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

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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-tetramethylcyclobutene[1]

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-methylpropenylcesium[3] 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, $\mathrm{F(CCF_3{=}CCF_3)_{\mathit{n}}Br}$ 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]

$$\underset{\text{I}}{\mathrm{CF_3C{\equiv}CCF_3}} + \mathrm{Br_2} \xrightarrow{h\nu} \underset{\text{II}}{\mathrm{CF_3CBr{=}CBrCF_3}} \qquad (1)$$

$$\mathrm{CF_3CBr{=}CBrCF_3} + \mathrm{CsF} \xrightarrow[\mathrm{CH_3CN}]{} \underset{\text{III,}}{\mathrm{CF_3CF{=}CBrCF_3}} + \mathrm{CsBr} \qquad (2)$$

54% cis, 46% trans

(a) at reflux, slow[4]

(b) at 30° with I as a catalyst, fast

$$\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{CsF} \rightleftarrows \mathrm{CF_3CF{=}CCsCF_3} \qquad (2a)$$

$$\mathrm{CF_3CF{=}CCsCF_3} + \mathrm{CF_3CBr{=}CBrCF_3} \longrightarrow \mathrm{CF_3CF{=}CBrCF_3} + \mathrm{CF_3CBr{=}CCsCF_3} \qquad (2b)$$

$$\mathrm{CF_3CBr{=}CCsCF_3} \longrightarrow \mathrm{CF_3C{\equiv}CCF_3} + \mathrm{CsBr} \qquad (2c)$$

$$\begin{tikzcd}
\textit{cis}\text{-}\mathrm{CF_3CF{=}CBrCF_3} + \mathrm{CsF} \arrow[dr, shift left] & \\
& \mathrm{CF_3CF_2CBrCsCF_3} \arrow[ul, shift left] \arrow[dl, shift left] \qquad (2d) \\
\textit{trans}\text{-}\mathrm{CF_3CF{=}CBrCF_3} + \mathrm{CsF} \arrow[ur, shift left] &
\end{tikzcd}$$

$$\mathrm{CF_3CF{=}CBrCF_3} + (n-1)\mathrm{CF_3C{\equiv}CCF_3} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{CsF}} \underset{\text{IV, } n\,=\,2}{\mathrm{F(CCF_3{=}CCF_3)_{\mathit{n}}Br}} \qquad (3)$$

$$\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{CsF} \rightleftarrows \mathrm{CF_3CF{=}CCsCF_3} \qquad (3a)$$

$$\mathrm{CF_3CF{=}CCsCF_3} + \mathrm{CF_3CF{=}CBrCF_3} \rightleftarrows \mathrm{CF_3CF{=}CBrCF_3} + \mathrm{CF_3CF{=}CCsCF_3} \qquad (3b)$$

$$\mathrm{CF_3CF{=}CCsCF_3} + (n-1)\mathrm{CF_3C{\equiv}CCF_3} \longrightarrow \mathrm{CF_3CF{=}CCF_3(CCF_3{=}CCF_3)_{\mathit{n}-1}Cs} \qquad (3c)$$

$$\mathrm{F(CCF_3{=}CCF_3)_{\mathit{n}}Cs} + \mathrm{CF_3CF{=}CBrCF_3} \rightleftarrows \mathrm{F(CCF_3{=}CCF_3)_{\mathit{n}}Br} + \mathrm{CF_3CF{=}CCsCF_3} \qquad (3d)$$

$$\mathrm{F(CCF_3{=}CCF_3)_{\mathit{n}}Br} + \mathrm{CsF} \longrightarrow \underset{\text{V, } n\,=\,2}{\mathrm{F(CCF_3{=}CCF_3)_{\mathit{n}}F}} + \mathrm{CsBr} \qquad (4)$$

$$\underset{\text{IV, 54\%}}{\textit{trans,trans}\text{-}\mathrm{CF_3CF{=}CCF_3CCF_3{=}CBrCF_3}} \underset{}{\overset{100\text{–}150^\circ}{\rightleftarrows}} \underset{\text{VI, 46\%}}{\textit{trans}\text{-}\overline{\mathrm{CF_3CFCBrCF_3CCF_3}}\mathrm{{=}CCF_3}} \qquad (5)$$

All of the compounds prepared were derived from $\mathrm{CF_3C{\equiv}CCF_3}$.[9] Reaction 1 yielded the pure dibromide, $\mathrm{CF_3CBr{=}CBrCF_3}$,[10] which was converted into an equilibrium mixture of *cis*- and *trans*-$\mathrm{CF_3CF{=}CBrCF_3}$ 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 $\mathrm{CF_3C{\equiv}CCF_3}$ 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

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[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 $\mathrm{CF_3C{\equiv}CCF_3}$ 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 $\mathrm{CF_3C{\equiv}CCF_3}$ 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 pathway of major importance to CFX chemistry which is facilitated by the formation of stabilized carbanions and steric inhibition of the $\mathrm{S_N2}$ mechanism.[8]

[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 $\mathrm{CF_3C{\equiv}CCF_3}$ was observed with irradiation at reflux temperature without the formation of $\mathrm{CF_3CBr_2CBr_2CF_3}$.

[11] The exclusive formation of $\mathrm{CF_3CF_2CBrCsCF_3}$ 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 $-\mathrm{CF_2}-$ relative to $-\mathrm{CFX}$.

effective trapping reagent for *trans*-$CF_3CF{=}CCsCF_3$ the polymerization of $CF_3C{\equiv}CCF_3$ 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 $CF_3CF{=}CBrCF_3$, faster than they added to $CF_3C{\equiv}CCF_3$ as well as upon the structural relationships of the reactants. Since $CF_3CF{=}CCsCF_3$ was not consumed by the first such exchange (eq 3b) its addition to $CF_3C{\equiv}CCF_3$ took place exclusively to form $CF_3CF{=}CCF_3CCF_3{=}CCsCF_3$ (eq 3c) which gave the diene IV as the first isolable product (eq 3d, $n = 2$) and, with excess $CF_3CF{=}CBrCF_3$, in high yield.[13] Higher telomers, produced by the addition of more than one butyne molecule (eq 3), were prepared as mixtures utilizing lower $CF_3CF{=}CBrCF_3$ concentrations.[17] The BrF telomers were shown also to add $-CCF_3{=}CCF_3-$ units by reaction with $CF_3C{\equiv}CCF_3$ and CsF due to the reversibility of reaction 3d. Substitution of bromine by fluorine by reaction with CsF yielded $F(CCF_3{=}CCF_3)_nF$ products, *e.g.* $CF_3CF{=}CCF_3CCF_3{=}CFCF_3$ (eq 4) but more slowly than telomerization.[18] No products formed by loss of CsF from the $F(CCF_3{=}CCF_3)_nCs$ 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 process[20] 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 $CF_3C{\equiv}CCF_3$ 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.

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(12) First prepared with Harold Goldwhite.

(13) The hexadiene synthesis was carried out by charging $CF_3C{\equiv}CCF_3$ (I) and either $CF_3CF{=}CBrCF_3$ (III) or $CF_3CBr{=}CBrCF_3$ (II) and CsF with CH_3CN in a sealed glass ampoule and shaking at 30°. With $CF_3CBr{=}CBrCF_3$, 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 CH_3CN, 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 CH_3CN and distilled from P_2O_5 at 0.1 mm to yield 78.8 g of volatile product. Glpc 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 $F(CCF_3{=}CCF_3)_3Br$ (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 V[14] (~85% trans,trans) by CsF in CH_3CN (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 spectra[16] 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, $CF{=}CCF_3$), 1625 (w, $CBr{=}CCF_3$), 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 ^{19}F (CH_2Cl_2) 63.0 (d, $CF{=}CC\mathit{F}_3$, $J_{cis\text{-}F,CF_3} = 13.9$ Hz), 64.0 (s, $CBrCF_3$), 64.2 (s, $CBr{=}CCF_3$), 72.0 (s/c, $CFC\mathit{F}_3$), 106.0 (broad, $C\mathit{F}CF_3$) ppm upfield from external $CFCl_3$. *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 ^{19}F (neat) 57.2 (c, $CF{=}CC\mathit{F}_3$, $J_{cis\text{-}F,CF_3} = 13.1$ Hz), 62.4 (s, $CBrCF_3$), 62.7 (s, $CBr{=}CCF_3$), 64.2 (d/q, $CFC\mathit{F}_3$), 103.1 (c, $C\mathit{F}CF_3$) 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 ^{19}F (CCl_4, 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 ^{19}F (neat) 62.8 (d, $CF{=}CC\mathit{F}_3$, $J_{cis\text{-}F,CF_3} = 16.1$ Hz), 70.9 (s/c, $CFC\mathit{F}_3$), 104.4 (br, $C\mathit{F}CF_3$) ppm. *trans*-**3-Bromoperfluoro-1,2,3,4-tetramethylcyclobutene:** bp 54° (100 mm); mp −42 to −43°; ir (gas) 1716 (w, $CF_3C{=}CCF_3$), 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 (w), 677 (w), 645 (w) cm^{-1}; nmr ^{19}F (neat) 64.6 (s/c, $CBrCCF_3{=}$), 65.2 (s/c, $CFCC\mathit{F}_3{=}$), 70.6 (d/q, $CBrCF_3$, $J_{cis\text{-}F,CF_3} = 17.2$ Hz), 75.9 (s/c, $CFCF_3$), 167.3 (br q, $C\mathit{F}CF_3$) ppm. *trans,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 ^{19}F (neat) 60.9, 61.4, 62.6, 62.2, 64.5, 72.0, 105.0 ppm. *trans,trans,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 ^{19}F ($CFCl_3$) 57.5, 58.8, 59.3, 60.8, 61.3, 68.2, 99.2 ppm. *trans,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 ^{19}F ($CFCl_3$) 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 CH_2Cl_2.

(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 CH_3CN after shaking at 30° for 3.5 hr as above[13] were completely converted into a viscous semisolid product. The BrF telomers, $F(CCF_3{=}CCF_3)_nBr$, 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 $CF_3CF{=}CCF_3CCF_3CsCBrFCF_3$ as compared with $CF_3CBrFCFCsCF_3$.[11]

(19) The thermal cyclization of a 1,3-diene was first observed with $CF_2{=}CFCF{=}CF_2$; M. Prober and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, 71, 598 (1949); W. T. Miller, Jr., in National Nuclear Energy Series, VII-I, "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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