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Highly Fluorinated Dienes. I. The Novel Pyrolysis of 1-Acetoxymethyl-2-methyltetrafluorocyclobutene[1]

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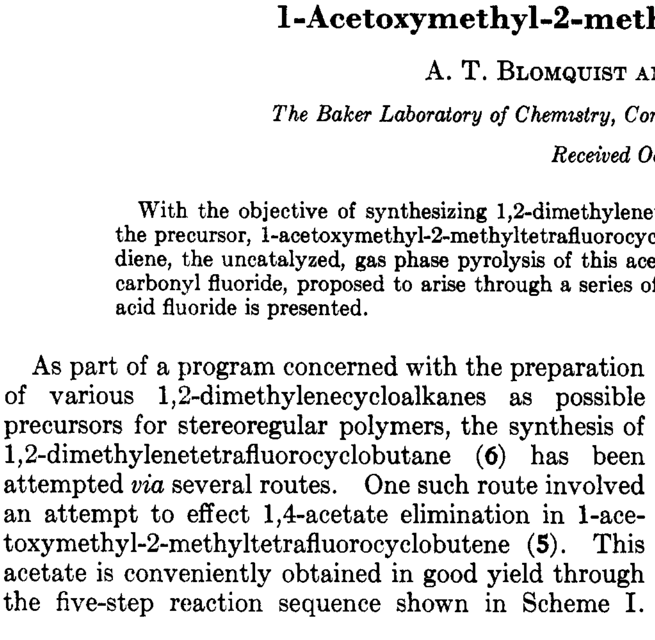
With the objective of synthesizing 1,2-dimethylenetetrafluorocyclobutane, the preparation and pyrolysis of the precursor, 1-acetoxymethyl-2-methyltetrafluorocyclobutene, has been carried out. Instead of the expected diene, the uncatalyzed, gas phase pyrolysis of this acetate at 606° gives 1,1-difluoro-2-methyl-1,3-butadiene-3-carbonyl fluoride, proposed to arise through a series of molecular rearrangements. The structure proof of this acid fluoride is presented.

As part of a program concerned with the preparation of various 1,2-dimethylenecycloalkanes as possible precursors for stereoregular polymers, the synthesis of 1,2-dimethylenetetrafluorocyclobutane (**6**) has been attempted *via* several routes. One such route involved an attempt to effect 1,4-acetate elimination in 1-acetoxymethyl-2-methyltetrafluorocyclobutene (**5**). This acetate is conveniently obtained in good yield through the five-step reaction sequence shown in Scheme I.

SCHEME I



Chlorotrifluoroethylene is dimerized under pressure to give the "head to head," "tail to tail" dimer, 1,2-dichlorohexafluorocyclobutane (**1**).[2] Dechlorination of the dimer **1** with zinc dust in refluxing ethanol occurs readily to give hexafluorocyclobutene (**2**)[3] which is subsequently converted into 1,2-dimethyltetrafluorocyclobutene (**3**) by reaction with methyllithium in ether at −50°.[4] Photolytic bromination of the cyclobutene **3** with bromine in carbon tetrachloride gives a single isolable product, 1-bromomethyl-2-methyltetrafluorocyclobutene (**4**). The structure assignment of the bromide **4** is based upon its proton nuclear magnetic resonance (pmr) which shows two singlets at τ 6.04 (2) and 8.70 (3), and its infrared spectrum which shows only a single band in the 5–6.8-μ region at 6.00 μ and no intense exomethylene absorption in the 11–12-μ region. Acetolysis of the monobromide **4** with silver acetate in acetic acid gives only one isolable acetate, compound **5**. The pmr spectrum of the acetate **5** shows three bands at τ 5.17, 7.92, and 8.02. Overlap of the last two bands requires a combined integration to give an area ratio of 1:3 for the bands τ 5.17:7.92 + 8.02. Analogous to the monobromide **4**, the infrared spectrum of the acetate shows no intense *exo*-methylene absorption in the 11–12-μ region. These data are in excellent agreement with the endocyclic double-bond structure **5**.

A number of allylic acetate pyrolyses involving 1,4 elimination have been reported.[5] For this reason the expected product from the uncatalyzed gas-phase pyrolysis of the acetate **5** at 606° was the diene **6**. Instead, a totally different compound was obtained which has been shown to be 1,1-difluoro-2-methyl-1,3-butadiene-3-carbonyl fluoride (**7**) (Scheme II). The following is a discussion of the reasoning which led us to this structural assignment.

The following physical data were obtained for **7**: mass (mass spectrum), 150; infrared, 5.50, 5.73, and 6.15 μ; ultraviolet (isooctane), λ_{max} 251 mμ (log ϵ 3.26); pmr (*ca.* 15% in CCl_4), singlet at τ 3.50 (1) vinyl, singlet at 3.95 (1) vinyl, triplet at 8.16 (3) (J = 3.2 cps) methyl. Compound **7** polymerizes very rapidly

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[1] Abstracted from part of the Ph.D. thesis of P. P. Nicholas, Cornell University, June 1964.

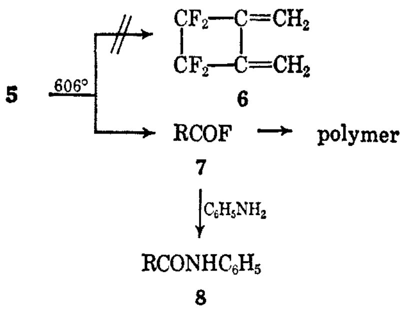
[2] A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[3] A. L. Henne and W. J. Zimmerschied, *ibid.*, **69**, 281 (1947).

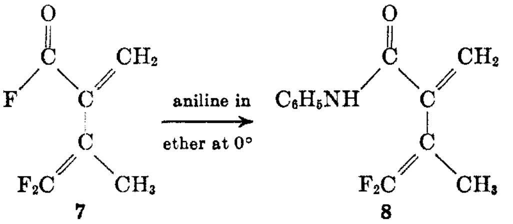
[4] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

[5] W. J. Bailey and R. Barclay, *ibid.*, **21**, 328 (1956); H. R. Snyder, J. M. Stewart, and R. L. Meyers, *J. Am. Chem. Soc.*, **71**, 1055 (1949); W. J. Bailey and J. C. Gossens, *ibid.*, **78**, 2804 (1956); S. A. Morell, H. H. Geller, and E. C. Lathrop, *Ind. Eng. Chem.*, **37**, 877 (1945); O. Grummitt and J. Splitter, *J. Am. Chem. Soc.*, **74**, 3924 (1952).

SCHEME II



at room temperature and also reacts spontaneously with aniline in ether at 0° to give a crystalline derivative **8** with the following physical properties: mass (mass spectrum), 223; elemental composition, $C_{12}H_{11}F_2ON$; infrared spectrum, 2.95, 3.08, 5.81, and 6.02 μ; pmr, multiplet at τ 2.83 (5) phenyl, singlet at 4.13 (1) vinyl, singlet at 4.60 (1) vinyl, triplet at 8.23 (3) (J = 3.2 cps) methyl.



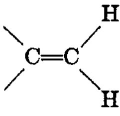
The infrared spectrum of the product **8** clearly demonstrates that it is an anilide. The N-H stretch at 2.95 and 3.08 μ, together with the hydrogen-bonded carbonyl band at 6.02 μ are characteristic of mono-N-substituted amides.[6] Furthermore, the striking similarity between the pmr spectra of **7** and **8** demonstrates the incorporation of **7** into aniline. Accordingly, only ten of the eleven protons present in the anilide **8** are observed in the pmr spectrum, since amido protons are occasionally not observed.[7] Heating an acetone solution of the anilide with excess D_2O results in no change in the pmr spectrum in the τ 4–5 region thus demonstrating that neither of the bands which have been assigned vinylic character can result from this amido proton. The infrared bands at 5.73 and 5.81 μ in the spectra of **7** and **8**, respectively, are attributed to a fluoro-substituted double bond.[8] Assigning the band at 5.50 μ in the infrared spectrum of the product **7** to an acid fluoride carbonyl group[9] satisfactorily explains the spontaneous reaction between product **7** and aniline.

The mass and elemental composition of the anilide **8** shows that "R" must have the composition $C_5H_5F_2$. This gives a predicted mass of 150 for the acid fluoride **7** which is indeed observed experimentally.

The data are now sufficient to elucidate the structure of the group R. The composition $C_5H_5F_2$ indicates that R must have two degrees of unsaturation and, therefore, must have a carbon configuration which falls into one of the following four categories: I, acetylenes; II, dienes [(a) allenes, (b) 1,3-dienes, (c) 1,4-dienes]; III, monocyclic alkenes [(a) cyclopropenes, (b) methylenecyclopropanes, (c) vinylcyclopropanes, (d) cyclobutenes, (e) methylenecyclobutanes, (f) cyclopentenes]; IV, bicycloalkanes.

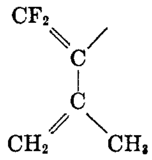
Acetylenes are immediately eliminated since the infrared spectra of **7** and **8** do not show the characteristic acetylene band at 4.76 μ.[10] Similarly, allene structures, IIa, are eliminated since the characteristic allene band at 5.07 μ is also missing.[11] Since two unsplit vinyl protons are present in the pmr spectra of **7** and **8**, all structures of the type III and IV are eliminated with the exception of IIIb, c, and e. For a structure of type IIIb to satisfy this latter condition, the *exo*-methylene group must be unsubstituted. Such a structural feature would give rise to a band at 11.2 μ in the infrared[12] which is not present in the spectra of either **7** or **8**. Further examination of the pmr spectra reveals that R must contain a methyl group and, thus, structures of the type IIc, IIIc, and IIIe are eliminated.

Of the remaining structures, IIb, only derivatives which have both vinyl protons on the same terminal methylene group could give rise to two unsplit vinyl protons in the pmr. Such protons are known to undergo very weak interaction with one another. Of course, it is further required that there be no group on the adjacent carbon atom capable of significant coupling with the terminal methylene protons. Thus,

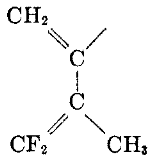


(J_{ab} = 0–3.5 cps[13])

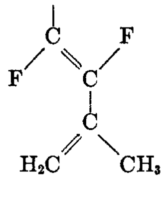
the following structures A–D are possible for group R.



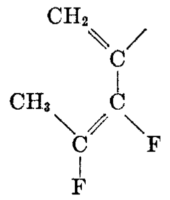
A



B



C



D

The splitting of the methyl protons into a triplet in the pmr spectrum of R is clearly the result of coupling between these protons and two equivalent or nearly equivalent fluorine atoms. This portion of the pmr spectra of **7** and **8** is adequately explained only by structure B. This structure also explains the absence of the terminal methylene band in the infrared at 11.2 μ. Normally, disubstituted ethylenes of the type $R_1R_2C{=}CH_2$ give rise to a characteristic band at 11.2 μ; however, a carbonyl group attached directly to the double bond results in an increase in the absorption

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[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 209, 207.

[7] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 72.

[8] R. N. Haszeldine, *J. Chem. Soc.*, 4426 (1952).

[9] Reference 6, p 126.

[10] Reference 6, p 59.

[11] J. H. Wotiz and W. D. Celmer, *J. Am. Chem. Soc.*, **74**, 1860 (1952).

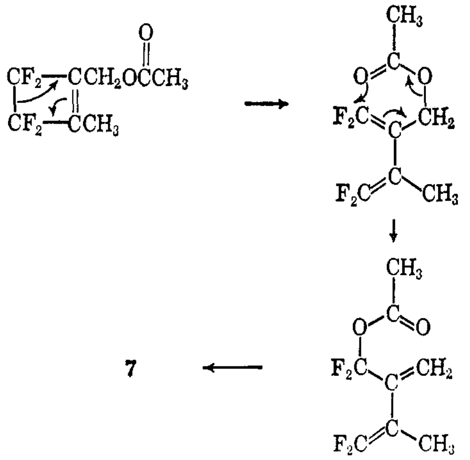
[12] J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **75**, 3344 (1953).

[13] Reference 7, p 85.

frequency to approximately 10.7 μ.[14] The infrared spectra of the acid fluoride **7** and the anilide derivative **8** have bands at 10.4 and 10.8 μ, respectively.

It is, therefore, concluded that the structure of **7** is the acid fluoride, 1,1-difluoro-2-methyl-1,3-butadiene-3-carbonyl fluoride, which is proposed to arise *via* the route shown in Scheme III.

Scheme III



The final step in this mechanism could occur in several ways. Hydrolysis during work-up or bond migration from the oxygen atom in the ester linkage with resulting fluoride displacement would provide the observed product. There is some precedent for the given mechanism. The first step, valence tautomerism, is well known for highly fluorinated cyclobutanes, and several examples have been reported.[15] The subsequent rearrangement finds its analogy in the gas phase isomerization of allyl vinyl ether to β-vinyl propionaldehyde[16] and the allylic rearrangement of certain allylic acetates.[17]

Experimental Section[18]

1,2-Dichlorohexafluorocyclobutene (**1**).—In a modification of the procedure of Henne and Ruh,[2] 2100 g of chlorotrifluoroethylene was placed in a 4-l. stainless steel bomb and heated in a rocker for 24 hr at 125°, 48 hr at 150°, and 24 hr at 200°. The contents were distilled and 1620 g (77.0%) of the dimer **1**, bp 59–59.5°, was obtained.

Hexafluorocyclobutene (**2**).—In accordance with the general procedure outlined by Henne and Zimmerschied,[3] 554 g (2.38 moles) of the dichloride **1** was slowly added to a stirred refluxing mixture of 332 g (5.08 g-atoms) of zinc dust in 700 ml of absolute ethanol. The flask was equipped with an efficient condenser through which the low-boiling product (bp 4°) passed, and was collected in a Dry Ice trap. Distillation at room temperature through a column packed with glass helices gave 317 g (1.95 moles, 82.0%) of hexafluorocyclobutene.

1,2-Dimethyltetrafluorocyclobutene (**3**).—The procedure used was a modification of one described by Dixon.[4] A 5-l. three-necked flask was fitted with two Dry Ice condensers and a paddle stirrer. One condenser contained two side arms for the introduction of methyl bromide and nitrogen. The other condenser contained a single side arm leading to a mercury well for maintaining a slight static nitrogen pressure. The system was flushed with nitrogen and flash dried with a burner. A slight nitrogen flow was then maintained. The flask was charged with 5 lb of anhydrous ether and 120 g (15.9 g-atoms) of lithium wire cut into 1-in. sections. The mixture was stirred and cooled to 0–5° with a Dry Ice–acetone bath. Methyl bromide was slowly condensed into the mixture, and this addition was continued until the lithium had completely reacted (*ca.* 2 hr). The bath was maintained at 0–5° throughout this reaction.

The bath was then cooled to −50° with Dry Ice and the two-arm condenser was replaced with a gas inlet tube also containing two side arms, one of which extended into the ethereal mixture. Through this arm was slowly distilled 603 g (3.72 moles) of hexafluorocyclobutene; nitrogen was passed through the second arm. The bath temperature was maintained at −45 to −50° by the incremental addition of Dry Ice to the acetone bath. After addition of hexafluorocyclobutene was completed (1–1.5 hr), the reaction mixture was maintained at −50° with stirring for an additional 0.5 hr. It was then allowed to warm gradually to room temperature.

The excess methyllithium was decomposed by the gradual addition of a 1:1 solution of water and concentrated hydrochloric acid. Addition was carried out until the stirred reaction mixture became clear brown in color. The ether phase was removed and washed twice with cold water followed by treatment with saturated sodium bicarbonate solution. The resulting ethereal solution was distilled to remove the ether.

The reaction was repeated with 576 g (3.55 moles) of hexafluorocyclobutene and 114 g (15.2 g-atoms) of lithium. The reaction products, free of ether, were combined and added to two volumes of saturated sodium bicarbonate solution. This resulting mixture was distilled under reduced pressure through a take-off head which led to a water-cooled condenser. The pressure was adjusted so that the heat temperature was maintained at 45–50°. The clear, colorless organic distillate was removed from the aqueous phase and dried over calcium chloride. Distillation was performed from calcium carbonate through a 2-ft vacuum jacketed column packed with glass helices. Three fractions were obtained: (1) bp 32–62° (179 mm), 105 g; (2) bp 62–64° (179 mm), 505 g; (3) bp 64–74° (179 mm), 75 g. The distillation was followed by gas chromatography (vpc) to assure purity of the collected fraction (2). The following vpc conditions were employed: Aerograph A-90-P; column, 5 ft × 0.25 in., 20% GE-SF-96 Si oil on 60–80 mesh fire brick; column temperature, 70°; injector temperature, 210°; sample volume, 3 μl; attenuation, 4; flow rate, 26 ml/min. The main fraction (2) was collected when the concentration of cyclobutene **3** in the distillate reached 87% and was continued until the concentration dropped below 87%. Redistillation of fraction 1 gave an additional 58 g of 95% pure **3** thus giving a total of 606 g (3.93 moles, 54.1%) of 91% pure **3**.

Based upon vpc data, four products were obtained from this reaction. The major product **3** was found to be present in 80% concentration and was third in order of retention time. An analytically pure sample of the cyclobutene **3** was obtained by preparative vpc: $n^{20.0}_{\mathrm{D}}$ 1.3489.

Anal. Calcd for $C_4H_6F_4$: C, 46.76; H, 3.92. Found: C, 46.81; H, 4.00.

The proton nmr spectrum at high resolution showed a quintuplet at τ 8.22 (J = 1.0 cps) indicating that the four fluorine atoms must couple equivalently with the methyl protons.

1-Bromomethyl-2-methyltetrafluorocyclobutene (**4**).—A solution of 100 g (0.650 mole) of the cyclobutene **3** in 250 ml of carbon tetrachloride was added to a three-necked, 500-ml flask equipped with a magnetic stirring bar, addition funnel, and a water-cooled condenser. The solution was stirred and heated to reflux by irradiation with a GE sun lamp. To the refluxing solution was added a solution of 104 g of bromine (0.650 mole) in 50 ml of carbon tetrachloride in increments of 5 ml. Addition was made as rapidly as bromine was consumed (solution turns to pale orange from deep red). Addition was completed in 5 hr and the stirred solution was allowed to cool to nearly room temperature. The reaction mixture was then washed with saturated aqueous sodium bisulfite and dried over calcium chloride. The carbon tetrachloride was removed by distillation and the residue distilled under reduced pressure. All material boiling up to 50° (2.5 mm) was collected and redistilled. There was obtained 66.5 g (0.286 mole, 44%) of the monobromide **4**, bp 62–65° (15 mm), n^{26}_{D} 1.4178. *Caution:* this material is a powerful lacrimator.

Anal. Calcd for $C_6H_5F_4Br$: C, 30.92; H, 2.16; Br, 34.30. Found: C, 31.76; H, 2.41; Br, 34.64.

1-Acetoxymethyl-2-methyltetrafluorocyclobutene (**5**).—A mixture of 150 ml of acetic acid, 40 g (0.171 mole) of the mono-

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[14] Reference 6, p 51.

[15] J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 382 (1961).

[16] L. Stein and G. W. Murphy, *ibid.*, **74**, 1041 (1952).

[17] W. J. Bailey and R. Barclay, *J. Org. Chem.*, **21**, 328 (1956).

[18] All boiling points and melting points are uncorrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

bromide **4**, and 37.07 g (0.222 mole) of silver acetate was stirred at reflux for 24 hr. The mixture was filtered and the filtrate distilled under reduced pressure. The acetate **5** was collected at 75–76° (9 mm). There was obtained 22.5 g (0.107 mole, 62.5%) of the product: $n^{17}D$ 1.3890; infrared spectrum, 3.45, 5.72, 6.05 μ.

Anal. Calcd for $C_8H_8F_4O_2$: C, 45.31; H, 3.80. Found: C, 45.04; H, 3.85.

1,1-Difluoro-2-methyl-1,3-butadiene-3-carbonyl Fluoride (7).—A Basic Products Corp. multiple unit (70-T type), 115-v electric furnace was vertically mounted on a platform. A 20-in.-long, 25-mm-diameter Vycor tube was inserted and fitted at the top with a take-off head leading to a flask fitted with a nitrogen inlet capillary. A thermocouple well with a 6-in. immersion into the heated portion of the tube was fused to the take-off head and extended vertically through the center of the Vycor tube. All temperature measurements were made at the base of this well. At the outlet of the Vycor tube was placed a series of two traps in liquid nitrogen. The acetate **5** was placed in the flask and heated to 60° by an oil bath. Airco Seaford grade nitrogen was passed into the system which was evacuated to 2-mm pressure.

In a typical experiment, 4.00 g (0.0189 mole) of the acetate **5** was pyrolyzed at 606° at 2 mm of nitrogen pressure over a 77-min period. The pyrolysate was washed with cold water and dried over calcium chloride. A total of 3.41 g of pyrolysate was obtained. Gas chromatography was performed under the following conditions: Aerograph A-90-P_2; column, 7 ft × $^3/_8$ in., 30% five-ring poly-*m*-phenyl ether on 80–100 mesh acid-washed Chrom P; column temperature, 85°; detector temperature, 235°; injector temperature, 220°; flow rate, 150 ml/min; attenuation, 1; 4-μl sample. The column temperature was manually programmed to 160° after the appearance of the acid fluoride **7** peak. The composition of this pyrolysate was found to be the following (in order of retention time): 1,1-difluoro-2-methyl-1,3-butadiene-3-carbonyl fluoride (61%), unknown (25%), unreacted acetate **5** (14%).

The pure acid fluoride **7** was collected by preparative gas chromatography at attenuation 64 using 300-μl somples. Total yield of pure acid fluoride was 1.13 g (0.00754 mole, 40.0%), $n^{25}D$ 1.3827.

1,1-Difluoro-2-methyl-1,3-butadiene-3-carboxanilide (8).—To an ice-cold stirred solution of 0.46 g (0.00306 mole) of the acid fluoride **7** in 4 ml of anhydrous ether was slowly added 1.0 g of aniline. After addition was complete, the reaction mixture was allowed to warm to room temperature. The ether was evaporated and the solid residue was treated with 150 ml of carbon disulfide. The mixture was heated to boiling and filtered. The filtrate was concentrated and allowed to crystallize. The resulting crystalline anilide was recrystallized from carbon disulfide to give 0.50 g (73.2%) of white plates, mp 96.5–97°.

Anal. Calcd for $C_{12}H_{11}F_2ON$: C, 64.56; H, 4.97; F, 17.03; N, 6.27. Found: C, 64.08; H, 4.99; F, 17.08; N, 5.98.

Registry No.—**5**, 7718-49-2; **3**, 356-58-1; **4**, 7704-56-5; **7**, 7704-57-6; **8**, 7704-58-7.

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Highly Fluorinated Dienes. II.[1] 1,2-Dimethylenetetrafluorocyclobutane[2]

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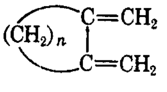
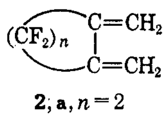
The uncatalyzed, gas phase pyrolysis of 1-bromomethyl-2-methyltetrafluoro-1-cyclobutene at 630° in a fast-flowing nitrogen stream gives a mixture of 1,2-dimethylenetetrafluorocyclobutane (19%), 1,1-difluoro-2-methylene-3-difluoromethylenecyclobutane (25%), and 1,2-dimethyltetrafluoro-1-cyclobutene (5%). Physical and chemical properties of the two dienes are in accord with the structures given. The intermediate formation of 1,1-difluoroallene is considered to account for the formation of the unsymmetrical diene. Although both dienes fail to form normal Diels–Alder-type adducts, they do give crystalline adducts with diphenylnitrilimine.

In recent years some of the work in this laboratory has been concerned with the synthesis of 1,2-dimethylenecycloalkanes of type **1**, with the ultimate objective of examining *cis* 1,4-addition polymers derived therefrom.[3] These studies have now been extended to include certain related fluorinated dienes of type **2**.



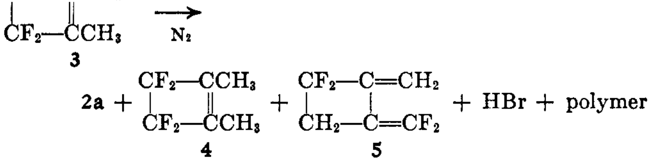
1, $n = 2, 3, 4$



2; **a**, $n = 2$
b, $n = 3$
c, $n = 4$

Although syntheses of the three 1,2-dimethylene perfluoroalkanes **2** have been achieved, the present report is an account of the work done on the four-membered-ring diene **2a**. Dienes **2b** and **2c** will be described in subsequent articles.

Of the several routes examined for the preparation of the diene **2a** only the fast-flow pyrolysis of 1-bromomethyl-2-methyltetrafluoro-1-cyclobutene (**3**)[1] proved to be successful. The uncatalyzed, gas-phase pyrolysis of the bromo compound **3** in a fast flowing nitrogen stream at 630° gives the diene **2a**, 1,2-dimethyltetrafluoro-1-cyclobutene (**4**), 1,1-difluoro-2-methylene-3-difluoromethylenecyclobutane (**5**), hydrogen bromide, and a small amount of nonvolatile, polymeric material. Gravimetric analysis for hydrogen bromide indicates that a 71% conversion is achieved under suitable conditions.



Because of the instability of the dienes **2a** and **5**, pure samples of the volatile organic products were isolated by preparative vpc. The structural assignment for the cyclobutene **4** is based upon its vpc retention time and its proton magnetic resonance spectrum (pmr) which

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[1] Part I of this series: A. T. Blomquist and P. P. Nicholas, *J. Org. Chem.*, **32**, 863 (1967).

[2] Abstracted from part of the Ph.D. thesis of P. P. Nicholas, Cornell University, June 1964.

[3] A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **77**, 1806 (1955); A. T. Blomquist, Y. C. Meinwald, and D. T. Longone, *ibid.*, **78**, 6057 (1956); A. T. Blomquist and D. T. Longone, *ibid.*, **79**, 3916 (1957).