analysis of the crude products was the only feasible method of identification. The spectra of both products exhibited the typical features of fluorinated cyclopropanes. The presence of 1-trifluoromethylcyclopropane in the crude reaction mixture was further confirmed by comparison of its spectrum with the spectrum of the same substance satisfactorily prepared by the diazomethane method.

An attempt to prepare 1-ethyl-2-trifluoromethylcyclopropane by the Freund reaction was unsuccessful. The β -diketone $\text{CF}_3\text{COCH}_2\text{COCH}_2\text{CH}_3$ (XV) was reduced to the glycol XVI which was converted into a monobromide, but attempted replacement of the second hydroxyl group with bromine led to a mixture of bromoolefins.

(20) We are indebted to Dr. Mabel Wilson for the interpretation of the infrared spectra.

(21) V. A. Slabey, *THIS JOURNAL*, **76**, 3004 (1954).

(22) F. Swarts, *Compt. rend.*, **197**, 1261 (1933).

(23) F. Swarts, *Bull. soc. chim. Belg.*, **38**, 99 (1929).

(24) K. N. Campbell, J. O. Knobloch and B. K. Campbell, *THIS JOURNAL*, **72**, 4380 (1950).

(25) H. Gilman and R. G. Jones, *ibid.*, **65**, 2037 (1943).

(26) E. T. McBee and O. R. Pierce, Abstracts of the 124th Meeting of the American Chemical Society, Chicago, Ill., September 1953, p. 24-O.

(27) G. V. Tiers, H. A. Brown and T. S. Reid, *ibid.*, p. M 30.

Attempts to apply the Perkin reaction by condensation of acetoacetic or malonic ester with the dibromides 1,1,1-trifluoro-2-methyl-2,3-dibromopropane (XVII), 1,1,1,2,3,3-hexafluoro-2,3-dibromopropane (XVIII) and 1,1,1,3,3-pentafluoro-2-chloro-2,3-dibromopropane (XIX) failed in every case.

The three fluorocyclopropanes III, VI and VIII as well as many of the intermediates used in this work were tested for anesthetic activity by Dr. J. C. Krantz, Jr., and co-workers at the Department of Pharmacology, University of Maryland. Some of the results have already been reported.²⁸

Experimental²⁹

1,1,1-Trifluoropropene (I) was prepared in good yield by the procedure of Campbell, *et al.*,²⁴ *i.e.*, by the pyrolysis of 1,1,1-trifluoro-2-acetoxypropane²⁵ over glass wool at 530–550°.

1-Trifluoromethylcyclopropane (III). (1) **Diazomethane Method.**—Reaction of 50 g. (0.51 mole) of I with about the equivalent amount of diazomethane³⁰ in ether, in a flask provided with a Dry Ice-acetone cooled condenser, was catalyzed by irradiation with a quartz mercury arc ultraviolet lamp. After the color of diazomethane had disappeared (2 hr.), distillation yielded 58 g. (89%) of 5-trifluoromethyl-2-pyrazoline (II), b.p. 146.5°, n_D^{20} 1.3870.

Anal. Calcd. for $\text{C}_4\text{H}_5\text{N}_2\text{F}_3$: C, 34.78; H, 3.65; N, 20.28; F, 41.28. Found: C, 34.98; H, 3.82; N, 20.78; F, 41.09.

Forty-two grams (0.3 mole) of II was heated in a flask provided with a column, 1 in. in diameter and 3 in. high, packed with 2 g. of powdered potassium hydroxide and 4 g. of 10% platinized asbestos and electrically heated at 260°. The material which collected in the Dry Ice-acetone cooled receiver, connected to the top of the column, was distilled to give 17 g. (51%) of III, b.p. 21.6°.

Anal. Calcd. for $\text{C}_4\text{H}_5\text{F}_3$: C, 42.85; H, 4.50. Found: C, 43.64; H, 4.54.

(2) **The Freund Reaction.**—The improved procedure³¹ described for the synthesis of cyclopropane was applied to 20 g. of XIII. After 9 hr. at 145–155°, about 2 ml. of low-boiling material had collected in the Dry Ice-acetone cooled receiver. The crude product was subjected to infrared analysis.

2-Methyl-3,3,3-trifluoropropene (IV).—One hundred and nineteen grams of crude 1,1,1-trifluoro-2-methyl-2-propanol³² was heated under stirring with 70 ml. of concentrated sulfuric acid up to 110° (2 hr.). After the evolution of ethylene had subsided, an additional 70 ml. of sulfuric acid was added and the dehydration was complete after 0.5 hr. at 110–135°. The product, collected in a Dry Ice-acetone cooled receiver connected to the top of the condenser, was bubbled through 5% sodium hydroxide and dried; yield 46.5 g. Dehydration was faster when the pure carbinol³³ was used, and the yield of IV was 80%. This method for the preparation of IV was superior to previously described methods.^{32,33}

1-Methyl-1-trifluoromethylcyclopropane (VI). 5-Methyl-5-trifluoromethyl-2-pyrazoline (V) was prepared by reaction of IV with about the equivalent amount of diazomethane, according to the procedure described for compound II and irradiated 13 hr. The yield ranged between 60 and 88%, b.p. 141.2–141.5°, n_D^{20} 1.3791.

Anal. Calcd. for $\text{C}_5\text{H}_7\text{N}_2\text{F}_3$: C, 39.50; H, 4.64; N, 18.41. Found: C, 39.34; H, 5.03; N, 18.66.

Fifteen grams (0.1 mole) of V was slowly added to a mixture of 3.6 g. of potassium hydroxide and 2 g. of 10% plati-

(28) Go Lu, S. L. Ling and J. C. Krantz, Jr., *Anesthesiology*, **14**, 466 (1953).

(29) All boiling points are uncorrected.

(30) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

(31) H. B. Hass, E. T. McBee, G. E. Hinds and E. W. Gluesenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

(32) The azeotrope ($\text{C}_2\text{H}_5\text{OH}-\text{C}_4\text{F}_7\text{H}_6\text{OH}$) was used. A. L. Heine, J. W. Shepard and E. J. Young, *THIS JOURNAL*, **72**, 3577 (1950).

(33) F. Swarts, *Bull. soc. chim. Belg.*, **36**, 191 (1927).

nized asbestos at 150–220° and the product collected in a Dry Ice-acetone cooled receiver connected to the top of the condenser; b.p. 37–38°, n_D^{20} 1.3228, yield 64%. By the method used for compound II the yield was 92%. Failure to add bromine was evidence for the lack of unsaturation and in favor of the cyclic structure.

Anal. Calcd. for $C_5H_7F_3$: C, 48.41; H, 5.69. Found: C, 48.50, 48.80; H, 6.11, 5.69.

1-Trifluoromethyl-1,2,2-trifluorocyclopropane (VIII).—Ultraviolet light was not required to promote the reaction of diazomethane with 1,1,2,3,3-hexafluoropropene³⁴ (VII), although it cut down the reaction time from 20 to 5 hours. The product, collected in a Dry Ice-cooled receiver, fractionated by a low temperature Podbielniak column, gave compound VIII, b.p. –15.8°, in about 30% yield. Failure to decolorize bromine and to absorb ozone were indicative of a cyclic structure.

Anal. Calcd. for $C_4H_2F_6$: C, 29.27; H, 1.23. Found: C, 29.96; H, 1.07.

In one run, a substance of b.p. –65° was isolated in very small amount, and its structure was not ascertained.

4,5-Bis-trifluoromethyl-3-pyrazoline (X) was obtained in good yield from the reaction of IX with diazomethane, b.p. 131°, n_D^{20} 1.3562.

Anal. Calcd. for $C_5H_4N_2F_6$: C, 29.12; H, 1.94; N, 13.59. Found: C, 29.36, 28.93; H, 2.22, 2.05; N, 13.82.

Pyrolysis of the pyrazoline, by the method used for compound VI at 155–200°, was very sluggish in spite of the fact that triple quantities of potassium hydroxide and platinized asbestos were used. In one run, a small amount of a substance of b.p. 37–38° was obtained, presumably 1,2-bis-trifluoromethylcyclopropane in amount insufficient for further purification.

Ethyl (2-Methyl-2-trifluoromethyl)-cyclopropanecarboxylate (XI).—Thirty-four and two-tenths grams (0.3 mole) of diazoacetic ester³⁵ and 30 g. (0.3 mole) of IV were heated 7 hr. at 100–130° in a rocking bomb. The product consisted of a very small yield of compound XI, b.p. 58° (5 mm.), and a fraction of b.p. 105° (8 mm.) containing 8.2% of nitrogen, which was not identified. (The corresponding pyrazoline should contain 12.50% of nitrogen.)

Anal. Calcd. for $C_8H_{11}F_3O_2$: C, 48.98; H, 5.61; F, 29.08. Found: C, 48.43; H, 6.88; F, 28.73.

Ethyl γ,γ,γ -Trifluoroacetate.—Several runs were carried out substantially according to the literature³⁶ except that sodium hydride (twofold the calculated amount) was used as a condensing agent and ether as a solvent. The yield ranged between 54 and 78%.

1,1,1-Trifluoro-2,4-butanediol.—Fifty grams (0.27 mole) of ethyl β -hydroxy- γ,γ,γ -trifluorobutyrate³⁷ was slowly added to a suspension of 10.2 g. of lithium aluminum hydride in 500 ml. of ether. After hydrolysis with 30% sulfuric acid, the dried ethereal solution yielded 27 g. (70%) of the substance, b.p. 195°, 86° (5 mm.), n_D^{20} 1.3760, d_4^{20} 1.394. An attempt to prepare compound XIII in one step by reaction of this substance with phosphorus tribromide failed.

Anal. Calcd. for $C_4H_7O_2F_3$: C, 33.34; H, 4.89; F, 39.56; *MR*, 22.84. Found: C, 34.23; H, 5.26; F, 39.46; *MR*, 23.72.

Ethyl β -Bromo- γ,γ,γ -trifluorobutyrate.—A mixture of 186 g. (1 mole) of ethyl β -hydroxy- γ,γ,γ -trifluorobutyrate and 271 g. (1 mole) of phosphorus tribromide was heated slowly to 90°. The reaction became exothermic, the temperature rising to 130°. After 5 hr. at the same temperature (vigorous evolution of hydrogen bromide throughout), the mixture was poured into ice-water, extracted with carbon tetrachloride, washed, dried and vacuum distilled. One hundred and twenty-two grams (49%) of the bromo ester was obtained, b.p. 81–83° (45 mm.), d_4^{20} 1.5275, n_D^{20} 1.3934.

Anal. Calcd. for $C_6H_9O_2F_3Br$: C, 28.93; H, 3.24; Br,

(34) J. D. La Zerte, L. J. Hals, T. S. Reid and J. H. Smith, *THIS JOURNAL*, **75**, 4525 (1953). We are greatly indebted to Dr. Mathew W. Miller of Minnesota Mining and Manufacturing Co. for informing us of this work prior to its publication.

(35) W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1936, p. 282.

(36) F. Swarts, *Bull. classe sci. Acad. roy. Belg.*, [5], **12**, 692 (1926).

(37) R. G. Jones, *THIS JOURNAL*, **70**, 143 (1948).

32.10; *MR*, 39.26. Found: C, 28.55; H, 3.11; Br, 31.45; *MR*, 39.08.

A forerun (20 g., 19%) of b.p. 42–44° (45 mm.), n_D^{20} 1.3608, was identified as ethyl γ,γ,γ -trifluorocrotonate.

Anal. Calcd. for $C_6H_7O_2F_3$: C, 42.84; H, 4.20; F, 33.92. Found: C, 42.91; H, 4.30; F, 34.08.

Both substances have been recently prepared by different methods.³⁸

1,1,1-Trifluoro-2-bromo-4-butanol was prepared by the slow addition of 102 g. (0.4 mole) of ethyl β -bromo γ,γ,γ -trifluorobutyrate to a suspension of 8 g. of lithium aluminum hydride in 800 ml. of ether; b.p. 78–80° (40 mm.), yield 53 g. (64%), n_D^{20} 1.4025. The substance readily loses hydrogen bromide on standing, and no satisfactory analysis could be obtained. A forerun (10 g., 17%) of b.p. 59° (42 mm.) was probably 4,4,4-trifluoro-1-butanol.³⁹

Anal. Calcd. for $C_4H_7OF_3$: C, 37.51; H, 5.51; F, 44.50. Found: C, 38.22; H, 5.37; F, 44.70.

1,1,1-Trifluoro-2,4-dibromobutane (XIII).—Fifty-four grams (0.2 mole) of phosphorus tribromide was added dropwise to 62 g. (0.3 mole) of 1,1,1-trifluoro-2-bromo-4-butanol under stirring and cooling, keeping the temperature below 50°. After stirring 1 additional hour, the mixture was poured into ice-water, extracted with carbon tetrachloride and dried. Distillation gave, in addition to 8 g. of the starting material, 20 g. (25%) of XIII, b.p. 60° (35 mm.), n_D^{20} 1.4349.

Anal. Calcd. for $C_4H_6F_3Br_2$: C, 17.80; H, 1.87; Br, 59.22. Found: C, 18.23; H, 2.08; Br, 58.95.

1,1,1-Trifluoro-2,4-hexanediol (XVI).—Sixty-seven grams (0.4 mole) of XV⁴⁰ in 100 ml. of ether was shaken at 3 atmospheres of hydrogen with 7 g. of 10% palladized charcoal; only one molar equivalent of hydrogen was absorbed. The dried ethereal solution was added to a stirred suspension of 22 g. of lithium aluminum hydride in 1200 ml. of ether. The product of b.p. 75–78° (3 mm.) gave a negative test for a carbonyl group; yield 50 g. (72%).

Anal. Calcd. for $C_6H_{11}O_2F_3$: C, 41.86; H, 6.39. Found: C, 41.60, 41.80; H, 6.63, 6.45.

Several other methods were tried, such as lithium aluminum hydride, moist sodium, platinum oxide, copper chromite at 100° and 100 atmospheres, but they resulted in mixtures boiling over a wide range. The test for carbonyl group was positive, and the hydroxyl content was very low, indicating that some reduction of one of the two carbonyl groups to the hydrocarbon stage had occurred. Similar difficulties have been reported by other workers in the reduction of β -diketones.⁴¹

Replacement of one OH with Br resulted when 52 g. of XVI (0.3 mole) was heated in a closed vessel 3.5 hr. at 60–70° with 170 ml. of a solution, prepared by saturating water at 0° with hydrogen bromide, b.p. 63–65° (7 mm.), yield 31 g. (30%). The test for unsaturation was negative.

Anal. Calcd. for $C_6H_{10}OBrF_3$: OH, 7.23. Found: OH, 7.45, 7.30.

It was not determined whether the hydroxyl group in position 2 or 4 had undergone replacement.

1,1-Difluorocyclopropane (XII).—Forty-seven and six-tenths grams (0.2 mole) of 1,3-dibromo-2,2-difluoropropane (XIV)⁸ was added (1 hr.) to a mixture of 64 g. of acetamide, 0.8 g. of sodium iodide, 9.5 g. of anhydrous sodium carbonate and 18 g. of zinc dust, previously heated to 125° in a flask provided with thermometer, stirrer, dropping funnel and condenser, the top of which was connected to a Dry Ice-acetone cooled receiver. After 18 hours, the condensate, distilled through a low-temperature Podbielniak, yielded two fractions of b.p. –33 and –23.5°, respectively. The –23.5° fraction exhibited the typical bands of fluorinated cyclopropanes and it is believed to be XII. The contaminant, the –33° fraction, was probably allene, deriving from the elimination of zinc fluoride or zinc bromofluoride.

1,1,1,3,3-Pentafluoro-2-chloro-2,3-dibromopropane (XIX).—The following method was used also for compounds XVII and XVIII.

(38) H. M. Walborsky and M. Schwarz, *ibid.*, **75**, 3241 (1953).

(39) E. T. McBee, A. E. Kelley and E. Rapkin, *ibid.*, **72**, 5071 (1950).

(40) J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).

(41) A. S. Dreiding and J. A. Hurtman, *ibid.*, **75**, 939 (1953).

Twenty-four grams (0.15 mole) of bromine was added over a period of 2 hr. to 25 g. (0.149 mole) of 1,1,1,3,3-pentafluoro-2-chloropropene⁴² in a flask provided with mechanical stirrer, dropping funnel and a Dry Ice-acetone cooled con-

denser. The reaction proceeded rapidly and exothermically as soon as ultraviolet light was applied. After washing with aqueous sodium bisulfite and drying, 27 g. (82%) of XIX was obtained, b.p. 104°, or 46° (71 mm.).

Anal. Calcd. for C₃F₅Br₂Cl: Cl, 10.86. Found: Cl, 10.81. RARITAN, N. J.

(42) A. L. Henne, A. M. Whaley and J. K. Stevenson, *THIS JOURNAL*, **63**, 3478 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cyclic Dienes. XVII. 3-Methylenecyclohexene^{1,2}

BY WILLIAM J. BAILEY AND JOHN C. GOOSSENS³

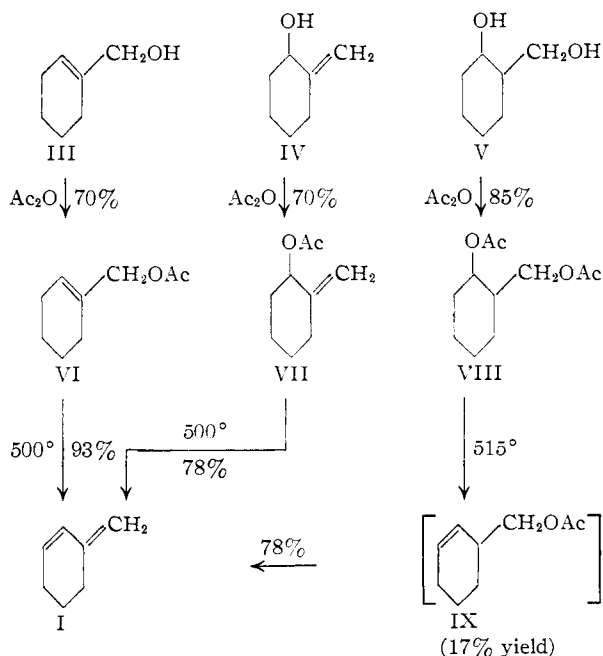
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3-Methylenecyclohexene was prepared in three steps from 2-hydroxymethylcyclohexanone in an over-all yield of 42%. In the final step the pyrolysis of each of three esters, 1-cyclohexenylmethyl acetate, 2-methylenecyclohexyl acetate and 2-acetoxymethylcyclohexyl acetate, produced the diene in 78 to 95% yields. The structure of the 3-methylenecyclohexene was proved by analysis, infrared and ultraviolet absorption spectra and ozonolysis to known derivatives.

In a research program designed to correlate the structure and properties of hydrocarbon polymers, an all-*cis* diene polymer related to natural rubber was prepared.⁴ In contrast to natural rubber, poly-1,2-dimethylenecyclohexane was a high melting crystalline solid. Since the structure of balata (or gutta percha) differs from that of natural rubber only in the configuration around the double bonds,⁵ the high melting point of balata has been attributed to its all-*trans* configuration. It was of interest, therefore, to prepare a synthetic all-*trans* diene polymer related in structure to balata. The all-*cis* polymer was prepared by the synthesis and polymerization of a diene in which the 2- and 3-positions were connected through a six-membered ring.⁶ In this polymer the six-membered ring containing the double bond must have the *cis* configuration and at every monomer unit the polymer chain must, as a consequence, enter and leave from the same side of the double bond. It was reasoned, therefore, that a diene with a six-membered ring connecting the 1- and 3-positions should produce an all-*trans* polymer. Thus the ring would restrict one end of the polymer chain and the substituent in the 3-position to the *cis* configuration, so that at every monomer unit the polymer chain must enter and leave from opposite sides of the double bond. The simplest diene that has a six-membered ring connecting the 1- and 3-positions is 3-methylenecyclohexene (I).

3-Methylenecyclohexene (I) was synthesized from 2-hydroxymethylcyclohexanone (II) in three steps in an over-all yield of 42%. By a modification of the procedure of Dreiding and Hartman,⁷ 2-hydroxymethylcyclohexanone (II) was reduced by the reflux of an ether solution with lithium aluminum hydride for 24 hr. to produce a mixture of an 11% yield of 1-cyclohexenylmethanol (III), a 34% yield of 2-methylenecyclohexanol (IV)

and a 21% yield of 2-hydroxymethylcyclohexanol (V). The unsaturated alcohols III and IV were acetylated with acetic anhydride to produce 70% yields of 1-cyclohexenylmethyl acetate (VI) and 2-methylenecyclohexyl acetate (VII), respectively. The saturated diol V was converted with acetic anhydride to 2-acetoxymethylcyclohexyl acetate (VIII) in an 85% yield. The acetate VI⁸ previously had been prepared in a low yield by the reaction of cyclohexene and formaldehyde in the presence of acetic anhydride, while VII⁹ was prepared in an unreported yield by the oxidation of methylenecyclohexane with selenium dioxide in acetic acid. VIII¹⁰ had been prepared from V in an unreported yield. The three acetates VI, VII and VIII previously were characterized only by their boiling points.



3-Methylenecyclohexene (I) was prepared by

(1) Previous paper in this series, *THIS JOURNAL*, **78**, 670 (1956).
 (2) Presented before the Division of Polymer Chemistry at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955.

(3) Office of Naval Research Fellow, 1951-1954.
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