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

1,1-Difluoroallene[1]

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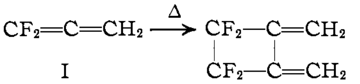
1,1-Difluoroallene has been prepared using, as starting material, 1,3-dibromo-1,1-difluoropropane obtained from the free adical-catalyzed addition of dibromodifluoromethane to ethylene. The structure of the allenic product was confirmed by its chemical and physical properties, including its infrared and mass spectra. 1,1-Difluoroallene slowly polymerizes at room temperature and under pressure to give a clear, colorless, viscous liquid.

The thermal dimerization of allene has been shown to yield the conjugated exocyclic diene, 1,2-dimethylenecyclobutane.[3] Persulfate-initiated polymerization of this diene gave a rubber-like high polymer with a preponderance of *cis*-1,4-units.[4] The unique properties of this parent exocyclic diene encouraged us to examine some of its polyfluoro derivatives. One such derivative, 1,2-dimethyleneperfluorocyclobutane, could be obtained from the "head-to-head" dimerization of 1,1-difluoroallene (I).



The remarkable stability and ease of formation of fluorocyclobutanes would be expected to favor the dimerization of I relative to that of allene.[5] Also, thermal dimerization of polyfluoroethylenes has been shown to give exclusively "head-to-head" cyclizations.[6]

The pyrolysis of 1-methylene-2,2,3,3-tetrafluorocyclobutane in a quartz tube at 800° and at pressures below 10 μ has been reported to give I and vinylidene fluoride as volatile products.[7] No boiling point was reported for I thus obtained and it was described as a gas with a very strong infrared absorption at 4.95 μ. A more convenient laboratory synthesis for the desired fluoroallene was sought for our investigations and is reported here as

$$\underset{\text{II}}{CF_2BrCH_2CH_2Br} \longrightarrow \underset{\text{III}}{CF_2BrCH{=}CH_2} \longrightarrow$$
$$\underset{\text{V}}{CF_2BrCHBrCH_2Br} \longrightarrow \underset{\text{IV}}{CF_2BrCBr{=}CH_2} \longrightarrow$$
$$\underset{\text{I}}{CF_2{=}C{=}CH_2}$$

1,3-Dibromo-1,1-difluoropropane (II) was obtained in about 50% yield (38% conversion) from the free radical-catalyzed addition of dibromodifluoromethane to ethylene. Dehydrobromination of II with aqueous potassium hydroxide gave 3-bromo-3,3-difluoropropene (III) (60%). Photobromination of III gave 1,2,3-tribromo-1,1-difluoropropane (IV) (86%). Dehydrobromination of IV can yield three isomeric olefins

$$\underset{\text{V}}{CF_2BrCBr{=}CH_2} \qquad \underset{\text{VI}}{CF_2{=}CBrCH_2Br} \qquad \underset{\text{VII}}{CF_2BrCH{=}CHBr}$$

It is well known that both the halogen, X, in the group $-CF_2X$ and the halogen on a carbon atom adjacent to a fluorine-substituted carbon are of reduced reactivity.[8] The latter is probably due to the increased acidity of a hydrogen alpha to the fluorine-substituted carbon atom which facilitates its removal in nucleophilic attack. In view of the above considerations, isomer V would clearly be the expected olefin. The boiling point of V may be predicted with a fair degree of accuracy. Substitution of a bromine atom for a chlorine atom in fluorohalopropenes and propanes increases the boiling point by *ca.* 21°. For example[9]

$CF_2ClCH_2CH_2Cl$ b.p. 81°	$\longrightarrow$	$CF_2ClCH_2CH_2Br$ b.p. 100°	$\Delta T = 19°$
$CF_2ClCH_2CH_2Br$	$\longrightarrow$	$CF_2BrCH_2CH_2Br$[10] b.p. 122°	$\Delta T = 22°$
$CF_2ClCCl{=}CH_2$ b.p. 58°	$\longrightarrow$	$CF_2ClCBr{=}CH_2$ b.p. 79°	$\Delta T = 21°$
$CF_2ClCBr{=}CH_2$	$\longrightarrow$	$CF_2BrCBr{=}CH_2$[10] (V) b.p. 101°	$\Delta T = 22°$

On this basis, the olefin V should boil at *ca.* 100°. The boiling point of V prepared here was found to be 101°, in good agreement with the expected value. Also, the boiling points of isomeric fluorohalopropenes and propanes are lower when the fluorine and halogen atoms are concentrated at one end of the molecule or on the least number of carbon atoms.[9] Thus the other two possible isomers of V, $CF_2{=}CBrCH_2Br$ and $CF_2BrCH{=}CHBr$, would be expected to boil higher than *ca.* 100° (*ca.* 15–30° higher). When V was treated with antimony trifluoride, the allylic bromine was replaced readily by fluorine to give the known olefin, 2-bromo-1,1,1-trifluoropropene (VIII). The formation of VIII identifies conclusively the structure of V.

Debromination of V with zinc in refluxing ethanol occurred readily to give the fluoroallene I, b.p. −21° (56%). The infrared absorption spectrum of the gas confirmed the allenic structure. In addition to the expected carbon–fluorine and carbon–hydrogen peaks, strong absorption was observed at 4.95 μ which may be assigned to double bond stretching in an allenic system. Allene itself absorbs at 5.13 μ. The presence of fluorine on the allenic carbon atoms shifts the peak to the observed higher frequency (perfluoroallene absorbs at 4.87 μ).[11] The absence of the triple bond absorption at 4.6 μ excludes the possibility that the gaseous product is an acetylenic isomer of the expected allene. Chemical evidence for the allenic

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[1] The work reported here was supported in part by the B. F. Goodrich Co.

[2] E. I. du Pont Teaching Fellow, 1956–1957.

[3] A. T. Blomquist and J. A. Verdol, THIS JOURNAL, **78**, 109 (1956).

[4] A. T. Blomquist and J. A. Verdol, *ibid.*, **77**, 1806 (1955).

[5] *Cf.* D. D. Coffmann, P. L. Barrick, R. D. Cramer and M. S. Raasch, *ibid.*, **71**, 490 (1949).

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

[7] U. S. Patent 2,733,278; *C. A.*, **50**, 15,575 (1956).

[8] J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1954, p. 219.

[9] *Cf.* R. N. Haszeldine, *J. Chem. Soc.*, 3371 (1953).

[10] This work.

[11] T. L. Jacobs and R. S. Bauer, THIS JOURNAL, **78**, 4815 (1956)

structure was conclusive. Addition of bromine to I at −80° took place vigorously to give its precursor, V.

The mass spectrum of I showed the following mass to charge peaks with percentage intensities relative to the parent peak: *26* (C_2H_2), 14%; *31* (CF), 40%; *37* (C_3H), 5%; *50* (CF_2) 5%; *55* (C_3F), 4%; *56* (C_3FH), 8%; *57* (C_3FH_2) 27%; *74* (C_3F_2), 4%; *75* (C_3F_2H), 60%; *76* ($C_3F_2H_2$), 100%. No peaks were observed above 76.

At room temperature, under pressure and absence of oxygen, 1,1-difluoroallene slowly polymerizes to a water-white viscous liquid.

Experimental Part

1,3-Dibromo-1,1-difluoropropane (II).[12]—A two-liter stainless steel autoclave was charged with 2270 g. (10.8 moles) of dibromodifluoromethane and 50 g. of benzoyl peroxide. The autoclave was then assembled and purged with ethylene, 100 p.s.i. and pressured with ethylene, 100 p.s.i. Heat was applied and reached 65° in 35 minutes at which point pressure had risen to 150 p.s.i. Heating was discontinued and about 20 minutes later the temperature was 95° and the pressure 85 p.s.i. When the temperature had dropped to 80° and the pressure to 70 p.s.i., the heat control was set for 90° and ethylene pressurized to 200 p.s.i. and so maintained for 24 hr. This time limit was purely arbitrary.

The charge was removed and II flash distilled at 50 mm., b.p. 58–65°. The crude material was fractionated to give pure II (38% conversion, 50% yield), b.p. 81.5–82.0° (173 mm.), n^{25}_D 1.4467, d^{25}_4 2.0262; M_D calcd. for $C_3H_4Br_2F_2$ 31.36, found 31.37 (reported[13] b.p. 62° (86 mm.), n^{25}_D 1.4450, d^{25}_4 2.0353).

3-Bromo-3,3-difluoropropene (III).—Into 200 cc. of 15 *M* aqueous potassium hydroxide at 80° was added dropwise 116.8 g. (0.491 mole) of II with vigorous stirring. During addition crude product distilled at 42–52°. The distillate contained some water which was separated from the lower oil layer. The latter was dried over magnesium sulfate and distilled to give 46.5 g. (60%) of pure III, b.p. 41–42°, n^{25}_D 1.3786 (reported[14] b.p. 42°, n^{25}_D 1.3773).

1,2,3-Tribromo-1,1-difluoropropane (IV).—To 92.0 g. (0.586 mole) of III at the reflux temperature was added dropwise the stoichiometric amount of bromine. The reaction flask was illuminated with two General Electric blue light lamps. After a short induction period bromine absorption was rapid. The reaction charge was washed with 10 ml. of 5% sodium sulfite solution to remove residual bromine. The oil layer, which was milky white, was dried over calcium sulfate to give a clear liquid which was then distilled to give pure IV, 158.9 g. (86%), b.p. 78.5–79.0° (25 mm.), n^{25}_D 1.5035, d^{25}_4 2.4081; M_D calcd. for $C_3H_3Br_3F_2$ 39.12; found 39.04.

Anal. Calcd. for $C_3H_3Br_3F_2$: Br, 75.68. Found: Br, 75.34.

1,2-Dibromo-1,1-difluoropropene (V).—To 44.5 g. (0.140 mole) of IV at 0° was added dropwise ice-cold 10% potassium hydroxide in 95% ethanol (10% excess) with vigorous stirring. After total addition of base, the mixture was stirred vigorously for an additional 2 hr. at 0°. Excess water was then added to dissolve potassium bromide and separate out the oil layer (bottom). The oil layer was drawn off, washed with water, dried over magnesium sulfate and distilled to give 20.5 g. (62%) of pure V, b.p. 100–101°, 65–66° (148 mm.), n^{25}_D 1.4498.

Anal. Calcd. for $C_3H_2Br_2F_2$: C, 15.27; H, 0.86; Br, 67.76. Found: C, 15.50; H, 1.00; Br, 67.86.

2-Bromo-1,1,1-trifluoropropene (VIII).—To a mixture of 10 g. of antimony trifluoride and 2 g. of antimony pentachloride at 90° was added dropwise 14.0 g. (0.059 mole) of V. Product vapor came off at 35–50° and after distilling gave 5.0 g. of pure VIII, b.p. 33.5–34.5°, n^{25}_D 1.3519 (reported[15] b.p. 33.0–33.5°, n^{25}_D 1.3503).

Anal. Calcd. for $C_3H_2BrF_3$: C, 20.59; H, 1.15; Br, 45.68. Found: C, 20.67; H, 1.19; Br, 45.83.

1,1-Difluoroallene (I).—In a 100-ml., three-necked flask equipped with stirrer, reflux condenser and dropping funnel was placed 40 g. of zinc dust in 40 ml. of abs. ethanol. The condenser outlet led to a series of traps immersed in Dry Ice. After heating the mixture to gentle reflux of alcohol, 20.3 g. (0.0852 mole) of V in 30 ml. of 95% ethanol was added slowly over a 2 hr. period. Formation of a gaseous product was immediate and after total addition of olefin solution no additional product was evolved on continued heating. The gas was purified by several vaporization distillations to give 3.6 g. (56%) of product, b.p. −21 to −20° (thermocouple immersion).

Bromination of I.—To 3 g. (0.04 mole) of I condensed in a test-tube at −80° was added dropwise one equivalent of chilled bromine. Decolorization was immediate and reaction very vigorous with some loss of material due to spattering. The product formed was V as shown by refractive index and infrared spectrum which was identical in all respects with authentic V.

Infrared Spectra.—Spectra were taken with a Perkin-Elmer model 21 instrument, liquids as films on sodium chloride plates and gases in a 10-cm. gas cell: w = weak, m = medium, s = strong, vs = very strong.

1,3-Dibromo-1,1-difluoropropane(II)

3.32w	8.61vs	10.96vs
6.90, 6.97m	9.07vs	12.09m
7.43s	9.36s	12.63w
7.77s	9.58s	12.96w
8.05, 8.11s	9.87vs	13.55w
8.39vs	10.54s	14.68m

3-Bromo-3,3-difluoropropene (III) (at 20 and 62 mm.)

3.21w	7.04s	9.07s
3.32w	7.41, 7.44m	9.82s
4.44w	7.75m	10.6vs, broad
5.25m	8.10vs	13.48s, broad
5.74s	8.43s	
6.07w	8.83vs	

1,2,3-Tribromo-1,1-difluoropropane (IV)

3.29w	8.83s	11.19m
3.37w	8.99vs	11.42s
7.00m	9.26m	11.57m
7.59s	9.13m	11.87m
8.12s	9.29m	13.03s
8.38s	9.94vs	14.22m
8.62s	10.63vs	14.57m

1,2-Dibromo-1,1-difluoropropene (V)

3.24w	8.17m	10.75vs, broad
5.71w	8.30m	13.10m
6.13m	8.88s	14.58m
7.14w	9.33vs	

1,1-Difluoroallene (I) (10 and 276 mm.)

3.04w	5.45w	10.08m
3.28, 3.36, 3.44m	5.70w	10.70s
3.58w	6.18w	10.87s
3.95w	6.60m	11.41, 11.50, 11.60, 11.71, 11.82w
4.10m	6.72, 6.76, 6.80vs	
4.32w	7.17m	
4.41w	7.47, 7.52, 7.57vs	12.34s
4.72m	8.02, 8.12vs	12.47s
4.95vs	9.90m	14.97w

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[12] We are indebted to the Organic Chemicals Research Department of B. F. Goodrich Co. for carrying out this reaction.

[13] P. Tarrant and A. M. Lovelace, THIS JOURNAL, **76**, 3466 (1954).

[14] P. Tarrant, A. M. Lovelace and M. R. Lilyquist, *ibid.*, **77**, 2783 (1955).

[15] A. L. Henne and M. Nager, *ibid.*, **73**, 1042 (1951).