The temperature rose quickly to 90° and was maintained at 85–95° for 4 hr. The cooled solution was poured into 2 l. of water and the resulting brown solution extracted with four 500-ml portions of ether. The combined ether extracts were washed with two 400-ml portions of water and dried over sodium sulfate. Distillation through a 30-cm Vigreux column gave a small fore-run, 8.49 g of clear oil, bp 48–50° (7 mm), and 9.42 g, bp 50–51° (7 mm) [lit.[14] bp 58–63 (7 mm)], $n^{25}\text{D}$ 1.4569, $\nu$ neat 2250 $\text{cm}^{-1}$. Vapor phase chromatography on the silicon gum rubber column indicated that the lower boiling fraction contained *ca.* 10% more volatile impurity. The nitrile discolored slowly at room temperature and therefore was stored under nitrogen at −10°.

**3-Cyclopentenecarboxylic Acid.**—To a solution of 86.0 g (0.924 mol) of the slightly impure 4-cyanocyclopentene in 270 ml 95% alcohol was added 90 ml of 40% aqueous sodium hydroxide solution and the mixture refluxed under nitrogen for 20 hr. The black solution was poured into 2 l. of water containing 90 ml of glacial acetic acid. Extraction with four 500-ml portions of ether followed by drying and removal of the solvent gave a brown oil. This was distilled through a 30-cm Vigreux column to give 66.3 g of yellow oil, bp 56–66° (0.3 mm). This material was redistilled through a 30-cm Podbielniak column to give 64.0 g (60%) of light yellow oil, bp 46–48° (0.3 mm), $n^{25}\text{D}$ 1.4669 [lit.[15] bp 83–84° (2 mm), $n^{23}\text{D}$ 1.4673]. The anilide was prepared according to the published[16] procedure, mp 138–140° (lit.[16] mp 139–140°).

**4-Hydroxymethylcyclopentene.**—To a stirring suspension of 4.15 g (0.113 mol) of lithium aluminum hydride in 100 ml of dry tetrahydrofuran[13] was added a solution of 11.6 g (0.110 mol) of 3-cyclopentenecarboxylic acid in 55 ml of dry tetrahydrofuran. The mixture refluxed vigorously during the course of the addition. Heating under reflux was continued for 20 hr. The reaction was worked up by the addition of 50 ml of saturated sodium potassium tartrate solution. Extraction with solid with ether, followed by drying over sodium sulfate and removal of the solvent, yielded 11.0 g of a yellow oil. The oil was distilled through a Vigreux column to give 8.00 g (82%) of a clear oil, $n^{29}\text{D}$ 1.4665, bp 82–85° (30 mm) [lit.[16] bp 98–99° (57 mm), $n^{22}\text{D}$ 1.4670].

**$\Delta^3$-Cyclopentenylmethyl *p*-Bromobenzenesulfonate.**—To 5.00 g (51.0 mmol) of 4-hydroxymethylcyclopentene in 100 ml of pyridine stirring in an ice bath was added 15.0 g (58.5 mmol) of *p*-bromobenzenesulfoxyl chloride which had been dried at 40° (50 mm) overnight. After stirring in the ice bath for 1 hr, the solution was placed in a refrigerator at 4–5° for 10 hr. The yellow solution then was poured slowly into a rapidly stirring solution of ice water containing 80 ml of 12 *M* hydrochloric acid. Suction filtration and thorough washing of the filter cake with water gave 16.7 g of white solid, mp 39.5–46.0°. The material was recrystallized from pentane to give 12.5 g (96%) of white solid, mp 39.5–42.0°. An analytical sample was again recrystallized, mp 40.5–42.0°.

*Anal.* Calcd for $C_{12}C_{13}BrO_3S$: C, 45.44; H, 4.13. Found: C, 45.50; H, 3.97.

**3,4-Epoxycyclopentylmethyl *p*-Bromobenzenesulfonate.**—To a stirring solution of 6.50 g of 88% *m*-chloroperbenzoic acid in 80 ml of methylene chloride was added 8.50 g (26.7 mmol) of $\Delta^3$-cyclopentenylmethyl brosylate in small portions and the solution stirred for 25 min. A small amount of 10% sodium hydrogen sulfite solution was then added and the solution was suction filtered. The filter cake was washed thoroughly with methylene chloride and the layers were separated. The organic layer was washed with two portions of saturated sodium hydrogen carbonate solution and once with 1 *M* sodium hydroxide. After drying over sodium sulfate and evaporation of solvent a clear oil was obtained which slowly crystallized on standing, mp 50–80°. Thin layer chromatography failed to resolve the isomeric epoxides but did indicate the presence of a small amount of starting olefin.

***exo*-6-Hydroxy-2-thiabicyclo[2.2.1]heptane (15).**—A 6.65-g sample of the crude epoxide prepared above, dissolved in 50 ml of methanol, was added to 10.2 g (42 mmol) of sodium sulfide nonahydrate in 250 ml of methanol and the solution was refluxed for 44 hr. The majority of the methanol was removed by distillation, the residue diluted with 200 ml of water and the resulting slurry extracted with two 200-ml portions of ether. After drying over sodium sulfate and evaporation of the ether a brown oil was obtained; short-path vacuum distillation gave 0.51 g (14%) of a water white semisolid.

Addition of phenyl isocyanate to a sample of the alcohol gave a solid **urethan** which was twice recrystallized from methylene chloride–pentane, mp 123–124°.

*Anal.* Calcd for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.48. Found: C, 62.62; H, 6.28.

**Registry No.**—**7**, 18593-28-7; **8**, 18593-29-8; **9**, 18598-83-9; **10**, 6841-59-4; **12**, 279-26-5; **12** (sulfonium iodide), 18593-32-3; **13**, 18598-84-0; **14**, 18593-37-8; 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene-1-*d*, 18593-38-9; *endo*-3-chloro-2-thiabicyclo[2.2.1]-hept-5-ene-1,3-$d_2$, 18621-11-9; $\Delta^3$-cyclopentylmethyl *p*-bromobenzenesulfonate, 18593-39-0; **15** (urethan), 18598-85-1; 3,4-epoxycyclopentylmethyl *p*-bromobenzenesulfonate, 18593-40-3.

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[16] J. Meinwald, P. G. Gassman, and J. K. Crandall, *ibid.*, **27**, 3366 (1962).

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# The Peroxide-Initiated Addition of Some Polyfluorochloro- and Polyfluorobromoalkanes to Some Hydrocarbon Olefins

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Both $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ have been found to give reasonable yields of simple addition products with olefins in the presence of benzoyl peroxide. The products of dehydrohalogenations of the adducts are described. The preferred reaction of $CCl_3CF_2CF_2Br$ is by cleavage of the C–Br bond rather than the C–Cl bond. Other telogens such as $CF_2BrCF_2Br$, $CF_3CFBrCF_2Br$ and $CFClBrClCFClBr$ react with ethylene to give 1:1 adducts. Certain polyhaloalkanes such as $CF_3CFBrCFBrCF_3$ and particularly $CF_3CClBrCFBrCF_3$ lose bromine readily in the presence of peroxide.

The peroxide-initiated reaction of polyfluorobromoalkanes such as $CF_2Br_2$ and $CF_2BrCFClBr$ with a variety of olefins[1,2] and fluoro olefins[3,4] gives 1:1 addition products which are useful in the synthesis of reactive fluorine-containing molecules. For example, 1,1,2-trifluorobutadiene can be made relatively easily by the following series of reactions.

$$CF_2BrCFClBr + CH_2{=\!=}CH_2 \xrightarrow{Bz_2O_2}$$

$$CF_2BrCFClCH_2CH_2Br \xrightarrow[\text{2. Zn}]{\text{1. KOH}} CF_2{=\!=}CFCH{=\!=}CH_2$$

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[1] P. Tarrant and A. M. Lovelace, *J. Amer. Chem. Soc.*, **76**, 3466 (1954).

[2] P. Tarrant and E. G. Gillman, *ibid.*, **76**, 5423 (1954).

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

[4] P. Tarrant and M. R. Lilyquist, *ibid.*, **77**, 3640 (1955).

Some years ago attempts were made in our laboratories to add $CFCl_3$ to olefins in the presence of benzoyl peroxide. No adducts were obtained, which is a surprising result since $CCl_4$ adds readily to many olefins. Obviously the fluorine atom in $CFCl_3$ was rendering this molecule incapable of participating in a sustained chain reaction either by its inertness to radicals from the peroxide or from radicals such as $CFCl_2CX_2CX_2\cdot$ formed by the attack of the telogen radical on the olefin. It seemed desirable to determine whether a perfluoroalkyl chain would have the same effect as a fluorine atom upon a $-CCl_3$ group. Consequently a study was made of the reaction of $CF_3CF_2CCl_3$ with several olefins. About the time this study was completed, Burton and Kehoe[5] reported the formation of $CF_3CCl_2CH_2CHClC_6H_{13}$ in 83% yield from the reaction of $CF_3CCl_3$ and 1-octene in the presence of copper(I) chloride and ethanolamine.

In our laboratories a reaction was carried out using $CF_3CF_2CCl_3$ (1.0 mol) and ethylene (1.43 mol) in the presence of benzoyl peroxide and $CF_3CF_2CCl_2CH_2CH_2Cl$ was obtained in 15% yield along with the 2:1 adduct (21%) and the 3:1 adduct (10%). Using a greater amount of $CF_3CF_2CCl_3$ and propylene (1.2:1.0 molar ratio), $CF_3CF_2CCl_2CH_2CHClCH_3$ was obtained in 16% yield. With isobutylene under similar reaction conditions except a higher ratio of haloalkane to olefin (3:1), a 40% yield of the 1:1 adduct was obtained. In addition, an olefin, identified as $CF_3CF_2CClCH_2C(CH_3){=}CH_2$, was also formed.

The related compound $CF_2ClCF_2CCl_3$ was found to react with terminally unsaturated olefins in a similar manner in the presence of benzoyl peroxide to give adducts of the type $CF_2ClCF_2CCl_2CH_2CClR'R$. For instance, reaction with propylene produced the 1:1 adduct in 20% yield when a ratio of perhaloalkane to olefin was 1.1:1; the $CF_2ClCF_2CCl_3$ and isobutylene (3:1) gave a 13% yield of adduct and a 25% yield of $CF_2ClCF_2CCl_2CH_2C(CH_3){=}CH_2$.

Olefins have been formed before in addition reactions. Lovelace[6] found $CCl_3CH{=}C(CH_3)_2$ among the products of the reaction of $CCl_4$ with isobutylene. The reaction of $CCl_3Br$ with $CF_2BrCFClCH{=}CH_2$ led to the formation of $CCl_3CH_2CH{=}CFCF_2Br$ by loss of a chlorine atom.[7] The formation of the terminally unsaturated olefins from isobutylene and $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ is unexpected; however, these structures were clearly established by nmr analysis. Furthermore, as discussed below, these olefins were dehydrochlorinated to other derivatives which were identified.

It should also be noted that neither $CF_3CF_2CCl_3$ nor $CF_2ClCF_2CCl_3$ reacted with allyl chloride, indicating that they are not particularly reactive telogens.

The dehydrohalogenation of the adduct of $CF_3CF_2CCl_3$ and isobutylene, $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ was carried out using an excess of solid potassium hydroxide and seven new products were noted by analytical glpc. Only one was isolated (30%). It was felt that other products of the dehydrohalogenation would be similar to those obtained from $CF_2ClCF_2CCl_2CH_2CHClC(CH_3)_2$. It was identified as $CF_3CF_2CCl{=}C{=}C(CH_3)_2$ (VII) by ir spectrum ($C{=}C{=}C$, 5.07 $\mu$) and $^1H$ nmr singlet at $\tau$ 8.50 (TMS). Since appreciable quantities of $CF_2ClCF_2CCl_2CH_2C(CH_3){=}CH_2$ (X) were formed from $CF_2ClCF_2CCl_3$ and isobutylene, its dehydrohalogenation with potassium hydroxide pellets was also studied. Two major products were formed according to analytical glpc. These were identified as $CF_2ClCF_2C{\equiv}CC(CH_3){=}CH_2$ (XII) with peaks in the infrared spectra at 4.45 $\mu$ characteristic of $C{\equiv}C$ and 6.19 $\mu$ indicative of $C{=}C$, and the diene $CF_2ClCF_2CCl{=}CHC(CH_3){=}CH_2$ (XIII) with peaks at 6.14 and 6.24 $\mu$. The $^1H$ and $^{19}F$ nmr spectra were also consistent with these structural assignments.

The dehydrohalogenation of the adduct of $CF_2ClCF_2CCl_3$ and isobutylene led to the formation of five major products. Three of these were separated and identified as $CF_2ClCF_2C{\equiv}CC(CH_3){=}CH_2$ (XII), identified above, $CF_2ClCF_2C{\equiv}CCCl(CH_3)_2$ (XIV) with a characteristic $C{\equiv}C$ peak at 4.40 $\mu$ and $CF_2ClCF_2CCl{=}C{=}C(CH_3)_2$ with a characteristic ir band at 5.03 $\mu$ indicating $C{=}C{=}C$. Elemental analyses and $^1H$ and $^{19}F$ nmr data are consistent with these structures. The other compounds could not be separated for further analysis but glpc retention times indicated that one component was probably $CF_2ClCF_2CCl_2CH_2C(CH_3){=}CH_2$ (X), which was identified as the major product from the reaction of $CF_2ClCF_2CCl_3$ with isobutylene.

The dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2CHClCH_3$ with alcoholic potassium hydroxide gave seven products. Only one was isolated; it was identified as $CF_2ClCF_2CCl{=}CHCHClCH_3$ (IX) by elemental analysis and spectral data.

An attempt was made to add $CFCl_2CFCl_2$ to ethylene in the presence of benzoyl peroxide but no high boiling material was formed. Burton and Kehoe[5] have shown that $CF_2ClCFCl_2$ adds to 1-octene to give a 62% yield of the addition product in the presence of copper(I) chloride and ethanolamine.

Attention was next turned to a study of polyhaloalkanes in which multiple sites for reaction with olefins are present. Henne[8] has shown that $CCl_3Br$ reacts with $CF_2{=}CFCl$ to form $CCl_3CF_2CFClBr$. In our laboratory this compound was found to react with ethylene to give a 40% yield of $CCl_3CF_2CFClCH_2CH_2Br$ (XVI). Gas chromatography showed no significant amounts of any other addition product, indicating no cleavage of the C–Cl bond. The 1:1 adduct was readily dehydrobrominated by alcoholic potassium hydroxide to give a single product which was separated by preparative scale glpc and identified as $CCl_3CF_2CFClCH{=}CH_2$ (XVII).

A different set of reactions was found for $CCl_3CF_2CF_2Br$, made by adding $CCl_3Br$ to tetrafluoroethylene, for cleavage occurred at the carbon–chlorine bond as well as the carbon–bromine bond. Reaction with ethylene yielded three major products positively identified as $CCl_3CF_2CF_2CH_2CH_2Br$ (40%, XX), $CF_2BrCF_2CCl_2CH_2CH_2Br$ (9%, XXI), and $CCl_3CF_2CF_2CH_2CH_2Cl$ (7%, XIX). It should be observed that XXI and XIX are not 1:1 adducts. Another product (1.5%) had a retention time in an analytical glpc column between that of XX and XXI and is probably $CF_2BrCF_2CCl_2CH_2CH_2Cl$ (XXXIII).

Scheme I accounts for these products. The ratios

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[5] D. J. Burton and L. J. Kehoe, *Tetrahedron Lett.*, No. 42, 5163 (1966).

[6] A. M. Lovelace, M. S. Thesis, University of Florida, 1952.

[7] H. Muramatsu and P. Tarrant, *J. Org. Chem.*, **29**, 1796 (1964).

[8] A. L. Henne and D. W. Kraus, *J. Amer. Chem. Soc.*, **76**, 1175 (1954).

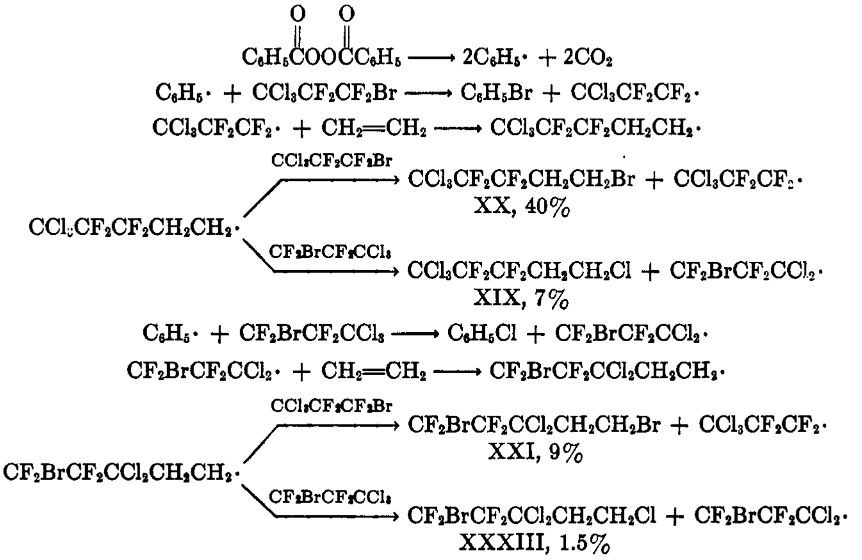
TABLE I

PHYSICAL PROPERTIES OF THE NEW COMPOUNDS PREPARED

| Compd no. | Compound | Yield, % | Bp (mm), °C | $n^{21}_D$ | $d^{21}_4$ | Calcd, % | | | Found, % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Cl | Br | F | Cl | Br | F |
| I | $CF_3CF_2CCl_2CH_2CH_2Cl$ | 15 | 33 (10) | 1.3942 | 1.5225 | 40.11 | | | 40.13 | | |
| II | $CF_3CF_2CCl_2(CH_2)_3CH_2Cl$ | 21 | 78 (9.5) | 1.4140 | 1.4461 | 36.32 | | | 36.15 | | |
| III | $CF_3CF_2CCl_2(CH_2)_5CH_2Cl$ | 10 | 67 (0.6) | 1.4238 | 1.3625 | 33.07 | | | 32.69 | | |
| IV | $CF_3CF_2CCl_2CH_2CHClCH_3$ | 16 | 70 (32) | 1.3970 | 1.4871 | 38.10 | | | 37.91 | | |
| V | $CF_3CF_2CCl_2CH_2C(CH_3){=}CH_2$ | 10 | 45 (6) | 1.3890 | 1.3819 | 27.62 | | | 27.41 | | |
| VI | $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ | 40 | 50 (6) | 1.4065 | 1.4397 | 36.28 | | | 36.12 | | |
| VII | $CF_3CF_2CCl{=}C{=}C(CH_3)_2$ | 30 | $118.5^a$ | 1.3855 | 1.2594 | 16.08 | | | 15.98 | | |
| VIII | $CF_2ClCF_2CCl_2CH_2CHClCH_3$ | 20 | 47 (2) | 1.4276 | 1.4902 | 47.93 | | | 48.15 | | |
| IX | $CF_2ClCF_2CCl{=}CHCHClCH_3$ | | $156.5^a$ | 1.4096 | 1.4166 | 41.04 | | | 40.73 | | |
| X | $CF_2ClCF_2CCl_2CH_2C(CH_3){=}CH_2$ | 25 | $172.5^a$ | 1.4421 | 1.4129 | 38.95 | | | 38.62 | | |
| XI | $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$ | 13 | 47 (0.5) | 1.4344 | 1.4301 | 45.81 | | | 44.88 | | |
| XII | $CF_2ClCF_2C{=}CC(CH_3){=}CH_2$ | 31 | $109^a$ | 1.3975 | 1.1960 | 17.69 | | | 17.62 | | |
| XIII | $CF_2ClCF_2CCl{=}CHC(CH_3){=}CH_2$ | 41 | $152^a$ | 1.4273 | 1.3451 | 29.95 | | | 29.96 | | |
| XIV | $CF_2ClCF_2C{\equiv}CCCl(CH_3)_2$ | | | | | 29.95 | | | 29.54 | | |
| XV | $CF_2ClCF_2CCl{=}C{=}C(CH_3)_2$ | | $152.5^a$ | 1.4212 | | 29.95 | | | 30.08 | | |
| XVI | $CCl_3CF_2CFClCH_2CH_2Br$ | 43 | 60 (0.5) | 1.4801 | 1.8218 | | 23.33 | | | 23.39 | |
| XVII | $CCl_3CF_2CFClCH{=}CH_2$ | 75 | $182^a$ | 1.4504 | 1.6357 | 54.10 | | | 53.90 | | |
| XVIII | $CCl_3CF_2CF_2Br$ | 58 | $134^a$ | 1.4301 | 1.9228 | | 26.81 | | | 26.82 | |
| XIX | $CCl_3CF_2CF_2CH_2CH_2Cl$ | 7 | $187^a$ | 1.4297 | | | | 26.92 | | | 27.18 |
| XX | $CCl_3CF_2CF_2CH_2CH_2Br$ | 40 | $209^a$ | 1.4486 | 1.8302 | | 24.48 | | | 24.87 | |
| XXI | $CF_2BrCF_2CCl_2CH_2CH_2Br$ | 9 | $216^a$ | 1.4664 | | | 43.12 | | | 42.40 | |
| XXII | $CFClBrCFClCH_2CH_2Br$ | 30 | 53 (2) | 1.4486 | 2.0020 | | 50.16 | | | 49.98 | |
| XXIII | $CFClBrCFClCH{=}CH_2$ | 75 | $144^a$ | 1.4571 | 1.7209 | | 33.30 | | | 33.29 | |
| XXIV | $CFCl{=}CFCH_2CH_2Br$ | | $138^a$ | 1.4514 | 1.6808 | | | | | | |
| XXV | $CFCl{=}CFCH{=}CH_2$ | 80 | | | | | | | | | |
| XXVI | $CF_2BrCF_2CH_2CH_2Br$ | 32 | 72 (80) | 1.4167 | 1.9702 | | 55.56 | | | 55.81 | |
| XXVII | $CF_2BrCF_2(CH_2)_3CH_2Br$ | 20 | 76 (10) | 1.4337 | 1.7902 | | 50.63 | | | 50.41 | |
| XXVIII | $CF_2BrCF_2CH{=}CH_2$ | 96 | 54.5 | 1.3556 | 1.6042 | | 38.65 | | | 38.44 | |
| XXIX | $CF_2BrCF_2(CH_2)_2CH{=}CH_2$ | 14 | $119.5^a$ | 1.3851 | | | 34.02 | | | 33.22 | |
| XXX | $CF_2BrCF_2(CH_2)_3CH_2OCH_2CH_3$ | 67 | $185.7^a$ | 1.3964 | 1.3670 | | 28.48 | | | 28.34 | |
| XXXI | $CF_2BrCF(CF_3)CH_2CH_2Br$ | 51 | $145^a$ | 1.4017 | 1.9920 | | 47.34 | | | 47.34 | |
| XXXII | $CF_2BrCF(CF_3)CH{=}CH_2$ | 54 | $79^a$ | 1.3469 | 1.6663 | | 31.17 | | | 31.58 | |

[a] Micro determination.

SCHEME I



$$C_6H_5\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow 2C_6H_5\cdot + 2CO_2$$

$$C_6H_5\cdot + CCl_3CF_2CF_2Br \longrightarrow C_6H_5Br + CCl_3CF_2CF_2\cdot$$

$$CCl_3CF_2CF_2\cdot + CH_2{=}CH_2 \longrightarrow CCl_3CF_2CF_2CH_2CH_2\cdot$$

$$CCl_3CF_2CF_2CH_2CH_2\cdot \xrightarrow{CCl_3CF_2CF_2Br} CCl_3CF_2CF_2CH_2CH_2Br + CCl_3CF_2CF_2\cdot$$

XX, 40%

$$CCl_3CF_2CF_2CH_2CH_2\cdot \xrightarrow{CF_2BrCF_2CCl_3} CCl_3CF_2CF_2CH_2CH_2Cl + CF_2BrCF_2CCl_2\cdot$$

XIX, 7%

$$C_6H_5\cdot + CF_2BrCF_2CCl_3 \longrightarrow C_6H_5Cl + CF_2BrCF_2CCl_2\cdot$$

$$CF_2BrCF_2CCl_2\cdot + CH_2{=}CH_2 \longrightarrow CF_2BrCF_2CCl_2CH_2CH_2\cdot$$

$$CF_2BrCF_2CCl_2CH_2CH_2\cdot \xrightarrow{CCl_3CF_2CF_2Br} CF_2BrCF_2CCl_2CH_2CH_2Br + CCl_3CF_2CF_2\cdot$$

XXI, 9%

$$CF_2BrCF_2CCl_2CH_2CH_2\cdot \xrightarrow{CF_2BrCF_2CCl_3} CF_2BrCF_2CCl_2CH_2CH_2Cl + CF_2BrCF_2CCl_2\cdot$$

XXXIII, 1.5%

of XX to XIX and XXI to XXXIII are about 6:1 indicating that the $RCH_2CH_2$ radical abstracts a bromine atom from the $-CF_2Br$ six times as readily as it does a chlorine from the $-CCl_3$ group. The ratios of the sum of XX and XIX to the sum of XXI and XXXIII, which is about 5, indicates the selectivity of the phenyl radical in attacking $-CF_2Br$ rather than $-CCl_3$.

Some years ago Hauptschein, *et al.*,[9] studied the thermal reaction of $CF_3CFBrCF_2Br$ with vinylidene fluoride and obtained a series of broad fractions from the distillation of the products. No structural assignments of the adducts were made, other that they were indicated to be 1:1, 2:1, etc., adducts. Hauptschein[10] also reported the formation of telomer bromides from perfluoropropene and $CF_3CFBrCF_2Br$ and indicated a preference for $CF_3CF(CF_2Br)CF_2CFCF_3)_nBr$ rather than $CF_3CFBrCF_2(CF_2CFCF_3)_nBr$ for the structures of

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[9] M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Amer. Chem. Soc.*, **80**, 846 (1958).

[10] M. Hauptschein, M. Braid, and A. H. Fainberg, *ibid.*, **80**, 851 (1958).

the adducts. In this laboratory $CF_3CFBrCF_2Br$ was found to react with ethylene to form a 51% yield of the 1:1 adduct, which was identified by $^1H$ and $^{19}F$ nmr spectra as $CF_3CF(CF_2Br)CH_2CH_2Br$. This compound was further readily dehydrobrominated to $CF_3CF(CF_2Br)CH{=}CH_2$. In the addition reaction, cleavage of the secondary carbon-bromine bond occurred. No reaction took place with $CF_2BrCFBrCF_3$ and allyl chloride or allyl ethyl ether.

The dibromide made from tetrafluoroethylene, $CF_2BrCF_2Br$, was found to give a 32% yield of 1:1 adduct, $CF_2BrCF_2CH_2CH_2Br$, and a 2:1 adduct, which was shown to be $CF_2BrCF_2(CH_2)_4Br$ rather than $(CF_2CH_2CH_2)_2Br$. Treatment of the 1:1 adduct with alcoholic potassium hydroxide gave $CF_2BrCF_2CH{=}CH_2$ while the 2:1 adduct gave primarily $CF_2BrCF_2(CH_2)_4OC_2H_5$ along with a small amount of $CF_2BrCF_2(CH_2)_2CH{=}CH_2$. These results demonstrated the unusual acidity of hydrogen adjacent to a $CF_2$ group.

Compounds such as $CFClBrCFClBr$, $CF_3CFBrCFBrCF_3$ and $CF_3CFBrCClBrCF_3$ which are "crowded" react chiefly to give the corresponding debrominated fluoro olefin and $CH_2BrCH_2Br$ in reaction with ethylene. For example, the reaction of $CF_3CFBrCFBrCF_3$ with ethylene in the presence of benzoyl peroxide gave a 20% yield each of $CH_2BrCH_2Br$ and $CF_3CF{=}CFCF_3$.

The physical properties of the new compounds prepared in this study are shown in Table I.

## Experimental Section[11]

**General.**—The reactants used were purchased from Du Pont or from Peninsular ChemResearch, Gainesville, Fla., and were not purified further. Vapor phase chromatographic separations were obtained using a silicone elastomer column with about 20% by weight of substrate on Chromosorb P. Helium was used to carry gas on the analytical apparatus and nitrogen was used on the preparative model. A 300-ml-capacity rocking autoclave was used in all experiments except in the addition of $CCl_3Br$ in tetrafluoroethylene for which a 1.4-l. autoclave was used. Nuclear magnetic resonance spectra were obtained on a Varian high-resolution nmr spectrometer operating at 60 Mc for hydrogen spectra and at 56.4 Mc for fluorine spectra. The interpretations were performed with the assistance of Dr. Wallace S. Brey, Jr. Infrared spectra were obtained using a Perkin-Elmer Infracord and a Beckman IR-10 and only those absorption peaks indicative of structural features are reported.

**The $^1H$ and $^{19}F$ Nmr Spectra of the New Compound Prepared.**—The $^1H$ and $^{19}F$ nmr spectra of the compounds shown in Table I are consistent with the assigned structures.

The $^{19}F$ nmr spectra of the new compounds with a $CF_3CF_2$ group showed the presence of two chemically shifted peaks in the area ratio 3:2 which did not show any fine structure. The peak at lower field was assigned to $CF_3$ and at higher fields was assigned to $CF_2$. The compounds with the $CF_2ClF_2$ group also showed the presence of two chemically shifted peaks in the area ratio of 1:1. These peaks were not resolved in compounds where a $CF_2ClCF_2$ group was attached to a saturated carbon atom but were resolved into triplets for compounds where $CF_2ClCF_2$ was attached to an unsaturated carbon atom. The $J_{F-F}$ values were larger for compounds in which a $CF_2ClCF_2$ group was attached to triple bonded carbon and double bonded carbon. The spectra of the compounds with the $CF_2BrCF_2$ groups showed the presence of two chemically shifted peaks in the area of a ratio of 1:1. These peaks showed the expected splitting in all compounds except in cases where $CF_2BrCF_2$ was attached to a carbon atom which had two or more highly electronegative chlorine atoms as substituents. In the compounds $CCl_3CF_2CFClCH_2CH_2Br$ and $CCl_3CF_2CFClCH{=}CH_2$ the two methylene fluorine atoms were magnetically nonequivalent and they showed the expected splitting. The $^{19}F$ spectrum of the compound $CCl_3CF_2CFClCH{=}CH_2$ showed some impurity which was suspected to be $CCl_3CFClCF_2C{=}CH_2$.

**The Addition of Perhaloalkanes to Olefins.**—A typical experiment is described below. The addition of $CF_3CF_2CCl_3$ to ethylene was carried out in a stainless steel, rocking autoclave (300 ml) heated to 100° for 16 hr. Ethylene (40 g, 1.43 mol) was vacuum transferred to the clave cooled in liquid nitrogen to which previously had been added $CF_3CF_2CCl_3$ (248 g, 1.05 mol) and benzoyl peroxide (5 g, 0.02 mol). After reaction, the autoclave was cooled and vented. Low-boiling material (22 g), mostly ethylene, was condensed in a cold trap.

Gas chromatography showed the presence of three new main products in the residual mixture. Distillation of the residual liquid yielded 25.6 g (15% yield) of 1:1 adduct, $CF_3CF_2CCl_2CH_2CH_2Cl$ (I) [bp 33° (10 mm), $n^{21}D$ 1.3942, $d^{21}{}_4$ 1.5225], 40 g (21% yield) of 2:1 adduct, $CF_3CF_2CCl_2(CH_2)_3CH_2Cl$ (II), and 32 g (10% yield) of 3:1 adduct, $CF_3CF_2CCl_2(CH_2)_5CH_2Cl$ (III).

**Addition of $CF_3CF_2CCl_3$ to Propylene.**—The haloalkane (244 g, 1.03 mol), propylene (33 g, 0.86 mol) and benzoyl peroxide (5 g, 0.02 mol) gave three main products according to glpc. The 1:1 adduct was purified by distillation and shown to be $CF_3CF_2CCl_2CH_2CHClCH_3$ (IV, 25.2 g, 16%).

**Addition of $CF_3CF_2CCl_3$ to Isobutylene.**—Haloalkane (382 g, 1.61 mol), isobutylene (27.5 g, 0.49 mol) and benzoyl peroxide (5 g, 0.02 mol) gave a mixture primarily of three new products. Two of these were separated and identified as $CF_3CF_2CCl_2CH_2C(CH_3){=}CH_2$ (V, 13 g, 10%) and the 1:1 adduct $CF_3CF_2CCl_2CH_2CCl(CH_3)_2$ (VI, 57.5 g, 40%).

**Dehydrohalogenation of $CF_3CF_2CCl_2CH_2CCl(CH_3)_8$ (VI) with Potassium Hydroxide.**—VI (20.6 g, 0.06 mol) was heated with KOH pellets (25 g, 0.45 mol) and the low-boiling material (15 g) distilled directly from the reaction mixture. Gas chromatography showed the presence of seven new main products in the reaction mixture. Only 4.4 g (30% yield) of one of them was isolated pure and identified as $CF_3CF_2CCl{=}C{=}C(CH_3)_2$ (VII). The $^1H$ and $^{19}F$ nmr spectra were consistent with the above structure. The $C{=}C{=}C$ band was found at 5.07 μ.

**The Addition of $CF_2ClCF_2CCl_3$ to Propylene.**—Haloalkane (266.5 g, 1.12 mol), propylene (42 g, 1.0 mol), and benzoyl peroxide (5.0 g, 0.02 mol) were heated at 100° for 4 hr. Gas chromatography showed the presence of three new products one of which was isolated by distillation and shown to be $CF_2ClCF_2CCl_2CH_2CHClCH_3$ (VIII).

**Addition of $CF_2ClCF_2CCl_3$ to Isobutylene.**—$CF_2ClCF_2CCl_3$ (381 g, 1.5 mol), isobutylene (28 g, 0.5 mol) and benzoyl peroxide (5 g, 0.02 mol) were heated in an autoclave at 100° for 4 hr with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of three new main products in the reaction mixture. Distillation yielded 33.6 g (25% yield) of $CF_2ClCF_2CCl_2CH_2C(CH_3){=}CH_2$ (X, ir 6.06 μ), and 20.42 g (13% yield) of 1:1 adduct, $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$ (XI).

**Dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2CHClCH_3$ (VIII) with Potassium Hydroxide.**—VIII (29 g, 0.1 mol) was dropped slowly into a mixture of KOH (11.2 g, 0.2 mol) and ethanol (23 g, 0.5 mol) at reflux temperature. It was kept for another 30 min at reflux temperature. The reaction mixture was poured into water and the organic layer was separated, washed and dried. Crude material (15 g) was obtained. Gas chromatography showed the presence of seven new products in this crude material. Only one of them was isolated pure; it was identified as $CF_2ClCF_2CCl{=}CHCHClCH_3$ (IX). The $^1H$ and $^{19}F$ nmr spectra were consistent with the above structure. The $C{=}C$ absorption was found at 6.08 μ.

**Dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2C(CH_3){=}CH_2$ (X) with Potassium Hydroxide.**—X (13.7 g, 0.05 mol) was heated with KOH pellets (11.2 g, 0.2 mol) and the low-boiling material (7 g) distilled directly from the reaction mixture. Gas chromatography showed the presence of two new main products, in yields of 31 and 41%. These were separated by preparative scale vpc and identified as follows: $CF_2ClCF_2C{\equiv}C{-}C(CH_3){=}CH_2$ (XII) [bp 109° (micro), $n^{21}D$ 1.3975, $d^{21}{}_4$ 1.1960 (ir $C{\equiv}C$ 4.45 μ, $C{=}C$ 6.19 μ)]; $CF_2ClCF_2CCl{=}CHC(CH_3){=}CH_2$ (XII) [bp 152° (micro), $n^{21}D$ 1.4273, $d^{21}{}_4$ 1.3451 (ir $C{=}C$ 6.14, 6.24 μ)]. The $^1H$ and $^{19}F$ nmr spectra were consistent with the above structure.

**Dehydrohalogenation of $CF_2ClCF_2CCl_2CH_2CCl(CH_3)_2$ (XI) with Potassium Hydroxide.**—XI (17.8 g, 0.06 mol) was heated with

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[11] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

KOH pellets (20 g, 0.36 mol) and the low-boiling material (11.5 g) distilled directly from the reaction mixture. Gas chromatography showed the presence of five new main products in the reaction mixture. Three were separated by preparative scale vpc and were identified as follows: $CF_2ClCF_2C{\equiv}CC(CH_3){=}CH_2$ (XII) (its properties are reported in the previous experiment); $CF_2ClCF_2C{\equiv}CCCl(CH_3)_2$ (XIV, ir C≡C 4.4 μ); $CF_2ClCF_2CCl{=}C{=}C(CH_3)_2$ (XV), $n^{21}{}_D$ 1.4212 (ir C=C=C 5.03 μ). Two other fractions could not be separated pure; hence, they were not positively identified; however, glpc analysis indicated that one was probably $CF_2ClCF_2CCl_2CH_2CCH_3{=}CH_2$ (X) which was obtained above.

**The Addition of $CCl_3CF_2CFClBr$ to Ethylene.**—$CCl_3CF_2CFClBr$ (109 g, 0.35 mol), ethylene (4.2 g, 0.15 mol) and benzoyl peroxide (0.5 g, 0.002 mol) were heated in an autoclave at 100° for 3 hr with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of one new main product in the residual mixture. Distillation yielded 20 g (43% yield) of 1:1 adduct, $CCl_3CF_2CFClCH_2CH_2Br$ (XVI).

**Dehydrohalogenation of $CCl_3CF_2CFClCH_2CH_2Br$ (XVI) with Potassium Hydroxide.**—XVI (17 g, 0.05 mol), KOH (8 g, 0.14 mol) and ethanol (11.5 g, 0.25 mol) were heated in a 50-ml flask fitted with water reflux condenser at reflux temperature for 30 min. The reaction mixture was poured into water and the organic layer was separated, washed and dried. Crude material (9 g, 75% yield) was obtained. Gas chromatography showed the presence of one new main product in this impure material. This was purified by preparative scale gas chromatography and identified as $CCl_3CF_2CFClCH{=}CH_2$ (XVII, ir C=C 6.1 μ).

**The Preparation of $CCl_3CF_2CF_2Br$.**—$CCl_3Br$ (1668 g, 8.4 mol), tetrafluoroethylene (200 g, 2.0 mol) and benzoyl peroxide (10.0 g, 0.04 mol) were heated in a 1.4-l. autoclave at 100° for 8 hr. Distillation of the reaction mixture gave the 1:1 adduct $CCl_3CF_2CF_2Br$ (350 g, 58%): bp 134° (micro); $n^{21}{}_D$ 1.4301; $d^{21}{}_4$ 1.9228 (*Anal.* Calcd for $C_3BrCl_3F_4$: Br, 26.81. Found: Br, 26.82).

**The Addition of $CCl_3CF_2CF_2Br$ to Ethylene.**—$CCl_3CF_2CF_2Br$ (325 g, 1.1 mol), ethylene (13 g, 0.46 mol) and benzoyl peroxide (2.5 g, 0.01 mol) were heated in an autoclave at 100° for 8 hr with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of four new main products in the reaction mixture. These were separated by distillation and preparative scale gas chromatography. Their amounts were estimated by glpc. The new compounds were $CCl_3CF_2CF_2CH_2CH_2Cl$ (XIX, 8.6 g, 7% yield) (*Anal.* Calcd for $C_5Cl_4F_4H_4$: C, 21.24; H, 1.42; F, 26.92, Br, 0.00. Found: C, 21.36, H, 1.46, F, 27.18, Br, 0.50); $CCl_3CF_2CF_2CH_2CH_2Br$ (XX, 60 g, 40% yield); and $CF_2BrCF_2CCl_2CH_2CH_2Br$ (XXI, 15 g, 9% yield). A second fraction was unidentified and is probably $CF_2BrCF_2CCl_2CH_2CH_2Cl$ (2.3 g, 1.5% yield).

**Addition of $CF_2BrCFBrCF_3$ to Ethylene.**—$CF_2BrCFBrCF_3$ (236 g, 0.76 mol), ethylene (7 g, 0.25 mol) and benzoyl peroxide (1 g, 0.004 mol) were heated in an autoclave at 100° for 16 hr with constant rocking. On venting the autoclave no low-boiling material was obtained. Gas chromatography showed the presence of one new main product in the reaction mixture. Distillation yielded 43 g (51% yield) of 1:1 addition product, $CF_2BrCF(CF_3)CH_2CH_2Br$ (XXXI).

**Dehydrohalogenation of $CF_2BrCF(CF_3)CH_2CH_2Br$ (XXXI) with Potassium Hydroxide.**—XXXI (20.2 g, 0.065 mol) was dropped slowly into a mixture of KOH (7 g, 0.13 mol) and ethanol (4.6 g, 0.1 mol) at room temperature. The reaction mixture was refluxed for 1 hr and poured into water. The organic layer was separated, washed and dried. Crude material (8 g, 54% yield) was obtained. Gas chromatography showed the presence of one new main product in this material. This was separated by preparative glpc and identified as $CF_2BrCF(CF_3)CH{=}CH_2$ (XXXII, ir C=C 6.08 μ).

**The Addition of $CF_2BrCF_2Br$ to Ethylene.**—$CF_2BrCF_2Br$ (401 g, 1.54 mol), ethylene (17.5 g, 0.63 mol) and benzoyl peroxide (2.5 g, 0.01 mol) were heated at 100° for 12 hr. Gas chromatography showed the presence of two new main products in the residual liquid. Distillation yielded 57 g (32% yield) of 1:1 adduct, $CF_2BrCF_2CH_2CH_2Br$ [XXVI, bp 72° (80 mm)], and 38.5 g (20% yield) of 2:1 adduct, $CF_2BrCF_2(CH_2)_3CH_2Br$ (XXVII).

**Dehydrohalogenation of $CF_2BrCF_2CH_2CH_2Br$ (XXVI) with Potassium Hydroxide.**—XXVI (21.7 g, 0.075 mol) was dropped slowly into a mixture of KOH (8 g, 0.14 mol) and ethanol (23 g, 0.5 mol) at reflux temperature. The olefin (15.2 g, 96% yield) was distilled directly from the reaction mixture as it was formed. This was purified by preparative glpc and identified as $CF_2BrCF_2CH{=}CH_2$ (XXVIII, ir C=C 6.06 μ). The $^1H$ and $^{19}F$ nmr spectr were consistent with the above structure.

**Dehydrohalogenation of $CF_2BrCF_2(CH_2)_3CH_2Br$ (XXVII) with Potassium Hydroxide.**—XXVII (9.6 g, 0.03 mol) was dropped slowly into a mixture of KOH (5.6 g, 0.1 mol), ethanol (9.2 g, 0.2 mol) and water (9 g, 0.5 mol) at reflux temperature. The reaction mixture was kept at reflux temperature for another 30 min and it was poured into water. The organic layer was separated, washed and dried. Gas chromatography showed the presence of two new main products in this material. Their amounts were estimated by vpc analysis. They were separated by preparative vpc and identified as $CF_2BrCF_2(CH_2)_2CH{=}CH_2$ (XXIX, 1.0 g, 14% yield, ir C=C 6.07 μ), and $CF_2BrCF_2(CH_2)_3CH_2OCH_2CH_3$ (XXX), 5.7 g, 67% yield.

**The Addition of CFClBrCFClBr to Ethylene.**—CFClBrCFClBr (293 g, 1 mol), ethylene (20 g, 0.72 mol) and benzoyl peroxide (5 g, 0.02 mol) were heated in an autoclave at 100° for 16 hr with constant rocking. On venting the autoclave no gaseous material was obtained. Gas chromatography showed the presence of three main products in the reaction mixture. These were separated by distillation and preparative scale gas chromatography. Their amounts were estimated by vpc analysis and they were identified as follows: CFCl=CFCl [26.5 g, 20% yield, bp 22°, $n^{21}{}_D$ 1.3763 (lit.[12] bp 22°, $n^0{}_D$ 1.3798)]; $CH_2BrCH_2Br$ [38 g, 20% yield, bp 131.2° (micro), $n^{21}{}_4$ 1.5377, $d^{21}{}_4$ 2.1647 (lit.[13] bp 131.6°, $n^{25}{}_D$ 1.5379, $d^{25}{}_4$ 2.1701)]; and $CFClBrCFClCH_2CH_2Br$ (XXII, 85 g, 30% yield).

**Dehydrohalogenation of $CFClBrCFClCH_2CH_2Br$ (XXII) with Potassium Hydroxide.**—XXII (10.3 g, 0.032 mol) was dropped slowly into a mixture of potassium hydroxide (5.6 g, 0.1 mol) and ethyl alcohol (4.6 g, 0.1 mol) at reflux temperature. The reaction mixture was refluxed for 30 min and poured into water and the organic layer separated, washed and dried. Crude material (6.8 g, 75% yield) was obtained. Gas chromatography showed the presence of one main product in this crude material. It was separated by preparative scale glpc and identified as $CFClBrCFClCH{=}CH_2$ (XXIII, ir C=C 6.1 μ).

**Dehalogenation of XXII with Zinc.**—XXII (16.1 g, 0.05 mol) was dropped slowly into a mixture of zinc (6.5 g, 0.1 mol), ethanol (4.6 g, 0.1 mol) and zinc chloride (0.1 g, 0.001 mol) at reflux temperature. The reaction mixture was refluxed for 30 min and the low-boiling material (12.9 g) was distilled directly from the reaction mixture. Gas chromatography showed the presence of one new main product in this material. This was separated by preparative vpc and identified as an isomeric mixture of *cis* (44%) and *trans* (56%) $CFCl{=}CFCH_2CH_2Br$ (XXIV).

**Dehydrohalogenation of $CFCl{=}CFCH_2CH_2Br$ (XXIV) with Potassium Hydroxide.**—XXIV (5 g, 0.025 mol) was dropped slowly into a mixture of potassium hydroxide (5.6 g, 0.1 mol) and ethanol (4.6 g, 0.1 mol). The low-boiling material (2.4 g, 80% yield) distilled directly from the reaction mixture as it was formed. Gas chromatography showed the presence of one new main product in this material. This was separated by preparative scale glpc and identificed as an isomeric mixture of *cis* (44%) and *trans* (56%) $CFCl{=}CFCH{=}CH_2$, which polymerizes on standing at room temperature. *Anal.* Calcd for $C_4ClF_2H_3$: Cl, 27.68. Found: Cl, 28.29.

**Addition of $CF_3CFBrCFBrCF_3$ to Ethylene.**—$CF_3CFBrCFBrCF_3$ (346 g, 0.96 mol), ethylene (14.5 g, 0.52 mol) and benzoyl peroxide (5 g, 0.02 mol) were heated at 100° for 8 hr with constant rocking. On venting the autoclave 30 g of low-boiling material was obtained. This consisted of ethylene and perfluorobutene-2. Gas chromatography showed the presence of two new materials in the reaction mixture. Their yields were estimated by distillation and vpc analysis. They were identified as $CF_3CF{=}CFCF_3$ [40 g, 20% yield, bp 2° (lit.[12] bp 0° (740 mm)] and $CH_2BrCH_2Br$ [37 g, 20% yield, bp 131° (micro), $n^{11}{}_D$ 1.5375, $d^{21}{}_4$ 2.1685 (lit.[13] bp 131.6°, $n^{25}{}_D$ 1.5379, $d^{25}{}_4$ 2.1701)].

**Preparation and Addition of $CF_3CFBrCClBrCF_3$ to Ethylene. Preparation of $CF_3CFBrCClBrCF_3$.**—$CF_3CFBrCClBrCF_3$ was

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(12) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," ACS Monograph Series, Reinhold Publishing Corp., New York, N. Y. 1958.

(13) "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958.

prepared from $CF_3CFClCCl_2CF_3$ by dechlorination followed by bromination of the product.

**Addition of $CF_3CFClCFBrCF_3$ to Ethylene.**—$CF_3CFBrCClBrCF_3$ (2.42 g, 0.64 mol), ethylene (7 g, 0.25 mol) and benzoyl peroxide (3 g, 0.012 mol) were heated in an autoclave at 100° for 4 hr with constant rocking. On venting the autoclave 50 g of low-boiling material was condensed. This consisted of $CF_3CF{=}CClCF_3$ with small amount of ethylene. Gas chromatography showed the presence of only one new chief product in the residual mixture. It was identified as $CH_2BrCH_2Br$. Glpc analysis indicated quantitative yields of the two products.

**Registry No.**—1, 18621-12-0; 2, 18621-13-1; 3, 18621-14-2; 4, 18599-02-5; 5, 18599-03-6; 6, 18599-05-8; 7, 18599-04-7; 8, 18599-06-9; 9, 18621-15-3; 10, 18599-07-0; 11, 18599-08-1; 12, 18599-09-2; 13, 18599-10-5; 15, 18599-11-6; 16, 18599-12-7; 17, 18599-13-8; 18, 812-31-7; 19, 18599-15-0; 20, 18599-16-1; 21, 18599-17-2; 22, 18621-16-4; 23, 18599-18-3; 24, 18599-19-4; 26, 18599-20-7; 27, 18599-21-8; 28, 18599-22-9; 29, 18599-23-0; 30, 18599-24-1; 31, 3871-35-0; 32, 2546-54-5.

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# Oxidation of Organic Compounds by Cerium(IV). VI. Oxidative Cleavage of Glycols by Cerium(IV) and Lead(IV). The Question of One- and Two-Electron Oxidative Cleavages[1]

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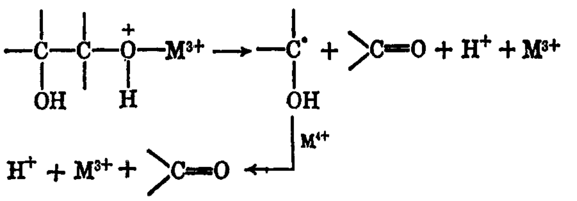
The yields of cyclohexanone obtained from the oxidation of bicyclohexyl-1,1′-diol in 75% aqueous acetic acid by cerium(IV) or lead(IV) in the absence of any addend and in the presence of acrylamide and acetamide have been measured. It is found that the yields of cyclohexanone are *ca.* 90% in all cases except for the cerium(IV) oxidation in the presence of acrylamide which gives a yield of 48%. These results clearly indicate that an intermediate radical can be trapped in the oxidation by cerium(IV) but no radicals are trapped by acrylamide in the oxidation of glycols by lead(IV). Mechanistic implications of these results are discussed.

The initial step of metal ion oxidative cleavage of glycols can be, in principle, either a one- or two-electron oxidation. These two pathways are outlined below for a tetrapositive metal ion. For simplicity monodentate glycol–metal complexes are drawn, but similar mechanisms could be drawn which involve bidentate glycol–metal complexes.[2] Since an intermediate radical is formed in the one-electron pathway, the presence of an effective radical trap should reduce the yield of ketone by a factor of 2.

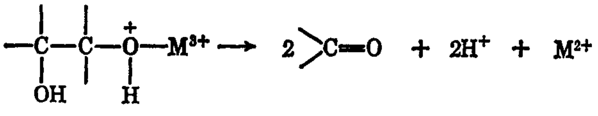
one-electron oxidative cleavage



$$-\underset{OH}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{H}{\overset{+}{O}}-M^{3+} \longrightarrow -\underset{OH}{\overset{|}{C}}{}^{\bullet} + {>}C{=}O + H^+ + M^{3+}$$

$$H^+ + M^{3+} + {>}C{=}O \xleftarrow{M^{4+}}$$

two-electron oxidative cleavage



$$-\underset{OH}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{H}{\overset{+}{O}}-M^{3+} \longrightarrow 2{>}C{=}O + 2H^+ + M^{2+}$$

Mino, Kaizerman, and Rasmussen[3] studied the oxidation of pinacol (2,3-dimethylbutanediol-2,3) by ceric sulfate in water at 25° in the presence and absence of acrylamide and concluded that the yield of acetone was decreased by a factor of 2 in the presence of acrylamide. They argued that the acrylamide was an effective trap for an intermediate radical which means that their results indicate that the first step of a cerium(IV) oxidation of a glycol is a one-electron oxidation. However, these workers quantitatively analyzed for acetone by an involved spectrophotometric method and carried out no control experiments to ascertain whether or not the high concentration of an amide affected the reaction. For these reasons, we felt that it was worthwhile to repeat this study using a glycol that produced a ketone that could be accurately analyzed directly by glpc methods that are now available and running a control run in the presence of a high concentration of some nonradical-trapping amide such as acetamide. Moreover, we wanted to carry out a similar set of experiments under identical conditions with a lead(IV) instead of cerium(IV) oxidizing agent. Since no evidence for cerium(II) or cerium(I) in aqueous solutions exists, it is reasonable that the cerium(IV) glycol cleavage goes by a one-electron oxidation. However, lead(IV) oxidations are known to go by both one- and two-electron pathways[4] and

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[1] (a) Part V: P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **90**, 4755 (1968). (b) This work was partially supported by Public Health Service Grant GM 13799 from the National Institutes of General Medical Sciences. (c) National Science Foundation Undergraduate Research Participant, Summer 1966.

[2] (a) H. L. Hintz and D. C. Johnson, *J. Org. Chem.*, **32**, 556 (1967); (b) L. B. Young and W. S. Trahanovsky, unpublished results.

[3] G. Mino, S. Kaizerman, and E. Rasmussen, *J. Amer. Chem. Soc.*, **81**, 1494 (1959).

[4] (a) R. Criegee in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter V; (b) W. H. Starnes, Jr., *J. Amer. Chem. Soc.*, **90**, 1807 (1968), and references cited therein.