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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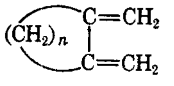
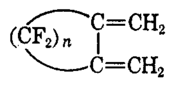
The uncatalyzed, gas phase pyrolysis of 1-bromomethyl-2-methyltetrafluoro-1-cyclobutene at 630° in a fast-flowing nitrogen stream gives a mixture of 1,2-dimethylenetetrafluorocyclobutane (19%), 1,1-difluoro-2-methylene-3-difluoromethylenecyclobutane (25%), and 1,2-dimethyltetrafluoro-1-cyclobutene (5%). 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.



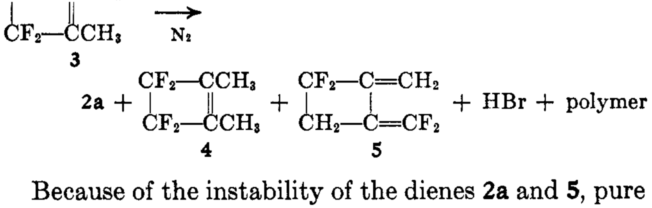
1, $n = 2,3,4$



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).

are identical with those of authentic material. Also, the structure of the diene **5** was established by comparing its infrared spectrum with that of authentic diene.[4]

Although the dienes **2a** and **5** polymerize rapidly at room temperature, they are somewhat stable at −80° and in dilute solutions of carbon tetrachloride at room temperature. The dienes are isomers of mass 152 (mass spectrometric analysis) and composition $C_6H_4F_4$ (elemental analysis of polymer). The pmr spectrum of **2a** shows a singlet at τ 4.18 while that of **5** shows a singlet at 4.44 (1), a singlet at 4.60 (1), and a multiplet at 6.82 (2) with $J = 5$ cps. The two dienes are excellent structural models for one another, and, accordingly, they have very similar ultraviolet spectra. The ultraviolet spectrum of **2a** in isooctane shows an absorption maximum at 244 mμ (log ϵ 3.97) and a shoulder at 244 mμ (log ϵ 3.75); diene **5** has an absorption maximum at 239 mμ (log ϵ 3.94) and a shoulder at 233 mμ (log ϵ 3.90). Conclusive chemical evidence for the structural assignment for the diene **2a** is its reaction with liquid hydrogen bromide. 1,4 addition occurs to give the starting monobromide **3** in 25.3% yield.

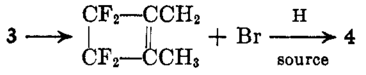
The low yields of the dienes **2a** and **5** as isolated (6.7 and 12.8%, respectively) appears to be due to their instability under preparative vpc conditions. This was verified by vpc analysis of several different volumes of injected pyrolysate with the stable cyclobutene **4** serving as an internal standard of reference. Gas chromatograms indicated that the ratio of the dienes **2a** and **5** to the cyclobutene **4** decreased markedly with increasing volume of the injected sample.

Since vpc analysis of the pyrolysate may be unreliable, pmr analysis was then used to establish the pyrolysate composition. This method is particularly advantageous for this system because these dienes are reasonably stable in dilute solutions and at room temperature. Furthermore, all three components in the volatile pyrolysate, **2a**, **5**, and **4**, have bands in the pmr that are in different regions of the spectrum. The mole per cent composition is obtained by weighting the relative integrated band areas in the spectrum of the pyrolysate by the number of protons in the reference absorption band and comparing the adjusted band areas. Using the bands at τ 4.18, 6.82, and 8.22 for **2a**, **5**, and **4**, respectively, it was found that the yields of the products **2a**, **5**, and **4** are 19, 25, and 5%, respectively. Comparison of these percentages with the per cent yields of the dienes actually isolated by preparative vpc indicates that only 39% of diene **2a** and 50% of diene **5** are recovered from the pyrolysate.

Mechanistic interpretation of the pyrolysis of the bromo compound, although speculative, may be made on the basis of known good analogies. The diene **5** has been prepared by other workers by the thermal dimerization of 1,1-difluoroallene; the latter was conveniently obtained by ring fission, at 800–950°, of 1-methylene-2,2,3,3-tetrafluorocyclobutane.[5] Accordingly, it is suggested that the formation of diene **5** in the pyrolysis of the bromo compound **3** occurs by dimerization of 1,1-difluoroallene, with the latter arising from

$$3 \longrightarrow 2a \longrightarrow 2CF_2{=}C{=}CH_2 \longrightarrow 5$$

homolytic cleavage of the diene **2a**. The small amount of the cyclobutene **4** is considered to arise from the allylic radical formed in the homolysis of the monobromide **3**.



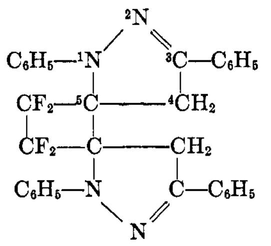
All efforts to obtain Diels–Alder adducts of the dienes **2a** and **5** with a variety of dienophiles have been unsuccessful. However, both dienes undergo 1,3-dipolar addition with diphenylnitrilimine to form crystalline adducts. Diene **2a** gives a 1:2 mole adduct **6** and diene **5** a 1:1 mole adduct **7** (7.5 and 29% yield, respectively). The addition reactions are carried out in

$$2a + 2C_6H_5C{\equiv}NNC_6H_5 \longrightarrow \underset{6}{C_{32}H_{24}N_4F_4}$$

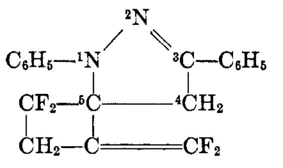
$$5 + C_6H_5C{\equiv}NNC_6H_5 \longrightarrow \underset{7}{C_{19}H_{14}N_2F_4}$$

refluxing benzene with the reagent, diphenylnitrilimine, generated *in situ* by dehydrochlorination of benzoyl chloride phenylhydrazone with triethylamine.[6] The adduct **7** is readily isolated from the reaction mixture by crystallization, whereas chromatography on silica gel is required to obtain the pure adduct **6**.

Generally, the addition of diphenylnitrilimine is a *cis* addition which gives 1,3-diphenyl-Δ^2-pyrazolines. According to Huisgen's studies, orientation in the addition product is such that the more highly substituted olefinic carbon atom becomes attached to the imine nitrogen of the adding reagent.[6] Accordingly, the adduct derived from the diene **2a** should have the structure **6** while the formulation **7** represents the adduct from the diene **5**.



6



7

The pmr absorption spectra of the two 1,3-dipolar adducts support the structural formulations **6** and **7**. The adduct **6** shows a phenyl grouping at τ 2.5–3 (5) and a singlet at 6.47 (1); the spectrum of adduct **7** has a phenyl grouping at τ 2.2–3.0 (10), a broad multiplet at 6.79 (2), and two singlets at 6.24 (1) and 6.47 (1) for the hydrogen atoms at the 4 position. The chemical shifts for the methylene protons attached to the 4 positions of the pyrazoline rings are consistent with those observed for the corresponding protons in the model compound, 1,3,5-triphenyl-Δ^2-pyrazoline, which appear at τ 6.31 and 7.05.[7]

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[4] D. D. Coffman, E. I. du Pont de Nemours and Co., Wilmington, Del., provided this spectrum.

[5] W. H. Knoth and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 3873 (1960).

[6] R. Huisgen, M. Seidel, G. Wollbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).

[7] Private communication from Dr. A. Hasner, University of Colorado, Boulder, Colo.

Experimental Section[8]

Pyrolysis of 1-Bromomethyl-2-methyltetrafluoro-1-cyclobutene (3).—Pyrolysis of the monobromide **3** was carried out at 35 mm with a continuous nitrogen sweep in the fast-flow apparatus previously described.[1] The sample flask, fitted with a nitrogen inlet capillary tube and containing the bromide **3**, was kept at room temperature throughout the pyrolysis. The two liquid nitrogen traps used to collect the total pyrolysate were warmed separately after completion of the pyrolysis and the hydrobromic acid vapor was passed into a solution of 4.38 g (0.0258 mole) of silver nitrate in 300 ml of water. The precipitated silver bromide was collected, dried *in vacuo* at 100° for 4 hr, and weighed. The water-insoluble organic phase that remained in the pyrolysis traps was transferred to a distillation flask containing hydroquinone and calcium chloride, and attached to a U tube trap, also containing a small amount of hydroquinone. With the trap cooled by liquid nitrogen, the system was evacuated and the material boiling up to room temperature at 5 mm was collected.

In a typical pyrolysis 7.00 g (0.30 mole) of the monobromide **3** was pyrolyzed at 630° over a 41-min period to give a total of 3.70 g of crude, water-washed pyrolysate free of hydrogen bromide. There was obtained, in addition, 2.12 g (71% conversion) of silver bromide as described above. The volatile portion of the crude pyrolysate amounted to 2.54 g (68.7% of the crude pyrolysate); the nonvolatile residue was a dark, viscous oil. The volatile fraction, kept at −80° to minimize polymerization, was examined by vpc under the following conditions: Aerograph A-90-P_2; column temperature, 70°; column 10 ft × $^1/_8$ in., 30% six-ring polyphenyl ether on 80–100 mesh Chrom P; injector temperature, 180°; detector temperature, 260°; flow rate, 80 ml/min. Three components were observed; they comprised the dienes **5** and **2a**, and the cyclobutene **4** (in order of retention times). All three products were collected by preparative vpc using 130-μl injections. The yields of the isolated dienes **2a** and **5** were 0.308 g (0.00202 mole, 6.7%) and 0.585 g (0.00385 mole, 12.87%), respectively. Subsequent studies showed that optimum resolution of the dienes could be achieved with a 10 ft × $^3/_8$ in. column containing 30% GE-SF-96 Si oil on 80–100 mesh Chrom P.

Refractive index measurements of the dienes were made as rapidly as possible on freshly isolated material. The values obtained were $n^{22.5}{}_D$ 1.3792 and 1.3786 for the dienes **2a** and **5**, respectively. However, these values may not be reliable since the dienes polymerize rapidly at room temperature. Elemental analyses were carried out on the respective polymers.

Anal. Calcd for $(C_6H_4F_4)_n$: C, 47.37; H, 2.65; F, 50.00. Found for diene **5**: C, 47.43; H, 2.63; F, 49.90. Found for diene **2a**: C, 46.99; H, 2.69; F, 47.94.

Hydrobromination of 1,2-Dimethylenetetrafluorocyclobutane (2a).—A mechanically sealed tube, charged at −80° with 4 ml of liquid hydrogen bromide and 0.5053 g (0.00331 mole) of the diene **2a**, was maintained at room temperature for 24 hr. The tube was then cooled to −80° and opened, and the hydrogen bromide was allowed to boil away as the sample gradually reached room temperature. The liquid residue was washed with water and dried over calcium chloride. A total of 0.5077 g of crude product was obtained which was examined by vpc under the following conditions: Aerograph A-90-P_2; column, 10 ft × $^3/_8$ in., 30% six-ring polyphenyl ether on 80–100 mesh Chrom P; column temperature, 115°; injector temperature, 225°; detector temperature, 240°; He flow rate, 150 ml/min; sample volume, 3 μl. Two components were observed, and the component with the longest retention time was identified by its infrared spectrum which was identical with that of authentic 1-bromomethyl-2-methyltetrafluorocyclobutene (**3**).

The concentration of the monobromide **3** in the reaction mixture was determined by vpc employing the calibrated response of the instrument determined with pure monobromide. It was found that 0.195 g (9.37 × 10^{-4} mole) was present (25.3% yield).

Preparation of the Adduct 6.[6]—A stirred solution containing 0.55 g (0.0037 mole) of the diene **2a**, 0.75 g (0.0032 mole) of benzoyl chloride phenylhydrazone, and a trace of hydroquinone in 7 ml of benzene was heated to reflux. To this solution was added 1.5 ml of triethylamine. An immediate reaction took place as indicated by darkening of the solution and the precipitation of triethylamine hydrochloride. The mixture was stirred at reflux for 1 hr, cooled to room temperature, and filtered.

Benzene was removed by a rotary evaporator and a dark, viscous oil remained. The oil was dissolved in a minimum amount of chloroform and deposited on a column packed with 42 g of 60–200 mesh silica gel (grade 950, Will Corp.). Elution was carried out with chloroform.

The first fraction was a yellow-brown oil (0.48 g) which would not crystallize from an ethanol–water mixture. The second fraction was a light red oil which gave white, hairlike crystals. Crystallization was carried out three times by dissolving the solid in boiling ethanol and adding water until the solution became turbid. After drying at 40° (2 mm) for 2 hr, there was obtained 0.066 g (1.22 × 10^{-4} mole) of the adduct **6** (7.5%), mp 175°.

Anal. Calcd for $C_{32}H_{24}N_4F_4$: C, 71.09; H, 4.48; F, 14.07; mol wt, 540. Found: C, 70.88; H, 4.41; F, 13.92; mol wt, 553 (Rast).

Preparation of the Adduct 7.—According to the above procedure, 1.47 g (0.00967 mole) of the diene **5** and 1.96 g (0.00839 mole) of benzoyl chloride phenylhydrazone in 15 ml of benzene was treated with 4 ml of triethylamine. Removal of benzene gave a viscous oil which crystallized immediately upon addition of a small amount of ethanol. The mother liquor was heated to boiling, and water was added until the solution became turbid. No further crystalline material was recovered.

The solid was dissolved in boiling 95% ethanol and treated with water until turbid. A crystalline solid was obtained which was recrystallized twice to give 0.84 g (0.00243 mole) of the adduct **7** (29.0%), mp 96–97.5°. Further recrystallization resulted in little change in the melting point (96.5–97.5°).

Anal. Calcd for $C_{19}H_{14}N_2F_4$: C, 65.88; H, 4.08; F, 21.96. Found: 65.91; H, 4.06; F, 21.78.

Registry No.—**2a**, 7704-59-8; **5**, 2557-72-4; **4**, 356-58-1; **6**, 7704-61-2; **7**, 7704-62-3.

Acknowledgment.—This work was supported by funds provided by the B. F. Goodrich Co., for which the authors are grateful. The authors also wish to thank Professor R. F. Porter, Cornell University, and D. Harvey of the B. F. Goodrich Research Center, for performing the mass spectrometric analyses.

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