nitrogen traps were attached to the system, nitrous oxide, identified by its characteristic infrared absorption at 4.5 μ, was also found as a product. Methyl benzoate was found in the filtrate from the recrystallization above.

When the reaction was repeated in tetrahydrofuran using sodium hydride as base, the yield of hydroxamic ester was increased to 82%.

Reaction of Nitro Compounds with Perchloryl Fluoride. **α-Phenylnitroethane.**—A solution of 6.6 g. (0.044 mole) of α-phenylnitroethane (prepared by the oxidation of acetophenone oxime[23]) in 50 ml. of tetrahydrofuran was added to a suspension of 1.2 g. (0.05 mole) of sodium hydride in 100 ml. of THF. This mixture was stirred under reflux for 30 min. It was then cooled to 0° and perchloryl fluoride was bubbled through at 0–16° for an hour. The mixture was then poured into water and worked up in the usual way **α-Fluoro-α-phenylnitroethane** (6.6 g., 82%) was obtained by distillation, b.p. 42–43° (0.5 mm.). Redistillation yielded an analytical sample, b.p. 46.5° (0.2 mm.), $n^{20}\text{D}$ 1.4996.

Anal. Calcd. for $C_8H_8FNO_2$: C, 56.81; H, 4.76; N, 8.28. Found: C, 56.73; H, 4.82; N, 8.34.

α-Nitro-α-phenylacetophenone.[24]—In the same manner a mixture of 1.1 g. (0.005 mole) of nitro compound and 0.2 g. (0.005 mole) of sodium hydride was treated with perchloryl fluoride. **α-Fluoro-α-nitro-α-phenylacetophenone** was obtained as a white solid, m.p. 74–76° (from ligroin); infrared spectrum: ν_{co}, 1695 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{10}FNO_3$: C, 64.86; H, 3.89; N, 5.40. Found: C, 64.78; H, 4.15; N, 5.37.

Diethyl Nitromalonate.—A solution of 8 g. (0.037 mole) of potassium diethyl nitromalonate in 150 ml. of dimethylformamide was treated with perchloryl fluoride at 0–15° for an hour. It was worked up in the usual way and 6.0 g. (80%) of diethyl fluoronitromalonate, identical with that prepared from diethyl oximinomalonate, was obtained.

5-Nitro-6-phenylnorbornene.—The nitro compound was prepared by the condensation of cyclopentadiene and β-nitrostyrene.[25] A mixture of 20 g. (0.1 mole) of nitro compound and 2.4 g. (0.1 mole) of sodium hydride in 250 ml. of THF was treated as described above. The crude product, 22.3 g., was chromatographed on silica in the usual manner. **5-Fluoro-5-nitro-6-phenylnorbornene** was eluted as a yellow oil with 1:1 ligroin–methylene chloride; yield 15.2 g. (70%). Distillation produced an analytical sample, b.p. 109–110° (0.05 mm.), $n^{20}\text{D}$ 1.5457.

Anal. Calcd. for $C_{13}H_{12}FNO_2$: C, 66.94; H, 5.19; N, 6.01; F, 8.15. Found: C, 67.14; H, 5.22; N, 6.20; F, 8.78.

Methylene chloride eluted 0.65 g. (3.5%) of **6-phenyl-5-ketonorbornene** ($\nu_{C=O}$ 1740 cm.$^{-1}$) which was converted to its orange dinitrophenylhydrazone, m.p. 174–176° dec. (from ethanol).

Anal. Calcd. for $C_{19}H_{16}N_4O_4$: C, 62.63; H, 4.43; N, 15.38. Found: C, 62.49; H, 4.79; N, 14.97.

Reduction of 4.6 g. of 5-fluoro-5-nitro-6-phenylnorbornene with iron in acetic acid produced 1.1 g. of 6-phenyl-5-ketonorbornene identified by comparison of its dinitrophenylhydrazone with that above.

2-Nitro-3-phenylnorbornane[9] was fluorinated in the same manner. From 4.4 g. of nitro compound was obtained 1.9 g. (40%) of colorless **2-fluoro-2-nitro-3-phenylnorbornane**, b.p. 101–105° (0.05 mm.), $n^{20}\text{D}$ 1.5341, by chromatography.

Anal. Calcd. for $C_{13}H_{14}FNO_2$: C, 66.37; H, 6.00; N, 5.95. Found: C, 66.40; H, 6.36; N, 5.76.

There was also obtained 0.25 g. (7%) of **phenylnorcamphor**, identified as its dinitrophenylhydrazone, m.p. 162–165° (lit.[9] m.p. 165–166°).

Catalytic reduction at atmospheric pressure of 2.46 g. of 5-fluoro-5-nitro-6-phenylnorbornene in 20 ml. of glacial acetic acid containing 0.08 g. of platinum oxide yielded 1.9 g. of 2-fluoro-2-nitro-3-phenylnorbornane identical to that prepared above.

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[23] W. D. Emmons and A. S. Pagano, THIS JOURNAL, **77**, 4557 (1955).

[24] This sample was generously provided by Dr. Travis E. Stevens; *cf.* T. E. Stevens, *ibid.*, **81**, 3593 (1959).

[25] W. E. Parham, W. T. Hunter and R. Hanson, *ibid.*, **73**, 5068 (1951).

HUNTSVILLE, ALA.

[CONTRIBUTION NO. 581 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Synthesis and Chemistry of 1,1-Difluoroallene

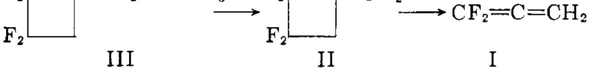
BY W. H. KNOTH AND D. D. COFFMAN

RECEIVED JANUARY 6, 1960

A convenient two-step synthesis of 1,1-difluoroallene has been found in the pyrolysis of 1-acetoxymethyl-2,2,3,3-tetrafluorocyclobutane obtained by cycloaddition of tetrafluoroethylene to allyl acetate. 1,1-Difluoroallene was converted to a dimer which polymerized spontaneously. The allene also reacted with acrylonitrile, maleic anhydride and ethyl azodiformate to form cyclobutanes and with cyclopentadiene to give a Diels–Alder adduct.

1,1-Difluoroallene (I) has been prepared by pyrolysis of 1-methylene - 2,2,3,3 - tetrafluorocyclobutane[1] (II) derived from tetrafluoroethylene and allene.[2] It has also been prepared from ethylene and dibromodifluoromethane in five steps by Blomquist and Longone.[3]

A convenient two-step synthesis of 1,1-difluoroallene has now been found in the pyrolysis of 1-acetoxymethyl-2,2,3,3-tetrafluorocyclobutane (III) prepared in 65–75% yield from allyl acetate and tetrafluoroethylene. Use of the acetoxymethylcyclobutane III in the pyrolysis provides a real advantage over the route from methylenetetrafluorocyclobutane[1] II since the acetoxymethylcyclobutane III can be obtained in yields about fourfold greater than those realized in the preparation of the methylenetetrafluorocyclobutane II. Pyrolysis of either the acetoxymethyltetrafluorocyclobutane (III) or the methylenetetrafluorocyclobutane II[2] at 800–950° gave 1,1-difluoroallene in yields ranging from 25–40%. The methylenetetrafluorocyclobutane II was a by-product in the pyrolysis of the acetoxytetrafluorocyclobutane III and was present in the crude pyrolyzate along with 1,1-difluoroallene.



III II I

1,1-Difluoroallene is a versatile compound which

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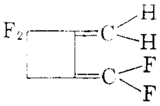
[1] J. L. Anderson, U.S. Patent 2,733,278 (1956).

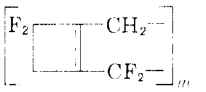
[2] D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949).

[3] A. T. Blomquist and D. L. Longone, *ibid.*, **79**, 4981 (1957).

displays some of the characteristics of allene[4,6] and of tetrafluoroethylene.[2,5] A dimer was obtained in 25–35% yield when 1,1-difluoroallene was passed through a quartz tube heated to 260–298°. The dimer polymerized spontaneously and completely in about an hour under ordinary conditions but could be stabilized by phenothiazine. The infrared spectrum of the dimer had bands at 5.65 μ for $CF_2=$ and at 5.95 and 11.3 μ for $CH_2=$. Nuclear magnetic resonance studies indicated the presence of two main types of fluorine in 1:1 ratio. One type was split into a weak-strong-strong-weak pattern indicating nearby asymmetry. This is in agreement with the structure 1,1-difluoro-2-methylene-3-difluoromethylenecyclobutane (IV). Further evidence for structure IV is found in the infrared spectrum of the polymer from the dimer. This spectrum contained a 5.9 μ band for C=C but showed no absorption in the 11.3 μ range for a terminal methylene group nor any indication of a terminal $CF_2=$ group. Thus, the spectrum of the polymer corresponds to that of structure V, which could be formed from the dimer IV by 1,4-polymerization. The polymer V, which was hard and colorless, softened at about 140° and could be hot-pressed at this temperature into clear, flexible films which were not attacked by boiling nitric acid.

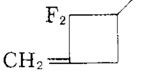


IV

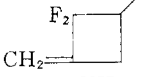


V

Like allene[6] and tetrafluoroethylene,[2] 1,1-difluoroallene also forms cyclobutanes by cycloaddition to certain unsaturated compounds. At 120–150° and autogenous pressure, 1,1-difluoroallene yields 1:1 cycloadducts with acrylonitrile, maleic anhydride and ethyl azodiformate. Infrared and nuclear magnetic resonance analyses indicate the adduct with acrylonitrile to be a mixture of VI with an isomer which contains a difluoromethylene group. However, hydrolysis of the mixture gave an almost pure compound of composition and spectral characteristics corresponding to 2,2-difluoro-3-methylenecyclobutanecarboxylic acid (VII). This acid had proton magnetic resonance peaks at +259, +30, −54 and −89 c.p.s. (referred to water) for COOH, $=CH_2$, CH and CH_2, respectively. The fluorine magnetic resonance spectrum had a weak-strong-strong-weak combination of peaks at −364, −568, −836 and −1040 c.p.s., using trifluoroacetic acid as a reference. This indicated that the fluorines are non-equivalent because of nearby asymmetry. These data fit structure VII in which the fluorine resonance would be split by the asymmetry due to the adjacent CHCOOH group.

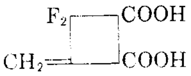


VI

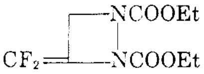


VII

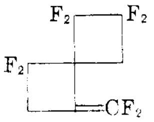
The 1,1-difluoroallene–maleic anhydride adduct was not isolated but was hydrolyzed immediately to obtain a dicarboxylic acid mixture which was predominantly compound VIII. The fluorine magnetic resonance was split into a weak-strong-strong-weak pattern which required the CF_2 group to be adjacent to the CHCOOH grouping. The adduct of 1,1-difluoroallene with ethyl azodiformate, on the other hand, showed only a single peak in its fluorine magnetic resonance and had no peak for $=CH_2$ in its proton magnetic resonance spectrum. Therefore, the structure is believed to be IX.



VIII



IX



X

The cycloaddition of 1,1-difluoroallene to tetrafluoroethylene gave an adduct composed of 2 moles of 1,1-difluoroallene and 1 mole of tetrafluoroethylene. Proton magnetic resonance analysis of this adduct showed the absence of terminal methylene unsaturation. Other spectral studies have been inconclusive. Structure X has been tentatively assigned to this adduct on the assumption that the difluoroallene dimer IV was an intermediate in its formation.

1,1-Difluoroallene also was found to be a potent dienophile. It reacted nearly quantitatively with cyclopentadiene to give a 1:1 Diels–Alder adduct. Comparison of the proton magnetic resonance spectrum of the adduct with the spectra of known compounds containing the [2.2.1]bicycloheptene ring system confirmed the Diels–Alder nature of the adduct. The infrared spectrum suggests the structure 5-difluoromethylene[2.2.1]bicyclo-2-heptene.

An examination of the possible explosion hazards involved in handling 1,1-difluoroallene has suggested that this diolefin is potentially more destructive than acetylene and should be handled with appropriate precautions. In brief tests, 1,1-difluoroallene was detonated by one no. 6 blasting cap and by a wire heated rapidly to about 270°. The total pressure rise in such detonations was comparable to that in an acetylene explosion but the rate of pressure buildup was more rapid with 1,1-difluoroallene.

Experimental

1-Acetoxymethyl-2,2,3,3-tetrafluorocyclobutane (III).—A pressure vessel was charged with allyl acetate (175 g., 1.75 moles) and tetrafluoroethylene (40 g., 0.40 mole) in the presence of small amounts of hydroquinone and Terpene B which were used as polymerization inhibitors. The vessel was heated to 215° for 3 hours under autogenous pressure. Distillation of the product gave 106 g. (66% yield) of 1-acetoxymethyl-2,2,3,3-tetrafluorocyclobutane, b.p. 121–123° (164 mm.), n^{25}D 1.3690. Yields of 65–75% were consistently obtained in this cyclobutane synthesis.

Anal. Calcd. for $C_7H_8F_4O_2$: C, 42.01; H, 4.03. Found: C, 42.15; H, 4.37.

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(4) A. T. Blomquist and J. A. Verdol, This Journal, **78**, 109 (1956). Allene dimer, 1,2-bis-(methylene)-cyclobutane, was prepared in a flow system at 500°.

(5) J. Harmon, U. S. Patent 2,404,374 (1946). Tetrafluoroethylene was dimerized to obtain octafluorocyclobutane.

(6) K. Alder and O. Ackerman, *Chem. Ber.*, **90**, 1697 (1957); H. N. Cripps, J. K. Williams and W. H. Sharkey, This Journal, **81**, 2723 (1959).

1,1-Difluoroallene (I). From 1-Acetoxymethyl-2,2,3,3-tetrafluorocyclobutane.—1-Acetoxymethyl-2,2,3,3-tetrafluorocyclobutane (III, 158 g., 0.79 mole) was passed dropwise at a rate of 35 g. per hour through a quartz tube which had a 28 cm. × 2 cm. i.d. section filled with quartz cylindrical packing and which was heated to 832–857°. The pressure was maintained at 0.7 to 1.3 mm., and the pyrolyzate was caught in a trap cooled in liquid nitrogen. Distillation of the product gave 19.0 g. (31.6% yield) of 1,1-difluoroallene, b.p. −27° (thermocouple immersion). 1-Methylene-2,2,3,3-tetrafluorocyclobutane (27 g. or 25% yield) and acetic acid (42 g., or 88% yield) also were formed. The 1,1-difluoroallene was identified by comparison of its various infrared absorption bands with the absorption wave lengths reported in the literature.[1,2] The yields of 1,1-difluoroallene obtained in a number of similar preparations ranged between 25 and 40%.

1,1-Difluoroallene. From 1-Methylene-2,2,3,3-tetrafluorocyclobutane.—1-Methylene-2,2,3,3-tetrafluorocyclobutane (II, 69 g., 0.49 mole) was passed dropwise at a rate of 2.7 g. per minute through the pyrolysis tube used in the above experiment. A temperature of 820° at 1 mm. pressure was maintained. Distillation of the pyrolyzate gave 8 g. (21% conversion, 27% yield) of 1,1-difluoroallene and 14.6 g. of recovered 1-methylene-2,2,3,3-tetrafluorocyclobutane.

1,1-Difluoro-2-methylene-3-difluoromethylenecyclobutane (Difluoroallene Dimer, IV).—The dimer was obtained by passage of 1,1-difluoroallene through a tube heated to 250–295°. This temperature is in the same region as the decomposition temperature of 1,1-difluoroallene (I), and frequently only decomposition products were obtained after short operating times. Flashing in the tube occurred infrequently but no explosions were experienced. In a typical experiment, 1,1-difluoroallene (I) was passed at a rate of 1 g. per minute through a 3 cm. i.d. Pyrex tube filled with quartz cylindrical packing of which an 84-cm. section was heated to 250–295°. After 21.5 g. of I had been passed, the reaction was discontinued because decomposition had started in the tube as shown by the formation of black tarry material. The pyrolyzate was collected in a trap which was cooled in liquid nitrogen and which contained 1 g. of phenothiazine to prevent polymerization of the dimer. Distillation of the crude product gave 6.4 g. (30% yield) of the dimer IV, b.p. 47–50° (300 mm.). In the absence of phenothiazine this dimer rapidly polymerized and it was analyzed as the polymer. The dimeric nature of the liquid product was inferred from its boiling point, 68–72°, which approximates the boiling point of allene dimer, 55–60°.[4]

Anal. Calcd. for $C_6H_4F_4$: C, 47.39; H, 2.66; F, 49.88. Found: C, 47.38; H, 2.85; F, 49.53.

1,1-Difluoroallene–Acrylonitrile Adduct (VI).—1,1-Difluoroallene (12.8 g., 0.17 mole), acrylonitrile (42 g., 0.8 mole), benzene (40 ml.) and hydroquinone (0.5 g.) were heated in an autoclave for 8 hours at 150°. Distillation gave 8.75 g. (43% yield) of a 1:1 difluoroallene–acrylonitrile adduct, b.p. 104–108° at 100 mm., $n^{28}D$ 1.4082–1.4120.

Anal. Calcd. for $C_6H_5F_2N$: C, 55.18; H, 3.88. Found: C, 55.27; H, 4.09.

2,2-Difluoro-3-methylenecyclobutanecarboxylic Acid (VII).—The 1,1-difluoroallene–acrylonitrile adduct VI (4.4 g., 0.034 mole) and concentrated hydrochloric acid (8 g.) were mixed and refluxed for 3 hours. The product was filtered, and the filtrate was extracted with ether. The extracts were dried and distilled to obtain 1.7 g. (34% yield) of 2,2-difluoro-3-methylenecyclobutanecarboxylic acid (b.p. 90–96° at 6 mm.) which solidified on standing; m.p. 35–40°.

Anal. Calcd. for $C_6H_6F_2O_2$: C, 48.66; H, 4.08; neut. equiv., 148. Found: C, 48.44; H, 4.20; neut. equiv., 144.

1,1-Difluoroallene–Maleic Anhydride Adduct and its Hydrolysis to 1,1-Difluoro-2-methylene-3,4-cyclobutanedicarboxylic Acid (VIII).—1,1-Difluoroallene (10 g., 0.13 mole), maleic anhydride (65 g., 0.66 mole), benzene (50 ml.) and hydroquinone (0.5 g.) were heated in an autoclave to 150° for 8 hours. Distillation gave 4.6 g. of a viscous yellow oil boiling at 112° (5.5 mm.). This adduct was heated on a steam-bath with 15 ml. of water until the mixture had become homogeneous. The water was evaporated to obtain a very viscous oil which crystallized reluctantly to a yellow solid, 3.6 g. (16% yield). This product was decolorized with charcoal in acetone solution to obtain a nearly colorless crystalline acid (VIII) that melted at 58–65°.

Anal. Calcd. for $C_7H_6F_2O_4$: C, 43.76; H, 3.15; neut. equiv., 96.1. Found: C, 43.16; H, 3.47; neut. equiv., 94.7.

1-Difluoromethylene-2,3-dicarbethoxy-2,3-diazacyclobutane (1,1-Difluoroallene–Ethyl Azodiformate Adduct, IX).—Ethyl azodiformate (54 g., 0.31 mole) and hydroquinone (0.5 g.) were charged into a Parr shaker bottle. This was flushed with nitrogen, evacuated and then pressured with 1,1-difluoroallene to 1.7 atm. and heated. At 120° an exothermic reaction commenced, and the temperature increased to 192°. Thirteen grams of 1,1-difluoroallene was absorbed in 35 minutes. Distillation gave 5.3 g. (6.8% yield) of the 1:1 difluoroallene–ethyl azodiformate adduct, b.p. 97° (1.4 mm.), $n^{26}D$ 1.4314.

Anal. Calcd. for $C_9H_{12}F_2N_2O_4$: C, 43.21; H, 4.84; N, 11.20; mol. wt., 250. Found: C, 44.02; H, 5.16; N, 11.15; mol. wt., 248.

1,1-Difluoroallene-Tetrafluoroethylene Adduct (X).—Tetrafluoroethylene (40 g., 0.4 mole), 1,1-difluoroallene (18 g., 0.24 mole) and hydroquinone (0.5 g.) were heated to 20° for 8 hours at autogenous pressure. Filtration and distillation of the reaction product gave 2.8 g. (9.2% yield) of a 2:1 difluoroallene–tetrafluoroethylene adduct, b.p. 118–124°.

Anal. Calcd. for $C_8H_4F_8$: C, 38.12; H, 1.52; mol. wt., 252. Found: C, 38.39; H, 1.89; mol. wt., 249.

1,1-Difluoroallene–Cyclopentadiene Adduct.[7]—Cyclopentadiene (100 g.) was stirred in a flask cooled by an ice-bath and fitted with a solid carbon dioxide condenser, thermometer and gas inlet tube. 1,1-Difluoroallene (23 g., 0.30 mole) was added through the gas inlet tube at a rate sufficient to keep the temperature near 20°. Distillation gave 39 g. (90% yield) of a 1:1 adduct, b.p. 117°.

Anal. Calcd. for $C_8H_8F_2$: F, 26.6. Found: F, 26.7.

Acknowledgments.—The authors thank Dr. Harlan Foster of this Laboratory for determining and interpreting the nuclear magnetic resonance spectra, and Mr. W. H. Johnson of the Explosives Department, E. I. du Pont de Nemours and Co., for ascertaining the explosion characteristics of 1,1-difluoroallene.

WILMINGTON, DEL.

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[7] We are indebted to Dr. D. C. England for this experiment.