at 100°. Distillation of the contents of the bomb yielded 29 g. of unreacted 2-H-perfluoropropene.

1,1-Difluoro-2,3-dimethylcyclopropane.—A three-liter flask was charged with 325 g. (5 moles) of zinc dust, 5 g. of zinc chloride and 250 ml. of 1-propanol. To the refluxing mixture was added 710 g. (2.3 moles) of 1,3-dibromo-1,1-difluoro-2-methylbutane.[2] The material distilling from the reaction flask at 54–60° was dried and fractionated to give 66 g. (39%) of the cyclopropane with the properties described in Table II.

1,1-Difluoro-2,2-dimethylcyclopropane.—In the manner described above 133 g. (0.5 mole) of 1,3-dibromo-1,1-difluoro-3-methylbutane[2] was treated with a mixture of 65 g. (1 mole) of zinc dust, 1 g. of zinc chloride and 250 ml. of 1-propanol. Fractionation of the crude product gave 27% of the 1,1-difluoro-2,2-dimethylcyclopropane.

3-Bromo-3,3-difluoropropene.—1,3-Dibromo-1,1-difluoropropane[2] (51 g., 0.21 mole) was treated with a solution of 56 g. of potassium hydroxide in 100 ml. of water contained in a 500-ml. flask. The product distilling from the reaction mixture at 42–52° was washed, dried and fractionated giving 21 g. (63.6%) of the desired 3-bromo-3,3-difluoropropene.

3-Bromo-1,1,1-trifluoropropane.—A 500-ml. stainless steel rocking autoclave was charged with 1,3-dibromo-1,1-difluoropropane[2] (1 mole), hydrogen fluoride (3.5 moles) and antimony pentachloride (6 ml.). It was heated and rocked 18 hours at 150°. The contents were then poured onto chipped ice, neutralized with dilute sodium hydroxide solution and steam distilled. The organic layer was separated, dried and fractionated using a 45-cm. column packed with glass helices to give 100 g. (56.5%) of the desired 1,1,1-trifluoro-3-bromopropane,[17] b.p. 62–64°, $n^{22}D$ 1.3606, and 40 g. of the unreacted dibromodifluoropropane.

1,1,1-Trifluoropropene-2.—3-Bromo-1,1,1-trifluoropropane (100 g., 0.57 mole) was refluxed with a saturated solution of 75 g. of potassium hydroxide in ethanol. The product was collected in a trap immersed in Dry Ice as it formed. Fractionation using a 40-cm. vacuum jacket column gave 41 g. (74.5%) of $CF_3CH{=}CH_2$,[18] b.p. −18 to −16°.

1,1,1-Trifluoropropane.—3-Bromo-1,1,1-trifluoropropane (90 g., 0.5 mole) was refluxed with 130 g. of zinc dust in 700 ml. of 1.5 *N* HCl solution for six hours. The product was collected in a trap immersed in Dry Ice and fractionated to give 20 g. (41%) of $CF_3CH_2CH_3$,[19] b.p. −12°.

3-Bromo-1,1,1-trifluorobutane.—1,3-Dibromo-1,1-difluorobutane[2] (236 g.), hydrogen fluoride (100 g.) and antimony pentachloride (5.6 ml.) were charged into the autoclave. The clave was sealed, heated and rocked 18 hours at 135°. The contents were poured onto cracked ice, neutralized and steam distilled. The organic layer (130 g.) was separated, dried and fractionated to give 90 g. (50%) of 3-bromo-1,1,1-trifluorobutane.

1,1,1-Trifluorobutene-2.—In the manner described, 3-bromo-1,1,1-trifluorobutane (37 g., 0.194 mole) was refluxed with a saturated solution of alcoholic potassium hydroxide. The product was collected in a trap immersed in Dry Ice as it was formed. Fractionation using a 40-cm. vacuum jacket column gave 17 g. (80%) of the desired 1,1,1-trifluorobutene-2,[20] b.p. 17.7°.

Acknowledgment.—We wish to acknowledge the assistance of Mr. B. E. Gray and Mr. F. F. Norris who carried out some of the fluorination reactions.

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GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE UNIVERSITY AND THE UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. IV. Thermal Cleavage of the Cyclobutane Ring[1]

BY WILLIAM J. BAILEY,[2] CARL H. CUNOV[3] AND LOUIS NICHOLAS[4]

RECEIVED AUGUST 23, 1954

When 1,2-di-(acetoxymethyl)-cyclobutane was pyrolyzed, cleavage of the cyclobutane ring took place in two different ways to produce allyl acetate and 2-vinylbutadiene (I). Pyrolysis of the corresponding methyl carbonate ester also produced the triene I. No 1,2-dimethylenecyclobutane was isolated. The structure of the triene I was proved by comparison of its physical properties with those of an authentic sample and conversion with maleic anhydride to the known Diels–Alder adduct.

Since the pyrolysis of diesters was used very successfully for the syntheses of cyclic dienes such as 1,2-dimethylenecyclohexane,[5a] 1,2-dimethylenecyclopentane[5b] and 1,2-dimethylene-4-cyclohexene,[5c] it was of interest to extend these pyrolyses to the cyclobutane series. This pyrolysis would help determine the relative thermal stabilities of the cyclobutane ring and the ester group. If the cyclobutane ring were stable to pyrolysis, the very interesting 1,2-dimethylenecyclobutane could be prepared very conveniently.

Cyclobutane-1,2-dicarboxylic anhydride (II)[6] was reduced with lithium aluminum hydride to 1,2-dimethylolcyclobutane (III) in an 88% yield. Heating III with acetic anhydride plus acetic acid produced an 89% yield of 1,2-di-(acetoxymethyl)-cyclobutane (IV). In order to prove that no rearrangement occurred during the esterification of the glycol, the ester IV was hydrolyzed back to the glycol III. The properties of the two samples of III were identical, and a mixed melting point of the corresponding di-α-naphthylurethans showed no depression.

When the diacetate IV was pyrolyzed over glass helices at 450° under such conditions that only 30% of two molar equivalents of acetic acid was liberated, a complex mixture of products was obtained. From this mixture was isolated 3.3% of allyl acetate (V), 2% of 2-vinylbutadiene (I), 19% of 1-methylene-2-acetoxymethylcyclobutane (VI), 2% of an isomeric diene VII plus a 63% recovery of the starting material IV. Even under these comparatively mild conditions no 1,2-dimethylenecyclobutane was isolated. If more vigorous conditions were employed so that a higher percentage of acetic acid

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[1] (a) Previous paper in this series, THIS JOURNAL, **77**, 1133 (1955). (b) Presented in part before the Michigan College Chemistry Teachers Association, Detroit, Mich., May, 1951, and the Philadelphia Organic Chemists Club, Philadelphia, Pa., February, 1954.

[2] Department of Chemistry, University of Maryland, College Park, Md.

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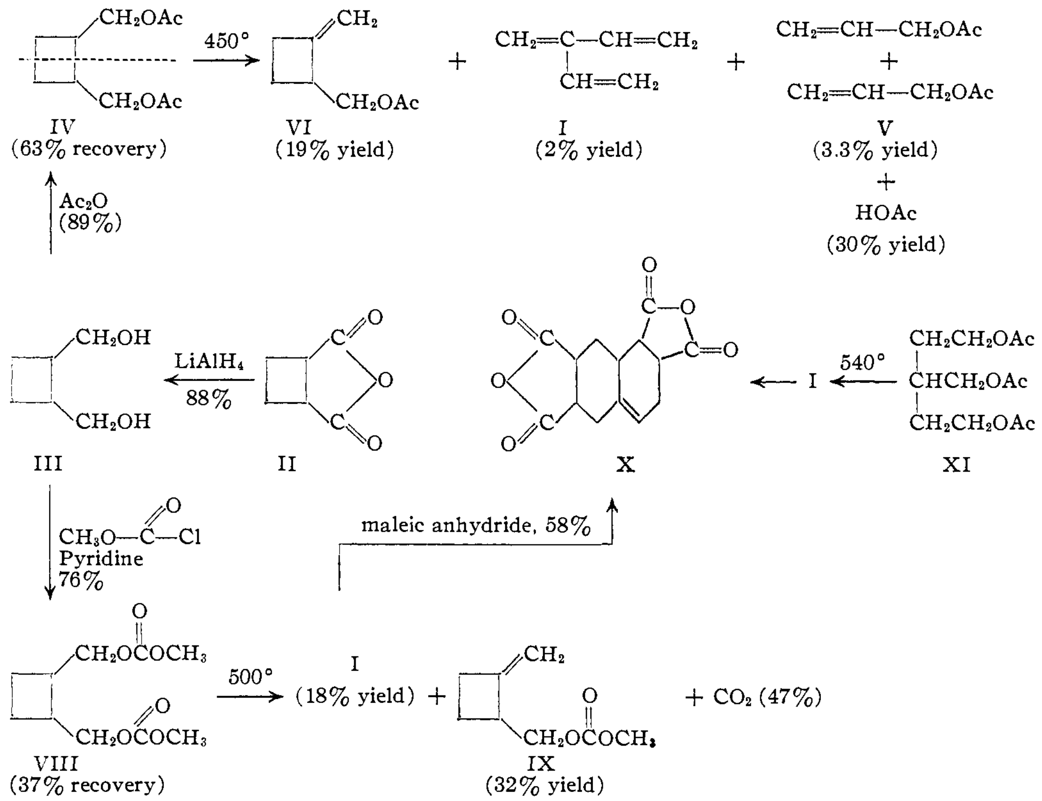
[4] Office of Naval Research Fellow, University of Maryland, 1951–1954.

[5] (a) W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953); (b) W. J. Bailey and W. R. Sorenson, *ibid.*, **76**, 5421 (1954); (c) W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

[6] E. R. Buchman, A. O. Reims, T. Skei and M. J. Schlatter, *ibid.*, **64**, 2696 (1952).



was eliminated, a higher yield of allyl acetate (V) was obtained, but the amount of the triene I was not increased substantially. The allyl acetate was identified by its physical and chemical properties plus analysis and saponification equivalent. Apparently, at temperatures above 450° the cyclobutane ring is cleaved thermally into two molecules of allyl acetate in a reaction reminiscent of a reverse Diels–Alder reaction. This cleavage competes favorably with pyrolysis of the acetate group. A more deep-seated rearrangement results in the formation of the triene I.

Since it was shown that in the pyrolysis of esters the alkyl methyl carbonates decompose about 50° lower than the corresponding acetates,[7] an attempt was made to prepare 1,2-dimethylenecyclobutane by the pyrolysis of a dicarbonate. When the 1,2-dimethylolcyclobutane (III) was treated with an excess of methyl chloroformate, there was obtained a 76% yield of the bis-(methyl carbonate) VIII. The methyl chloroformate was prepared conveniently by adding phosgene to cold methanol and removing the excess methanol by water extraction, followed by drying and distillation.

When the dicarbonate VIII was pyrolyzed at 500° under such conditions that 47% of the carbon dioxide was liberated and no carbonization occurred, an 18% conversion to 2-vinylbutadiene (I) was realized. At the same time a 32% yield of the olefin carbonate IX and a 37% recovery of the dicarbonate VIII were obtained. Surprisingly enough, no methyl allyl carbonate resulting from the cleavage of the cyclobutane ring was found.

The identity of the 2-vinylbutadiene (I) was proved by analysis, ultraviolet absorption and conversion to a known derivative through an intermediate Diels–Alder reaction. The properties of the triene I produced in this pyrolysis were very similar but not identical with those of the 2-vinylbutadiene prepared by the pyrolysis of 1,5-diacetoxy-3-acetoxymethylpentane (XI).[8] It undoubtedly was contaminated with a small amount of some isomeric hydrocarbon such as 1,2-dimethylenecyclobutane or 1,3,5-hexatriene. The ultraviolet absorption spectrum of the triene I possessed a broad maximum at 241 mμ. (The spectrum of the previously prepared triene I possessed the same general shape with an ϵ maximum at 231 mμ.[8]) That the two samples of the triene were essentially the same was proved by converting both of them to the identical Diels–Alder adduct X. When the triene I was treated with maleic anhydride, two moles of the anhydride added to form $\Delta^{1(9)}$-octalin-3,4,6,7-tetracarboxylic anhydride (X)[8] in a 58% yield.

All attempts to isolate a monoadduct resulting from 1,2-dimethylenecyclobutane failed. In one experiment a monoadduct was isolated in very small quantities but its structure was not established.

Other cleavages of a cyclobutane ring containing activating groups or steric strain have been noted. Fuson[9] reported the cleavage of diethyl 1-diethylaminocyclobutane-1,2-dicarboxylate into ethyl acrylate and ethyl α-diethylaminoacrylate. Cupery and Carothers[10] noted that divinylacetylene dimer on heating dissociated into two molecules of divinylacetylene. Truxillic and truxinic acids de-

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[7] J. J. Hewitt, Doctoral Dissertation, Wayne University, 1952.

[8] W. J. Bailey and J. Economy, This Journal, **77**, 1133 (1955).

[9] R. C. Fuson, *ibid.*, **50**, 1444 (1928); **51**, 599 (1929).

[10] M. E. Cupery and W. H. Carothers, *ibid.*, **56**, 1167 (1934).

compose into cinnnamic acid,[11] and ketoketene dimers[12] thermally dissociate into the corresponding ketene. Bailey and Daly[13] found that the vapor phase pyrolysis of ethyl 1-cyanocyclobutane-1-carboxylate produced a 57% yield of acrylonitrile. Cope, Haven, Ramp and Trumbull[14] found that 2,4-bicyclo[4.2.0]octadiene was in thermal equilibrium with 1,3,5-cycloöctatriene.

The present work clearly indicates that the cyclobutane ring will not withstand the high temperatures required for the convenient pyrolysis of an ester.

Experimental[15]

1,2-Dimethylolcyclobutane (III).—To 25.5 g. (0.67 mole) of lithium aluminum hydride dissolved in 800 ml. of anhydrous ether was added over a 2-hour period by means of an exhaustive ether extractor 63 g. (0.50 mole) of 1,2-cyclobutanedicarboxylic anhydride (II),[6] m.p. 77.0–77.5°.

After the reaction mixture had been stirred for an additional 3 hours, the excess hydride was decomposed with water and the complex was dissolved by the addition of just enough 10% hydrochloric acid to lower the *p*H to 2. The aqueous layer was extracted exhaustively with ether for 2 days and the extracts were combined with the original layer. The combined ether solution was washed with a sodium bicarbonate solution and dried over anhydrous sodium carbonate. After the ether was removed by distillation, the residue was fractionated through a 15 × 1.5-cm. Vigreux column to yield 50.7 g. (88%) of 1,2-dimethylolcyclobutane (III), b.p. 102–105° (2.8 mm.), n^{25}D 1.4744. (If the anhydride II was added in small amounts as a solid over a 2-hour period, followed by heating under reflux for an additional 6 hours, an 86% yield was obtained.)

Anal. Calcd. for $C_6H_{16}O_2$: C, 62.00; H, 10.34. Found: C, 62.02; H, 10.30.

1,2-Dimethylolcyclobutane di-α-naphthylurethan, m.p. 136–136.5°, was prepared from III and recrystallized from ethanol.

Anal. Calcd. for $C_{28}H_{26}O_4N_2$: C, 74.01; H, 5.72. Found: C, 73.72; H, 5.98.

1,2-Di-(acetoxymethyl)-cyclobutane (IV).—To a hot solution of 116 g. (1.0 mole) of 1,2-dimethylolcyclobutane (III) in 84 g. (1.4 moles) of glacial acetic acid was added 492 g. (4.8 moles) of acetic anhydride at such a rate as to maintain reflux. After the reaction mixture was heated for an additional 12 hours, the excess acetic acid and anhydride were removed by distillation and the residue was distilled through a 15-cm. Vigreux column to yield 176.6 g. (89%) of 1,2-di-(acetoxymethyl)-cyclobutane (IV), b.p. 94–101.5° (2.2 mm.) n^{25}D 1.4454, d^{30}_4 1.070.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00; sapn. equiv., 100. Found: C, 60.02; H, 8.10; sapn. equiv., 99.

Alkaline hydrolysis of IV gave a glycol indistinguishable from III.

Pyrolysis of 1,2-Di-(acetoxymethyl)-cyclobutane (IV).—At a rate of 1 g. per minute, 100 g. (0.50 mole) of 1,2-di-(acetoxymethyl)-cyclobutane (IV) was dropped through a pyrolysis tube packed with $^1/_8$-inch glass helices.[5a] The tube was externally heated at 480° and continuously flushed out with oxygen-free dry nitrogen. The pyrolysate, which was collected in a Dry Ice-bath, was diluted with ether containing a trace of *t*-butylcatechol, washed with water to remove the acetic acid and dried over anhydrous sodium carbonate. (Titration of an aliquot of the aqueous layer indicated that 30% of two molar equivalents of acetic acid had been liberated.) The ether was removed by distillation and all the material boiling below 110° (20 mm.) was flashed off and collected in Dry Ice traps. Refractionation of this low boiling fraction through an 8-inch, helix-packed column produced 0.8 g. (2%) of crude 2-vinylbutadiene (I), b.p. 72° (745 mm.), n^{25}D 1.4614, d^{25}_4 0.795 [reported[8] b.p. 32° (200 mm.), n^{25}D 1.4559].

Anal. Calcd. for C_6H_8: C, 90.00; H, 10.00. Found: C, 89.79; H, 10.06.

In addition to the triene I, fractionation of this low boiling fraction produced 0.8 g. (2%) of an isomeric diene VII, b.p. 78° (745 mm.), n^{25}D 1.4624, d^{28}_4 0.806.

Anal. Calcd. for C_6H_8: C, 90.00; H, 10.00. Found: C, 89.69; H, 9.98.

Further fractionation of this low boiling residue produced 3.3 g. (3.3%) of allyl acetate (V), b.p. 105–106° (745 mm.), n^{25}D 1.4001, d^{30}_4 0.921 [reported[16] b.p. 103–104° (734 mm.), n^{20}D 1.4049, d^{20}_4 0.928]. V rapidly decolorized bromine in carbon tetrachloride.

Anal. Calcd. for $C_5H_8O_2$: C, 60.00; H, 8.00; sapn. equiv., 100. Found: C, 60.31; H, 8.38; sapn. equiv., 98.

Fractionation of the high boiling residue from the pyrolysis through an 8-inch, helix-packed column produced 13.2 g. (19%) of 1-methylene-2-acetoxymethylcyclobutane (VI), b.p. 78.5° (29 mm.), n^{25}D 1.4452, d^{30}_4 0.969; and 63 g. (63% recovery) of 1,2-di-(acetoxymethyl)-cyclobutane (IV). VI readily decolorized bromine in carbon tetrachloride.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.57; H, 8.57. Found: C, 68.67; H, 8.48.

Increasing the temperature of pyrolysis increased the yield of allyl acetate but did not improve the yield of the hydrocarbon fraction.

Structure of the Diene VII.—The higher boiling diene VII, which analyzed for C_6H_8, was isomeric with 1,2-dimethylenecyclobutane. VII reacted readily with potassium permanganate solution. Its ultraviolet absorption spectrum, which possessed an ε maximum of 14,000 at 243 mμ, indicated the presence of a pair of conjugated double bonds. When 2 g. (0.025 mole) of diene VII and 2.5 g. (0.025 mole) of maleic anhydride were heated under reflux in 100 ml. of benzene for 24 hours, no reaction was observed and the maleic anhydride was recovered unchanged on evaporation of solvent. Since VII contains a conjugated double bond that will not undergo the Diels-Alder reaction, it can be concluded that one double bond is exocyclic and the other endocyclic. Two possibilities for the structure of VII are 1-methylene-2-methyl-2-cyclobutene and 1-methylene-2-cyclopentene.

1,2-Dimethylolcyclobutane Bis-(methyl Carbonate) (VIII).—To a mixture of 100.4 g. (0.86 mole) of 1,2-dimethylolcyclobutane (III), 500 ml. of dry chloroform and 158 g. (2 moles) of dry pyridine cooled to 0° was added 188 g. (2 moles) of methyl chloroformate. After the mixture had been stirred for 2 hours, the reaction mixture was washed successively with two 500-ml. portions of water, 250 ml. of 5% hydrochloric acid and 250 ml. of saturated sodium bicarbonate solution. After the chloroform solution was dried overnight with anhydrous magnesium sulfate, the chloroform was removed by distillation under reduced pressure. The residue was fractionated through a 6-inch, helix-packed column to yield 152 g. (76%) of 1,2-dimethylolcyclobutane bis-(methyl carbonate) (VIII), b.p. 92° (0.12 mm.), m.p. 23°, n^{25}D 1.4440.

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.72; H, 6.90. Found: C, 52.01; H, 6.78.

Pyrolysis of 1,2-Dimethylolcyclobutane Bis-(methyl Carbonate) (VIII).—At a rate of 1.2 g. per minute, 100 g. (0.43 mole) of 1,2-dimethylolcyclobutane bis-(methyl carbonate) (VIII) was dropped through a vertical pyrolysis tube packed with $^1/_8$-inch Pyrex helices and heated at 500°. The pyrolysate was collected in a side-inlet flask cooled in a Dry Ice-bath. The extent of pyrolysis was followed by passing the gas from the receiving flask through a tube packed with Ascarite. From the gain in weight of the Ascarite tube, it was found that 47% of the theoretical amount of carbon dioxide was eliminated. To the clear, colorless pyrolysate at 0° was added 50 mg. of *t*-butylcatechol, and the mixture

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(11) P. Karrer, "Organic Chemistry," 4th English Ed., Elsevier Publishing Co., New York, N. Y., 1950, p. 651.

(12) W. E. Hanford and J. C. Sauer in R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 119.

(13) W. J. Bailey and J. J. Daly, Jr., Abstracts of the 126th National Meeting of the American Chemical Society, New York, Sept., 1954.

(14) A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

(15) All melting points are corrected. The analyses were performed by Vivian Kapuscinski, James French, Robert Keen, Mary Aldrich and Kathryn Gerdeman.

(16) J. W. Brühl, *Ann.*, **200**, 179 (1879).

was washed with two 25-ml. portions of saturated calcium chloride solution and then with water to remove the methanol. After the mixture was dried for 16 hours over anhydrous magnesium sulfate and the drying agent removed, the low boiling fraction was flashed off under pressure of 15 mm. at 25° into a Dry Ice trap. At the Dry Ice temperature, about 1.5 g. of a solid, which was believed to be dimethyl carbonate, crystallized out. The crude triene was separated from this solid by a pipet, stabilized with 25 mg. of *t*-butylcatechol, and fractionated through a 6-inch, helix-packed column under nitrogen to yield 6.3 g. (18%) of impure 2-vinylbutadiene (I), b.p. 72° (752 mm.), n^{25}D 1.4634 [reported[8] b.p. 32° (200 mm.), n^{25}D 1.4559].

Anal. Calcd. for C_6H_8: C, 90.00; H, 10.00. Found: C, 90.20; H, 10.27.

The physical constants of this hydrocarbon plus the 58% yield of the Diels-Alder adduct X indicate that the 2-vinylbutadiene prepared in this manner is contaminated with isomeric hydrocarbons.

Fractionation of the higher boiling material from the pyrolysis through a 6-inch, helix-packed column produced 16.4 g. (32%) of methyl (2-methylenecyclobutyl)-methyl carbonate (IX), b.p. 56° (3 mm.), n^{25}D 1.4494, and 36.6 g. (37% recovery) of unreacted starting material VIII. IX readily decolorized bromine in carbon tetrachloride and could be pyrolyzed with the dicarbonate VIII to produce additional quantities of the triene I. No methyl allyl carbonate formed by cleavage of the cyclobutane ring was found.

$\Delta^{1(9)}$-Octalin-3,4,6,7-tetracarboxylic Anhydride (X).—To a solution of 2 g. (0.02 mole) of maleic anhydride and 25 mg. of *t*-butylcatechol in the smallest amount of toluene necessary for solution was added 0.5 g. of the crude 2-vinylbutadiene (I). Within 5 minutes a white flocculent precipitate formed and the solution became warm. After 1 hour the solid was removed by filtration and recrystallized three times from benzene-cyclohexane to yield 1.1 g. (58%) of $\Delta^{1(9)}$-octalin-3,4,6,7-tetracarboxylic anhydride (X), m.p. 240–242° (reported[8] m.p. 244–246°). Mixed melting point determination of X with an authentic sample[8] melted at 245–247°.

Simultaneous dehydrogenation and decarboxylation of the Diels-Alder adduct with 5% palladium-on-asbestos and copper chromite catalyst produced naphthalene, m.p. 78–79°. A mixed melting point with an authentic sample of naphthalene showed no depression.

All attempts to isolate an adduct resulting from the addition of 1 mole of 1,2-dimethylenecyclobutane and 1 mole of maleic anhydride were unsuccessful. Even in those experiments in which the diene was present in a molar excess, the product was always the adduct X.

In one case when 0.21 g. (0.0026 mole) of the triene I and 0.26 g. (0.0027 mole) of maleic anhydride were heated under reflux for 20 hours in benzene, a small amount, 134 mg. (26%), of a less-soluble adduct, m.p. 199–200°, was isolated. The adduct rapidly decolorized bromine in carbon tetrachloride. It is possible that the lower solubility of the diacid prevented the reaction from proceeding further.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.12; mol. wt., 196. Found: C, 60.84; H, 6.15; mol. wt. (Rast), 209.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY]

Studies on Polyvinyl Chloride. I. Reduction to a Hydrocarbon Polymer

BY JOHN D. COTMAN, JR.

RECEIVED OCTOBER 15, 1954

Polyvinyl chloride reacts with lithium aluminum hydride–lithium hydride in boiling tetrahydrofuran to yield a polyhydrocarbon. From the infrared spectrum of the product it was concluded that the product is quite similar to polyethylene. The reduction is complicated by atmospheric oxygen which is incorporated into the polymer as hydroxyl groups.

Marvel, Sample and Roy[1] have demonstrated the head-to-tail arrangement of monomer units in polyvinyl chloride by dechlorination with zinc.[2] The hydrocarbon product obtained is presumably a mixture of alicyclic structures. At high polymer dilution Freund dechlorination should yield a preponderance of cyclopropane structures. The removal of chlorines in pairs can result in complex three-dimensional structures at polymer concentrations favoring interchain reaction. In either case the molecular structures of the resulting hydrocarbons represent radical alterations of the polyvinyl chloride backbone.

Successful determination of branch ends in polyethylene by infrared analysis[3] and the possibility of chain branching in polyvinyl chloride revealed by the kinetic research of Bengough and Norrish[4] render highly desirable the conversion of polyvinyl chloride into a hydrocarbon of unchanged chain structure and molecular weight. Estimation of branches by infrared techniques on the polyhydrocarbon could be used as an index of branching in polyvinyl chloride if reduction did not involve chain cleavage, molecular rearrangement or extensive double bond formation.

It is uncertain whether procedures frequently employed for catalytic hydrogenation of chlorine compounds with chlorine removal, would result in molecular weight breakdown or rearrangement of polyvinyl chloride. Lack of accurate knowledge about adsorbed molecules on catalyst surfaces does not permit any judgement, *a priori*, on the probability of reduction without chain cleavage or rearrangement. Direct reduction with alkali metals or reduction through Grignard reagents do not offer clear routes to the desired polyhydrocarbon.

Eliel[5] has recently reported the preparation of optically active mono-α-deuteroethylbenzene by reaction between lithium aluminum deuteride and optically active phenyl methyl carbinyl chloride. The isolation of active hydrocarbon indicated nucleophilic displacement of chloride by the alumino deuteride as a preponderant, if not exclusive, reaction mechanism. The observations of Trevoy and Brown[6] suggest an SN2 mechanism in the reduction

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(2) P. J. Flory, *ibid.*, **61**, 1518 (1939); F. T. Wall, *ibid.*, **62**, 803 (1940).

(3) L. H. Cross, R. G. Richards and H. A. Willis, *Discs. Faraday Soc.*, **9**, 235 (1950); F. M. Rugg, J. J. Smith and L. H. Wartman, *J. Polymer Sci.*, **11**, 1 (1953); W. M. D. Bryant, and R. C. Voter, THIS JOURNAL, **75**, 6113 (1953).

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(5) E. L. Eliel, THIS JOURNAL, **71**, 3970 (1949).

(6) L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).