

conditions. We hope to utilize these methods for the synthesis of both *cis* and *trans* α -methylene- γ -butyrolactones.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Portions of this work were also supported by a Biomedical Sciences Support Grant to Rutgers University from the National Institutes of Health, by Research Corporation, and by the National Science Foundation. We thank Dr. Noal Cohen for providing some useful literature references, and Professor R. B. Miller for samples and helpful correspondence.

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Received June 28, 1973

Syntheses from Perfluoro-2-butyne. I. Fluoride Ion Promoted Telomerization of Perfluoro-2-butyne with 2-Bromoperfluoro-2-butene.

trans-3-Bromoperfluoro-1,2,3,4-tetramethylcyclobutene¹

Sir:

Although a virtually unlimited carbon-fluorine chemistry can now be visualized its realization is dependent upon the development of applicable synthetic methods particularly those for carbon-carbon bonds. We wish to report new results in this area centering around the synthesis of *trans,trans*-2-bromoperfluoro-3,4-dimethyl-2,4-hexadiene as a precursor for *trans*-3-bromoperfluoro-1,2,3,4-tetramethylcyclobutene and perfluorotetramethylcyclobutadiene.^{1,2} The desired hexadiene isomer was prepared in a single operation in ~80% yield from perfluoro-2-butyne, 2-bromoperfluoro-2-butene, and cesium fluoride with the intermediate formation of *trans*-perfluoro-1-methylpropenylcesium³ as shown in eq 1-5. The reaction process consists of an anionic telomerization and by increasing the ratio of butyne to butene was also utilized to prepare perfluoromethylated polyenes, $F(CCF_3=CCF_3)_nBr$ with $n > 2$. It provides a prototype for other syntheses with carbon-fluorine-halogen compounds in which fluoroorganometal intermediates generated by fluoride ion additions react as nucleophiles on unsaturated carbon and on halogen.⁷

(1) Presented in part at the 6th International Symposium on Fluorine Chemistry, Durham, England, July 1971, and at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract FLUO-011.

(2) Treatment of *trans*-3-bromoperfluoro-1,2,3,4-tetramethylcyclobutene with MeLi at -125° yielded the cyclobutadiene.

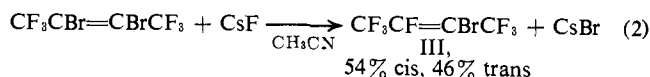
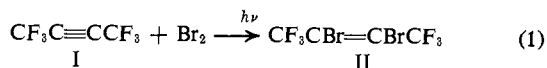
(3) Both CsF and AgF have been shown to add readily to $CF_3C\equiv CCF_3$ to form *trans* addition products.⁴ The facile addition of metal fluorides to unsaturated carbon-fluorine compounds to form perfluoroorganometallic compounds was first demonstrated with KF, i.e., the formation of perfluoroalkylpotassiums.⁵ Cesium fluoride and $CF_3C\equiv CCF_3$ have been utilized to prepare alkenyl and dialkenyl derivatives of perfluoro aromatics.⁶

(4) W. T. Miller, R. H. Snider, and R. J. Hummel, *J. Amer. Chem. Soc.*, **91**, 6532 (1969).

(5) J. H. Fried and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, **81**, 2078 (1959); W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

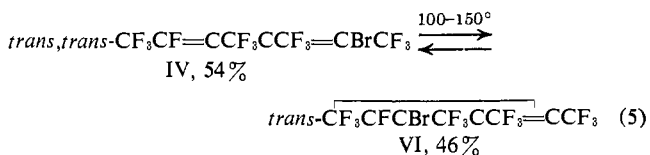
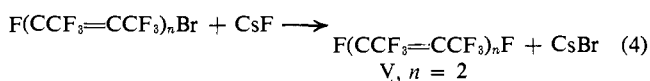
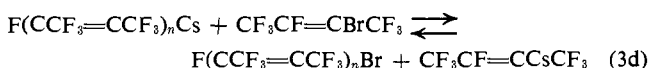
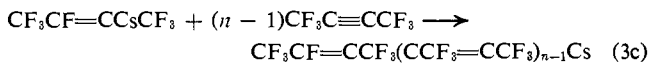
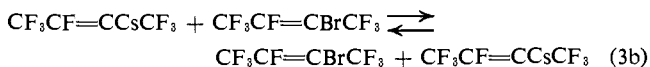
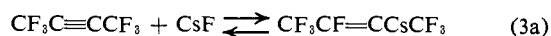
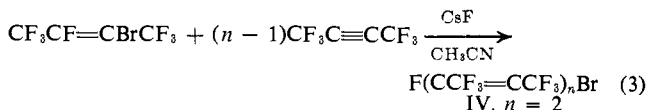
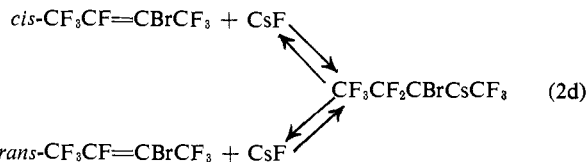
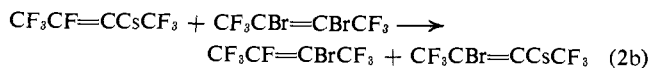
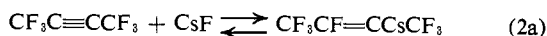
(6) W. T. Flowers, R. N. Haszeldine, and P. G. Marshall, *Chem. Commun.*, 371 (1970); R. D. Chambers, W. K. R. Musgrave, and S. Partington, *ibid.*, 1050 (1970).

(7) For the characteristic reactions of anionic nucleophiles on unsaturated carbon in carbon-fluorine-halogen compounds see ref 5. Bimolecular nucleophilic reactions on halogen also represent a reaction



(a) at reflux, slow⁴

(b) at 30° with I as a catalyst, fast



All of the compounds prepared were derived from $CF_3C\equiv CCF_3$.⁹ Reaction 1 yielded the pure dibromide, $CF_3CBr=CBrCF_3$,¹⁰ which was converted into an equilibrium mixture of *cis*- and *trans*- $CF_3CF=CBrCF_3$ with CsF (eq 2).⁴ Each isomer was rapidly equilibrated by CsF at 30° without bromine substitution, <1% after 30 hr.¹¹ Reaction with fluoride ion thus provides a general mechanism for the interconversion of *cis*-*trans* isomers of perfluoroolefins in addition to promoting their rearrangement.⁵ A small amount of $CF_3C\equiv CCF_3$ served as an effective catalyst for reaction 2 due to the ease with which the halogen-metal exchange reaction 2b took place. In the absence of an

pathway of major importance to CFX chemistry which is facilitated by the formation of stabilized carbanions and steric inhibition of the SN_2 mechanism.³

(8) W. T. Miller, Jr., and R. Becker, Abstracts of the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 14M.

(9) A. L. Henne and W. G. Finnegan, *J. Amer. Chem. Soc.*, **71**, 298 (1949).

(10) R. N. Haszeldine, *J. Chem. Soc.*, 2504 (1952). In our work rapid bromination of $CF_3C\equiv CCF_3$ was observed with irradiation at reflux temperature without the formation of $CF_3CBr_2CBr_2CF_3$.

(11) The exclusive formation of $CF_3CF_2CBrCsCF_3$ by addition of CsF to III was consistent with the expected greater effectiveness of α -Br as compared with α -F for stabilizing carbanions and with the greater stability of $-CF_2-$ relative to $-CFX$.

effective trapping reagent for *trans*-CF₃CF=CCsCF₃, the polymerization of CF₃C≡CCF₃ by anionic addition yielded an intractable solid.^{4,6,12} The success of the telomerization reaction (eq 3a-d) also depended upon the fluorovinylcesium intermediates undergoing halogen-metal exchange, with CF₃CF=CBrCF₃, faster than they added to CF₃C≡CCF₃ as well as upon the structural relationships of the reactants. Since CF₃CF=CCsCF₃ was not consumed by the first such exchange (eq 3b) its addition to CF₃C≡CCF₃ took place exclusively to form CF₃CF=CCF₃CCF₃=CCsCF₃ (eq 3c) which gave the diene IV as the first isolable product (eq 3d, *n* = 2) and, with excess CF₃CF=CBrCF₃, in high yield.¹³ Higher telomers, produced by the addition of

(12) First prepared with Harold Goldwhite.

(13) The hexadiene synthesis was carried out by charging CF₃C≡CCF₃ (I) and either CF₃CF=CBrCF₃ (III) or CF₃CBr=CBrCF₃ (II) and CsF with CH₃CN in a sealed glass ampoule and shaking at 30°. With CF₃CBr=CBrCF₃, reaction 2 took place first to yield III. For example, a 300-ml ampoule containing 28.5 g (176 mmol) of I, 54.5 g (208 mmol) of III, 1.6 g (10 mmol) of CsF, and 50 ml of CH₃CN, initially at -78°, was shaken at 30° ambient for 2 hr. The reaction mixture which contained an immiscible fluorocarbon layer and finely divided CsBr was washed with two 100-ml portions of cold water to remove CH₃CN and distilled from P₂O₅ at 0.1 mm to yield 78.8 g of volatile product. Gpc analysis, 0.25 in. × 12 ft, 20% squalene on silylated Chromosorb P, column A, showed: 8.52 g (32.5 mmol) of recovered III; 3.0 g (8.3 mmol) of V (4.7%); 66.8 g (157 mmol) of IV (89%); 1.7 g (2.9 mmol) of F(CCF₃=CCF₃)₂Br (3.0%); based upon I. The isomer composition of IV was: *trans,trans*, 88%; *cis,trans*, 2%; and *trans,cis*, 10%. The *trans,trans* and *trans,cis* isomers of IV were incompletely resolved by column A and their ratio was estimated from nmr peak areas for the single fluorine atoms. On heating the hexadiene fraction IV to 100-150°, or by distillation, the *trans,trans* isomer was partially cyclized to *trans*-3-bromoperfluoro-1,2,3,4-tetramethylcyclobutene (VI), bp ~102°, which was separable with column A or by spinning band distillation. Thermal equilibration of VI at 150° yielded 54% IV and 46% VI from which pure *trans,trans*-IV, bp 106°, was obtained. Pure *trans,cis*-IV, bp 109°, was preferably isolated from the distillation residue of IV, 0.25 in. × 30 ft, 25% eicosane on Chromosorb W at 60°, column B. Each of the hexadiene isomers was rapidly converted into the isolated equilibrium mixture, see above, and then into V¹⁴ (~85% *trans,trans*) by CsF in CH₃CN (eq 4). No evidence for the presence of *cis,cis*-IV was found, a result consistent with its spatial requirements. The properties of new compounds are given below.¹⁵

(14) See ref 4 and ref 14 therein cited.

(15) The assigned structures for new compounds were fully consistent with their chemical and spectral properties. All molecular formulas were established from mass spectra. Stereochemical assignments were made largely on the basis of nmr spectra¹⁶ with additional evidence from thermal, photochemical and fluoride ion catalyzed interconversions, the examination of molecular models, and experiments with related compounds. Ir and nmr values follow (c, complex). *trans,trans*-2-Bromoperfluoro-3,4-dimethyl-2,4-hexadiene: ir (gas) 1710 (w, CF=CCF₃), 1625 (w, CBr=CCF₃), 1380 (m), 1314 (w), 1282 (m), 1240 (vs), 1230 (vs), 1210 (vs), 1182 (s), 1138 (vw), 878 (m), 792 (m), 724 (m) cm⁻¹; nmr ¹⁹F (CH₂Cl₂) 63.0 (d, CF=CCF₃, *J*_{cis-F,CF₃} = 13.9 Hz), 64.0 (s, CBrCF₃), 64.2 (s, CBr=CCF₃), 72.0 (s/c, CFCF₃), 106.0 (broad, CFCF₃) ppm upfield from external CFCF₃. *trans,cis*-2-Bromoperfluoro-3,4-dimethyl-2,4-hexadiene: ir (gas) 1710 (w), 1635 (w), 1350 (m), 1285 (m), 1245 (vs), 1215 (vs), 1195 (vs), 1105 (m), 982 (m), 927 (w), 868 (w), 757 (w), 742 (m), 725 (w), 698 (m) cm⁻¹; nmr ¹⁹F (neat) 57.2 (c, CF=CCF₃, *J*_{cis-F,CF₃} = 13.1 Hz), 62.4 (s, CBrCF₃), 62.7 (s, CBr=CCF₃), 64.2 (d/q, CFCF₃), 103.1 (c, CFCF₃) ppm. *cis,trans*-2-Bromoperfluoro-3,4-dimethyl-2,4-hexadiene: ir (gas) 1725 (w), 1635 (w), 1393 (m), 1293 (s), 1259 (vs), 1220 (vs), 1200 (vs), 884 (m), 858 (m), 812 (w), 747 (w), 728 (w), 692 (m) cm⁻¹; nmr ¹⁹F (CCl₄, weak spectrum) 57.1, 59.3, 61.0, 70.5, 108.6 ppm. *trans,trans*-Perfluoro-3,4-dimethyl-2,4-hexadiene: ir (gas) 1706 (w), 1687 (m), 1370 (vs), 1279 (vs), 1259 (vs), 1234 (vs), 1213 (vs), 1189 (vs), 1149 (w), 894 (w), 875 (s), 738 (m), 735 (m), 680 (m), cm⁻¹; nmr ¹⁹F (neat) 62.8 (d, CF=CCF₃, *J*_{cis-F,CF₃} = 16.1 Hz), 70.9 (s/c, CFCF₃), 104.4 (br, CFCF₃) ppm. *trans*-3-Bromoperfluoro-1,2,3,4-tetramethylcyclobutene: bp 54° (100 mm); mp -42 to -43°; ir (gas) 1716 (w, CF₂C=CCF₃), 1564 (m), 1282 (vs), 1263 (s), 1241 (vs), 1227 (s), 1211 (s), 1202 (s), 1188 (s), 1138 (w), 1097 (w), 1035 (w), 1007 (vw), 905 (w), 816 (vw), 800 (vw), 734 (vw), 708 (m), 677 (w), 645 (w) cm⁻¹; nmr ¹⁹F (neat) 64.6 (s/c, CBrCCF₃), 65.2 (s/c, CFCF₃), 70.6 (d/q, CBrCF₃, *J*_{cis-F,CF₃} = 17.2 Hz), 75.9 (s/c, CFCF₃), 167.3 (br q, CFCF₃) ppm. *trans,trans*-2-Bromoperfluoro-3,4,5,6-tetramethyl-2,4,6-octatriene: ir (gas) 1707 (w), 1651 (w), 1617 (w), 1383 (m), 1333 (w), 1301 (w), 1251 (vs), 1233 (vs), 1291 (vs), 1210 (vs), 1194 (vs), 1175 (s), 1133 (vw), 1121 (vw), 971 (w), 878 (w), 845 (vw), 769 (w), 745 (w), 694 (w), 669 (w), 652 (w) cm⁻¹; nmr ¹⁹F (neat) 60.9, 61.4, 62.6, 62.2, 64.5, 72.0, 105.0 ppm. *trans,trans*,

more than one butyne molecule (eq 3), were prepared as mixtures utilizing lower CF₃CF=CBrCF₃ concentrations.¹⁷ The BrF telomers were shown also to add -CCF₃=CCF₃- units by reaction with CF₃C≡CCF₃ and CsF due to the reversibility of reaction 3d. Substitution of bromine by fluorine by reaction with CsF yielded F(CCF₃=CCF₃)_nF products, e.g. CF₃CF=CCF₃CCF₃=CFCF₃ (eq 4) but more slowly than telomerization.¹⁸ No products formed by loss of CsF from the F(CCF₃=CCF₃)_nCs intermediates with *n* > 1 were detected.

When the hexadiene fraction IV was heated at 100-150° the *trans,trans* isomer was partially cyclized to form the desired *trans*-3-bromoperfluoro-1,2,3,4-tetramethylcyclobutene (VI).^{13,19} Pure IV or VI yielded an equilibrium mixture (eq 5). At 150° the *cis,trans*- and *trans,cis*-hexadiene isomers were unchanged. These results were in accordance with the Woodward-Hoffmann rules for a concerted process²⁰ and the expected difficulty of forming the *cis*-cyclobutene.²¹

Our data bearing on the stereochemistry of the telomerization process are consistent with exclusive *trans* addition of CsF and of the intermediate alkenylcesiums to CF₃C≡CCF₃ and with retention of configuration during bromine transfers. The telomer products with "end" *cis* carbon-carbon double bonds are accounted for by fluoride ion catalyzed equilibration. "Internal" *cis* double bonds and double bond conjugation appear to be sterically excluded.

Acknowledgment. We are grateful for a grant from the National Science Foundation to support this work.

trans,trans-2-Bromoperfluoro-3,4,5,6,7,8-hexamethyl-2,4,6,8-decatetraene: mp 37-38°; ir (KBr) 1710 (w), 1630 (w), 1380 (m), 1240 (vs), 1200 (vs), 1170 (vs), 1120 (sh), 978 (w), 920 (m), 885 (m), 865 (w), 777 (vw), 754 (vw), 746 (vw), 728 (sh), 772 (m), 688 (m) cm⁻¹; nmr ¹⁹F (CFCl₃) 57.5, 58.8, 59.3, 60.8, 61.3, 68.2, 99.2 ppm. *trans,trans,trans,trans*-2-Bromoperfluoro-3,4,5,6,7,8,9,10-octamethyl-2,4,6,8,10-dodecapentaene: mp 126-128°; ir (KBr) 1720 (w), 1625 (w), 1380 (m), 1240 (vs), 1200 (vs), 1165 (vs), 1120 (sh), 978 (w), 883 (m), 840 (w), 772 (vw), 751 (vw), 738 (m), 730 (sh), 703 (m) cm⁻¹; nmr ¹⁹F (CFCl₃) 59.8, 61.3, 62.6, 64.0, 71.3, 110.5 ppm. *trans,trans,trans,trans,trans,trans*-2-Bromoperfluoro-3,4,5,6,7,8,9,10,11,12-decamethyl-2,4,6,8,10,12-tetradecahexaene: ir (KBr) 1700 (w), 1392 (m), 1249 (vs), 1210 (vs), 1183 (vs), 983 (w), 953 (vw), 889 (m), 778 (vw), 748 (vw), 726 (vw), 720 (m), 697 cm⁻¹; very slightly soluble in CH₂Cl₂.

(16) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, New York, N. Y., 1966, pp 909-916.

(17) For example, 2.5 g (15 mmol) of I, 1.38 g (5.3 mmol) of III, and 0.4 g (3 mmol) of CsF in 20 ml of CH₃CN after shaking at 30° for 3.5 hr as above¹³ were completely converted into a viscous semisolid product. The BrF telomers, F(CCF₃=CCF₃)_nBr, were present in the following relative amounts (column A) (*n*, %): 2, 7; 3, 23; 4, 38; 5, 20; 6, 11. The properties of the major isomers which were assigned all-*trans* configurations are given in ref 15.

(18) The greater ease of replacing bromine by fluorine observed with the telomer structure IV as compared with III was attributed to the greater stability and ease of formation of the intermediate allylic and more highly substituted cesium compound CF₃CF=CCF₃CCF₃Cs-CBrCF₃ as compared with CF₃CBrFCFCsCF₃.¹¹

(19) The thermal cyclization of a 1,3-diene was first observed with CF₂=CFCF=CF₂; M. Prober and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, 71, 598 (1949); W. T. Miller, Jr., in *National Nuclear Energy Series, VII-1, "Preparation, Properties and Technology of Fluorine and Organic Fluorine Compounds,"* McGraw-Hill, New York, N. Y., 1951, p 567.

(20) R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, 1, 17 (1968).

(21) We have prepared *cis*-3-bromoperfluoro-1,2,3,4-tetramethylcyclobutene by irradiating VI. Its chemistry will be reported separately.

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Received June 22, 1973