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The Synthesis and Polymerization of 1,1,2,3-Tetrafluoro-1,3-butadiene[1,2]

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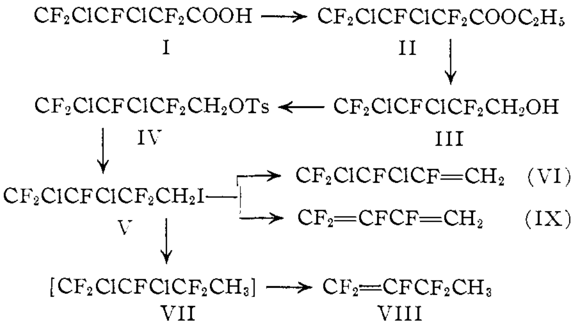
The synthesis and facile polymerization of the novel 1,1,2,3-tetrafluoro-1,3-butadiene are described.

Although considerable research has been carried out on dienes containing fluorine,[3] previous attempts to synthesize the much sought fluorocarbon diene monomer 1,1,2,3-tetrafluoro-1,3-butadiene, $CF_2{=}CFCF{=}CH_2$, bearing only a terminal $-CH_2$ group required for facile addition polymerization, have been unsuccessful.[4] It was predicted that this diene would readily form polymers of good thermal and oxidative stability since the residual double bond would be flanked by fluorines, *i.e.*, *via* 1,4-addition polymerization, $-(CF_2CF{=}CFCH_2)_n-$, and that the presence of a $-CH_2$ group in the polymer would improve the low temperature properties.[5]

We now wish to report the successful synthesis of 1,1,2,3-tetrafluoro-1,3-butadiene illustrated by the scheme.



Ethyl 3,4-dichloroperfluorobutyrate (II) was prepared in 88% conversion by conventional esterification of the acid I. Lithium aluminum hydride reduction of II afforded the alcohol III in 66% conversion. Preparation of the *p*-toluenesulfonate IV in 82% conversion was accomplished by the reaction of III with *p*-toluenesulfonyl chloride.[6] Reaction of the tosylate with excess sodium iodide in polyethylene glycol 200 gave 3,4-dichloro-1,1-dihydro-1-iodoperfluorobutane (V) in 54% conversion. A one-step dehalogenation of V involving concurrent loss of both chlorines and iodine + fluorine by the use of excess zinc in acetic acid resulted in a 54% conversion to 1,1,2,3-tetrafluorobutadiene (IX), b.p. −12° (300 mm.). In addition this reaction gave a 15% conversion to 3,4-dichloro-1,1-dihydroperfluorobutene-1 (VI), *i.e.*, the deiodofluorination product, one of the possible precursors of IX. Finally, there was an 11% conversion to the reduction product 3,3,3-trihydroperfluoro-1-butene (VIII). The failure to detect any of the other possible precursor of IX, *i.e.*, the dechlorination product $CF_2{=}CFCF_2CH_2I$, suggests that the main route to VIII is *via* VII, which represents reduction of the $-CH_2I$ group to $-CH_3$ as an initial side reaction.

While the structure of the tetrafluorodiene IX is unambiguously established by the mode of synthesis, its infrared spectrum furnishes additional support. The diene has the most intense double bond absorptions at 5.67 and at 6.05 μ. This is consistent with the assigned structure $CF_2{=}CFCF{=}CH_2$.[7] The two reported[5] isomers $CF_2{=}CFCH{=}CHF$, b.p. 16.5°, and $CF_2{=}CHCH{=}CF_2$, b.p. 7–8°, have bands at 5.62, 5.80, 6.02 μ for the former and at 5.85 μ for the latter. The absorption in IX at 11.76 μ with its typical three peaks, a major peak, and two side shoulders is assigned to the $-CH$ absorption in the $=CH_2$ group[8] and is consistent only with the 1,1,2,3-tetrafluorodiene isomer IX.

In contrast to the difficultly polymerizable perfluorobutadiene, the 1,1-dihydro analog IX polymerizes as predicted with great ease, even on standing at room temperature. Homopolymers were readily prepared by vinyl emulsion recipes and ultraviolet light activation, and were high melting, thermally stable strong elastomers. The fact that the only observable band in the C=C stretching vibration region of the infrared spectrum was at 5.8 μ is evidence that these polymerizations proceeded by 1,4-addition, *i.e.*, $-(CF_2CF{=}CFCH_2)_n-$. Various copolymers of IX with trifluoroethyl vinyl ether, perfluoropropene, 1-chloro-2,2-difluoroethylene and ethylene oxide[9] were prepared (see Experimental section).

Experimental

Ethyl 3,4-Dichloroperfluorobutyrate (II).—A solution of 400 g. of concentrated sulfuric acid and 325 g. of absolute ethanol was added while stirring and cooling to 865 g. (3.5 moles) of $CF_2ClCFClCF_2COOH$ (Kel-F Acid 452). The mixture was stirred at room temperature for 2 hr., allowed to stand overnight, and then refluxed for an additional 2.5 hr. The lower oil layer was separated, neutralized with so-

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[2] Presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 7 to 12, 1958.

[3] See, for example, P. Tarrant and M. R. Lilyquist, THIS JOURNAL, **77**, 3640 (1955).

[4] In this Laboratory several attempts at fluorinating $CF_2BrCFClCCl_2CH_2Cl$ to $CF_2BrCFClCFClCH_2Cl$ and $CF_2BrCFClCCl{=}CH_2$ to $CF_2BrCFClCFClCH_3$, obvious precursors of $CF_2{=}CF{-}CF{=}CH_2$, were unsuccessful.

[5] The preparation of the isomeric diene 1,1,2,4-tetrafluorobutadiene-1,3, $CF_2{=}CFCH{=}CHF$, has been reported by P. Tarrant and M. R. Lilyquist, THIS JOURNAL, **77**, 3640 (1955). Another isomer, 1,1,4,4-tetrafluorobutadiene-1,3, $CF_2{=}CHCH{=}CF_2$, has been reported by J. L. Anderson, U. S. Patent 2,743,303 (1956), and in British Patent 757,277.

[6] G. V. D. Tiers, H. A. Brown and T. S. Reid, THIS JOURNAL, **75**, 5978 (1953).

[7] $CF_2{=}CFCF{=}CF_2$ has its strongest double bond absorption at 5.66 μ. Also, the $-CF{=}CH_2$ stretching vibrations in the unconjugated olefins $CF_3CF{=}CH_2$ and $CF_2ClCFClCF{=}CH_2$, are at 5.89 and 5.95 μ, respectively.

[8] R. N. Haszeldine, private communication; $CF_3CF{=}CH_2$ has a similar band at 11.2 μ.

[9] See M. Hauptschein and J. M. Lesser, THIS JOURNAL, **78**, 676 (1956), for a description of the copolymerization of ethylene oxide with other highly fluorinated olefins

dium carbonate solution, washed with water and dried over anhydrous magnesium sulfate. (Additional product, which separated as a lower layer when the upper acid layer was added to 750 g. of ice, was added to the original oil layer.) On distillation there was obtained 845 g. (88%) of the ester II, b.p. 63–65° (20 mm.), middle cut b.p. 64° (20 mm.), $n^{30}\text{D}$ 1.3694.

Anal. Calcd. for $C_6H_5Cl_2F_5O_2$: C, 26.2; H, 1.8; F, 34.5. Found: C, 26.5; H, 1.6; F, 34.0.

Reaction of $CF_2ClCFClCF_2COOC_2H_5$ with Lithium Aluminum Hydride.—Four hundred and thirteen grams (1.5 moles) of II was dissolved in 200 ml. of anhydrous ether and added drop by drop at gentle reflux while stirring to 90 g. (95% pure, 2.25 moles) of lithium aluminum hydride in 1600 ml. of anhydrous ether during 4.5 hr. The mixture was stirred for one additional hour, cooled in an ice-bath, and cautiously decomposed by the dropwise addition of 110 ml. of water. It was then poured into 1500 ml. of ice-water and neutralized with 12 *N* sulfuric acid. The aqueous layer was separated, extracted with ether and the extract was combined with the organic layer from the reaction mixture. The combined material was washed with water, dried over anhydrous calcium sulfate and distilled. After removal of the ether there was obtained 20 g. of a low boiling fraction, b.p. 75–81°, and 16 g. of an intermediate cut boiling at 125–137°; both of these fractions were not further investigated. The principal product, the alcohol III (230 g., 66%), boiled at 63–67° at *ca.* 20 mm., $n^{25}\text{D}$ 1.3780. On refractionation at atmospheric pressure pure 3,4-dichloro-1,1-dihydroperfluorobutanol, b.p. 149–150°, $n^{23}\text{D}$ 1.3792, was obtained.

Anal. Calcd. for $C_4H_3Cl_2F_5O$: C, 20.6; H, 1.3; F, 40.8. Found: C, 20.9; H, 1.3; F, 40.4.

3,4-Dichloro-1,1-dihydroperfluorobutyl *p*-Toluenesulfonate (IV).—A solution of 8.2 g. of sodium hydroxide in 35 ml. of water was added dropwise to a stirred mixture of 38 g. (0.16 mole) of III and 38.1 g. of *p*-toluenesulfonyl chloride. The temperature was maintained at 50–55° during the addition and for 6 additional hours. The oil layer was separated, neutralized with concentrated ammonia, dried and filtered. The filtrate, after being heated at 110° at <1 mm., weighed 51 g. (82%). The tosylate IV is a colorless liquid, b.p. 130–131° (*ca.* 0.3 mm.), $n^{24}\text{D}$ 1.4698.

Anal. Calcd. for $C_{11}H_9Cl_2F_5O_3S$: C, 34.6; H, 2.2; Cl, 18.4. Found: C, 34.1; H, 2.3; Cl, 18.4.

3,4-Dichloro-1,1-dihydro-1-iodoperfluorobutane (V).—A solution of 126.5 g. (0.84 mole) of sodium iodide in 400 ml. of polyethylene glycol 200 (Carbide and Carbon Chemical Corp.) was added to 163 g. (0.42 mole) of IV. The mixture was refluxed while stirring for 10 hr. On distillation from the reaction flask at 80 mm. two layers boiling at 70–90° were obtained. The upper water-soluble glycol layer was discarded. The lower layer was dried and redistilled to give 78 g. (54%) of the iodide V, b.p. 86–91.5° (70 mm.), middle cut 86–87° (70 mm.), $n^{25}\text{D}$ 1.4397.

Anal. Calcd. for $C_4H_2Cl_2F_5I$: C, 14.0; H, 0.6; Cl, 20.7; I, 37.0. Found: C, 14.4; H, 0.7; Cl, 21.0; I, 37.4.

The Reaction of 3,4-Dichloro-1,1-dihydro-1-iodoperfluorobutane with Zinc and Acetic Acid.—Ninety-six grams (0.28 mole) of V was added slowly to a well stirred refluxing mixture of 325 g. of 30-mesh granular activated zinc, 480 ml. of glacial acetic acid and 1 g. of fused zinc chloride. The water-cooled condenser was connected at the outlet to a trap cooled in Dry Ice. After the addition was completed, the mixture was refluxed for 7.5 hr. The cold trap contained 35.5 g. of liquid which was rectified in a low temperature Podbielniak column (4.7 mm. × 38″) containing Heli-Grid packing. There were obtained: fraction A, 19 g. (54% conversion) of $CF_2{=}CFCF{=}CH_2$ (IX), b.p. −12° (300 mm.). *Anal.* Calcd. for $C_4H_2F_4$: C, 38.1; H, 1.6; mol. wt., 126. Found: C, 38.3; H, 1.8; mol. wt. (gas density balance), 126. Fraction B, 4.4 g. (11% conversion) of $CF_2{=}CFCF_2CH_3$ (VIII), b.p. 9° (333 mm.); mol. wt. calcd. for $C_4H_3F_5$ 146, found 146 (gas density balance). This compound has an intense band at 5.59 μ in the infrared. Fraction C, 8.4 g. (15% conversion) of $CF_2ClCFClCF{=}CH_2$ (VI), b.p. after refractionation 79°, $n^{19}\text{D}$ 1.3463. *Anal.* Calcd. for $C_4H_2Cl_2F_4$: C, 24.4; H, 1.0. Found: C, 24.0; H, 1.3. This compound has a strong band at 5.95 μ in the infrared spectrum.

General Polymerization Procedures.—The photochemical polymerizations were carried out in #7910 Vycor tubes of 30–50-ml. capacity placed 2 inches from a Hanovia Alpine Sun Lamp Type S-100. The tubes were cooled in liquid nitrogen, and evacuated after which the olefins were introduced by vacuum transfer, and the tubes were sealed *in vacuo*. After the exposure period, the contents of the tubes were heated in a vacuum oven at 85° for 24 hr.

The emulsion polymerization was conducted in a 10-ml. Carius tube which was also sealed *in vacuo* while cooled in liquid nitrogen. The tube was placed in a 300-ml. Aminco pressure reactor which was then pressured to 300 p.s.i. with nitrogen before it was sealed. The polymer was removed from the tube and washed with 2 l. of hot water on a sintered glass funnel and then dried at 85° in a vacuum oven.

Copolymer compositions were established by elementary analysis, preference being given to the more accurately determinable carbon content.

Homopolymerization of IX.—A mixture of IX (0.98 g.), water (deoxygenated, 2.0 ml.), potassium persulfate (0.003 g.) and Duponol ME (duPont, sodium lauryl sulfate) was heated at 60° for 16 hours. The polymer, obtained in 60% conversion, was a strong, white elastomer insoluble in 1,1,2-trichlorotrifluoroethane and slightly soluble in acetone. It softened at about 225° and gave a clear liquid melt at 265° with no discoloration to indicate decomposition. The infrared spectrum showed only a band at 5.8 μ in the C=C stretching region which indicates that the polymerization proceeded by 1,4-addition to give a polymer containing the recurring units $[CF_2CF{=}CFCH_2]$.

A rubbery crumb homopolymer was obtained in 86% conversion after 35-hr. exposure to ultraviolet light.

Copolymerization of IX with 2,2,2-Trifluoroethyl Vinyl Ether.—Compound IX (1.26 g., 0.01 mole) and 2,2,2-trifluoroethyl vinyl ether (1.26 g., 0.01 mole) were exposed to ultraviolet radiation for 40 hours. The polymer (44% conversion) was elastomeric, and softened at 72–80°. *Anal.* Found: C, 38.25; H, 2.01; F, 56.67. The mole fraction of IX in the copolymer (based on F) is 0.76. The infrared spectrum showed a major band at 5.8 μ and a weak band at 5.93 μ in the C=C stretching region which indicates primary copolymerization by 1,4-addition of the diene and partial 1,2-addition across the $—CF_2{=}CF—$ bond to leave a pendant $—CF{=}CH_2$ group.

Copolymerization of IX with Ethylene Oxide.—The diene IX (1.27 g., 0.01 mole) and ethylene oxide (0.48 g., 0.009 mole) were irradiated for 40 hours. The product (77% conversion) was a white elastomer, slightly soluble in 1,1,2-trichlorotrifluoroethane, which softens and melts at 250–270°. The infrared absorption spectrum showed a major band at 5.8 μ (1,4-addition) and a weak band at 5.93 μ (1,2-addition across the $—CF_2{=}CF—$ bond). A relatively strong band at 3.45 μ (CH_2) resulted from the presence of $(CH_2CH_2O)_n$-units. *Anal.* Found: C, 40.0; H, 2.69. This corresponds to a mole fraction of 0.73 for the tetrafluorobutadiene in the copolymer.

Copolymerization of IX with Perfluoropropene.—The diene IX (1.24 g.) and perfluoropropene (1.47 g.) were exposed to ultraviolet radiation for 166 hours. The polymer (19% conversion) was a transparent viscous oil. *Anal.* Found: C, 33.9; H, 1.22. This corresponds to 74 mole per cent. tetrafluorobutadiene in the copolymer. The infrared spectrum showed a strong band at 5.79 μ and a trace at 5.93 μ in the C=C stretching region.

Copolymerization of 1,1,2,3-Tetrafluorobutadiene with 1-Chloro-2,2-difluoroethylene.—The diene IX (1.24 g.) and 1-chloro-2,2-difluoroethylene (1.02 g.) were irradiated for 46 hours. The copolymer (31% conversion) was a viscous liquid. *Anal.* Found: C, 36.4; H, 1.34; F, 56.0. This corresponds to 84.5 mole per cent. IX in the copolymer. The absorption peaks in the double bond region of the infrared spectrum were at 5.8 and 5.93 μ. In this case the 5.8 μ band was only slightly more intense than the 5.93 μ band.

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