# Fluoro Olefins. IV. The Stereochemistry of Nucleophilic Displacement of Chloride Ion on β-Substituted 1-Chloroperfluoro Olefins[1]

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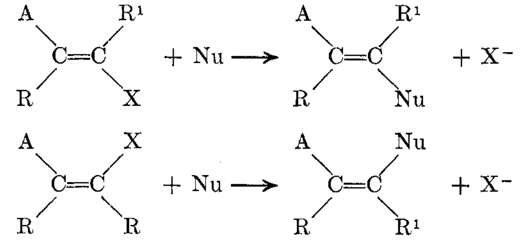
*Received December 7, 1970*

A series of cis- and trans-β-substituted 1-chloroperfluoro olefins were treated with methoxide ion (from methanol and potassium hydroxide) in methanol at room temperature. Retention of the original cis or trans configuration was observed in all cases. The type of β substituent (aromatic or alkyl), the type of para substituent in aromatic group (electron releasing or electron withdrawing), and the size of the perfluoro alkyl group had no effect on the stereochemical results. The results of these reactions can best be rationalized by an irreversible trans addition of methoxide to the olefin to give a short-lived carbonionic intermediate followed by a rapid cis elimination of halide ion.

Vinylic halogen is normally inert toward displacement by nucleophiles, but reaction will occur if the olefin is activated by an electron-withdrawing group. A number of workers have investigated the stereochemistry of nucleophilic displacement reactions on cis–trans pairs of such olefins. Vinyl halides activated by such diverse groups as sulfone,[3-7] carbonyl,[8-10] aromatic,[11-16] and cyano[17] have been investigated. A wide variety of nucleophilic reagents have been employed in these studies, including alkoxide,[4,8,10,15-17] azide,[5] iodide,[11] thiophenoxide,[3,5,9,10,12,13,17] diphenylarsine,[14] and diphenyl phosphide[18-20] ion and amines.[6,7,17]

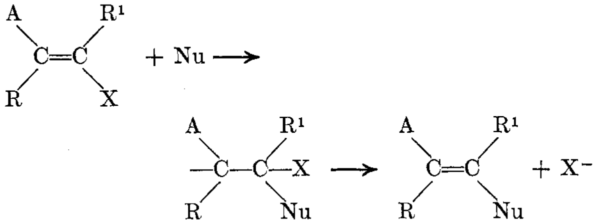
Displacement reactions using pure cis or trans vinyl halide usually proceeded quite stereospecifically, with retention of the original cis or trans configuration (eq 1).


(1)

A = activating group; Nu = nucleophile; X = Cl, Br

Nonstereospecific displacement of halide ion occurs when amines[6,7,17] are used as nucleophiles. This was also encountered when iodide ion[11] was used as the nucleophile, due to reversible reaction of the vinyl iodide product with other halide ion.

These reactions are usually postulated to take place *via* the addition–elimination mechanism shown in eq 2.


(2)

A = activating group; Nu = nucleophile; X = halogen

A number of workers[8,10,12,16,17] have observed clean second-order kinetics in these reactions, first order each in vinyl halide and nucleophile. In the first step of the reaction, the nucleophile adds to vinyl halide to form a carbanionic species. The addition is postulated to be irreversible,[16] with the incoming nucleophile and electron pair entering trans to the plane of the original $\pi$ orbital.[8,9,11] The carbanion carbon of this intermediate species has been proposed to be either tetrahedral[8,9,11] or planar.[21] In the second step, halide ion is eliminated either in a trans fashion *via* inversion of the carbanion center and rotation through 30°,[8,9,11] or by cis elimination *via* rotation through 30°.[8,9] The stereospecificity of the reaction indicates that the carbanionic intermediate has a very short lifetime.[17] Modena[15] has found that reaction of β-fluoro-4-methoxybenzoylstyrene with ethoxide ion is nonstereospecific due to slow breaking of the carbon–fluorine bond, yielding a relatively long-lived carbanionic species, which forms the most thermodynamically stable olefinic product. The possibility that the intermediate carbanionic species is protonated before going to product was eliminated by reaction of nucleophiles and β-halostyrenes labeled with deuterium in the α position[10] or with unlabeled β-halostyrene in deuterated ethanol.[8] No loss or incorporation of deuterium, respectively, was found to occur.

In the reaction of certain activated β-halostyrenes with an α hydrogen, an elimination–addition mechanism may be operative. Modena[10,22] observed that the very basic nucleophile, methoxide ion, reacted with *cis*-4-methoxybenzoyl-β-bromo- (or chloro-) styrene to substitute halide ion as shown in eq 3. In the corresponding trans isomer, the reaction proceeds *via* the normal addition–elimination sequence, due to the unfavorable cis elimination of hydrogen halide that would have to occur for the elimination–addition mechanism to operate. A whole spectrum of other mechanisms have also been proposed, including direct sub-

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[1] Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] National Institutes of Health Predoctoral Fellow, 1965–1968.

[3] G. Modena, *Ric. Sci.*, **28**, 341 (1958); *Chem. Abstr.*, **52**, 1543c (1958).

[4] L. Maioci and G. Modena, *Gazz. Chim. Ital.*, **89**, 854 (1959); *Chem. Abstr.*, **54**, 22451*i* (1960).

[5] G. Modena and P. E. Todesco, *Gazz. Chim. Ital.*, **89**, 866 (1959); *Chem. Abstr.*, **54**, 22452*f* (1960).

[6] G. Modena, P. E. Todesco, and S. Tonti, *Gazz. Chim. Ital.*, **84**, 878 (1960); *Chem. Abstr.*, **54**, 22453*f* (1960).

[7] F. Montanari, *Gazz. Chim. Ital.*, **87**, 149 (1957).

[8] D. E. Jones, *et al.*, *J. Chem. Soc.*, 2349 (1960).

[9] J. S. Pizey and W. E. Truce, *J. Org. Chem.*, **30**, 4355 (1965).

[10] G. Modena, *et al.*, *J. Chem. Soc. B*, 243 (1969).

[11] S. I. Miller and P. K. Yonan, *J. Amer. Chem. Soc.*, **79**, 5931 (1957).

[12] G. Marchese, F. Naso, and G. Modena, *Tetrahedron*, **24**, 663 (1968).

[13] P. Beltrame and P. L. Beltrame, *Gazz. Chim. Ital.*, **98**, 367 (1968).

[14] A. M. Aguir and T. G. Archibald, *J. Org. Chem.*, **32**, 2627 (1967).

[15] G. Modena, G. Marchese, and F. Naso, *J. Chem. Soc. B*, 290 (1969).

[16] E. F. Silversmith and D. Smith, *J. Org. Chem.*, **23**, 427 (1958).

[17] F. Scotti and E. J. Frazza, *ibid.*, **29**, 1800 (1964).

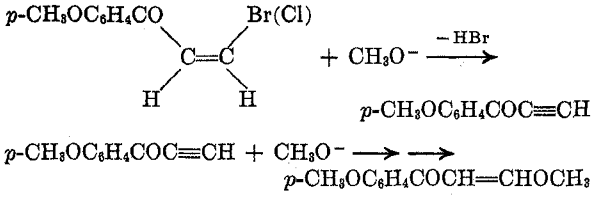
[18] A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, **86**, 2299 (1964).

[19] A. M. Aguiar and D. Daigle, *J. Org. Chem.*, **30**, 2826 (1965).

[20] A. M. Aguiar and D. Daigle, *ibid.*, **30**, 3527 (1965).

[21] J. S. Meek and J. S. Fowler, *ibid.*, **33**, 485 (1968).

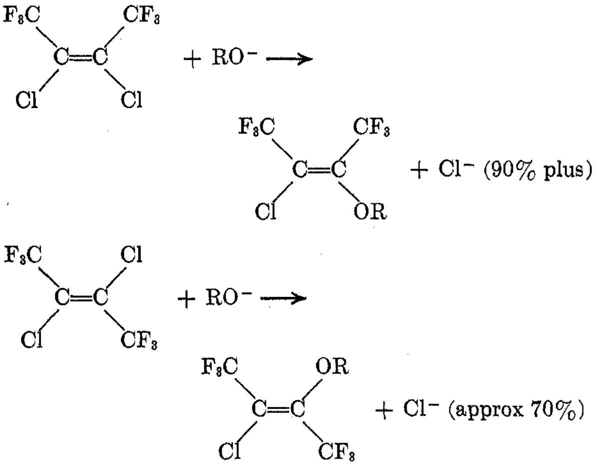
[22] G. Marchese, F. Naso, and G. Modena, *J. Chem. Soc. B*, 958 (1968).



(3)

stitution and a concerted mechanism. These are summarized by Miller[11] and Jones[8] among others.

Vinyl halides activated by polyfluorinated alkyl groups are also useful for this type of study. However, only a few reports have appeared describing the stereochemistry of nucleophilic displacement on such olefins. Park[23] has examined the reaction of alkoxide ion with *cis*- and *trans*-2,3-dichlorohexafluoro-2-butene. Displacement of chloride ion on the cis isomer occurred with greater than 90% stereospecificity; displacement of chloride ion on the trans isomer was approximately 70% stereospecific. Displacement proceeded with retention of the original cis or trans configuration (eq 4).



(4)

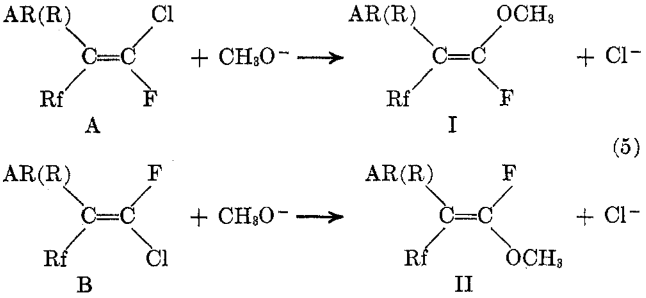
$R = CH_3-, C_2H_5-, i\text{-}C_3H_7-$

The authors concluded that alkoxide substitution on these olefins is governed by kinetic control. They postulated the formation of a planar carbanion as the reaction intermediate, which eliminated chloride ion stereospecifically, since rotation was prevented by the bulky trifluoromethyl groups. A similar investigation was carried out on these compounds using sodium borohydride in diglyme and lithium aluminum hydride in ether as nucleophiles.[24] Sodium borohydride reacted much more stereospecifically with the cis isomer than the trans isomer; displacement of chloride ion by hydride (as borohydride) ion took place 99% stereospecifically with the cis isomer with retention of configuration, but only 55% stereospecifically, with retention of configuration, with the trans isomer. Lithium aluminum hydride reacted less stereospecifically with cis starting material than did sodium borohydride, but more stereospecifically with the trans isomer. Fontanelli and coworkers[25] have investigated the reaction of 1-hydroperfluoropropene with alkoxide ion. They concluded that the stereochemical course of the reaction was "cis stereospecific."

## Results and Discussion

Because of this rather small number of reports on the stereochemical course of nucleophilic displacement reactions on polyfluorinated olefins, and because we had model compounds available,[26,27] it became desirable to us to make such an investigation. Several cis and trans $\beta$-substituted 1-chloroperfluoro olefins were used as model polyfluorinated olefins; methoxide ion, generated *in situ* from the dissolution of potassium hydroxide in methanol, was used as the nucleophilic reagent. The $\beta$ substituent and the size of the perfluoroalkyl group were both varied to determine what effect, if any, these would have on the overall stereochemistry of the displacement reaction. The general procedure used in these displacement reactions involved adding a solution of potassium hydroxide in methanol to a stirred solution of an equimolar amount of olefin (*vs.* potassium hydroxide) in methanol. The reaction was normally carried out at room temperature.

When methoxide ion was allowed to react with pure cis or trans olefin, chloride ion was displaced 90–96% stereospecifically. Retention of the original cis or trans configuration was always observed (eq 5). The reaction was quite clean; yields of methoxy product from chloride ion displacement ranged as high as 77%; only 3–4% yield each of products arising from displacement of fluoride ion or both fluoride and chloride ion were observed. The stereochemical results of these reactions is summarized in Table I. Cis–trans isomer ratios (and yields) were determined by glpc analysis of the reaction mixture, and the absolute configuration of the methoxy product was determined by $^{19}$F nmr spectroscopy (Table II). *cis*-Vinylfluorine–$CF_3(CF_2X)$ coupling constants were in the range of 24–27 cps, and the corresponding trans coupling constants were in the



(5)

TABLE I

RESULTS OF REACTION OF METHOXIDE ION WITH VARIOUS $\beta$-SUBSTITUTED 1-CHLOROPERFLUORO OLEFINS

| AR(R) | Registry no. | Rf | Isomer | % I | % II |
|---|---|---|---|---|---|
| $C_6H_5$ | 19302-03-5 | $CF_3$ | A | 96 | 4 |
| | 19302-02-4 | | B | 4 | 96 |
| $C_6H_5$ | 24165-18-2 | $C_2F_5$ | A | 90 | 10 |
| | 24165-19-3 | | B | 9 | 91 |
| $p$-$ClC_6H_4$ | 19302-07-9 | $CF_3$ | A | 94 | 6 |
| | 19302-06-8 | | B | 8 | 92 |
| $p$-$CH_3OC_6H_4$ | 19302-11-5 | $CF_3$ | A | 92 | 8 |
| | 19302-10-4 | | B | 6 | 94 |
| $c$-$C_6H_{11}$ | 24164-52-1 | $CF_3$ | A | 96 | 4 |
| | 24277-52-9 | | B | 4 | 96 |

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[23] J. D. Park and E. W. Cook, *Tetrahedron Lett.*, 4853 (1965).

[24] R. T. Bogan and D. J. Burton, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p K 29.

[25] R. Fontanelli, *et al.*, *Justus Liebigs Ann. Chem.*, 211 (1967); *Chem. Abstr.*, **71**, 60600w (1969).

[26] H. C. Krutzsch and D. J. Burton, Abstracts 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p K 2.

[27] D. J. Burton and H. C. Krutzsch, *Tetrahedron Lett.*, 71 (1968).

TABLE II

$^{19}F$ AND $^{1}H$ NMR[a] DATA ON β-SUBSTITUTED 1-METHOXYPERFLUORO OLEFINS

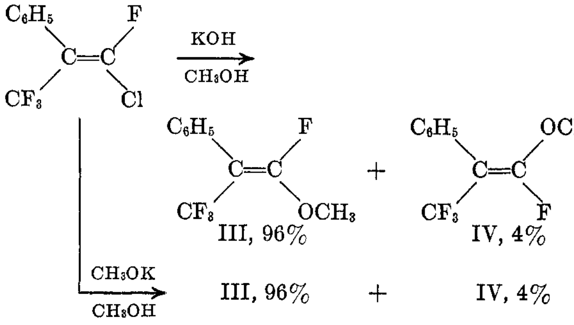
$\underset{(1)}{AR(R)C}(\underset{(2)}{CF_2X})\!=\!\underset{(3)}{CFOCH_3}$

| AR(R) | X | Registry no. | Isomer | $J$ (1),(2) | $\phi$ (1) | $\phi$ (2) | $J$ (2),(3) | $\delta$ (3) |
|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ | F | 29799-98-2 | A | 24 | 81.7 | 57.2 | 1.0 | 3.57 |
| | | 29799-99-3 | B | 13 | 80.0 | 57.2 | 0.9 | 3.71 |
| $C_6H_5$ | $CF_3$ | 29800-00-8 | A | 26 | 79.8 | 108.3 | 1.0 | 3.57 |
| | | 29800-01-9 | B | 10 | 75.3 | 108.0 | 1.0 | 3.78 |
| $p$-$ClC_6H_4$ | F | 29800-02-0 | A | 24 | 81.4 | 57.1 | 1.1 | 3.63 |
| | | 29800-03-1 | B | 13 | 80.8 | 57.7 | 1.0 | 3.79 |
| $p$-$MeOC_6H_4$ | F | 29800-04-2 | A | 24 | 80.7 | 56.8 | 1.0 | 3.68 |
| | | 29800-05-3 | B | 13 | 79.4 | 57.3 | 0.9 | 3.83 |
| $c$-$C_6H_{11}$ | F | 29800-06-4 | A | 27 | 82.8 | 57.4 | 1.0 | 3.75 |
| | | 29800-07-5 | B | 13 | 81.9 | 58.0 | 1.0 | 3.76 |

[a] The chemical shift values are expressed in $\phi$ values in parts per million upfield from $CCl_3F$ or in $\delta$ values in parts per million downfield from tetramethylsilane, and the coupling constant values are in cycles per second.

range of 10–13 cps. This is in agreement with data on similar compounds published by Swalen[28] and Stone.[29] Both infrared and elemental analysis are also in agreement with the assigned structures.

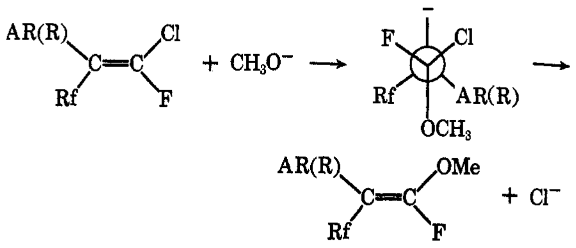
The method used for methoxide ion generation did not affect the stereochemical course of the reaction. Potassium methoxide generated from potassium metal and dry methanol displaced chloride ion with exactly the same stereochemistry and stereospecificity as did potassium methoxide generated from potassium hydroxide and methanol (eq 6).



(6)

As Table I illustrates, the overall stereochemical course and stereospecificity of the displacement reaction is largely unaffected by changing either of the substituents attached to the β-olefinic carbon. Thus, the reaction is not affected by electron-releasing or -withdrawing groups on the phenyl ring or by substitution of an aliphatic group in place of the phenyl ring. Furthermore, it is also largely unaffected by increasing the size of the perfluoroalkyl group from perfluoromethyl to perfluoroethyl. The only difference observed was a lower reactivity of the cyclohexyl substituted olefin toward the methoxide ion. Reaction required refluxing overnight, whereas the corresponding aryl-substituted olefins required only stirring for several hours at room temperature to effect reaction.

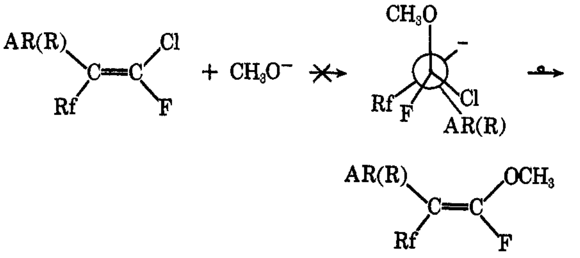
The stereochemical course of these reactions can be best rationalized by postulating an irreversible trans addition of the incoming nucleophile and electron pair across the double bond to form an unstable (short-lived) carbanionic species in the first step. Rapid cis elimination of chloride ion in the second step then forms the product methoxy olefin (eq 7).



(7)

The fact that no evidence of cis–trans isomerization was observed in recovered starting olefin demonstrated irreversible addition of nucleophile. Cis elimination of halide ion, although not common, has been documented;[30,31] a carbanionic intermediate is proposed for such cis eliminations. The possibility of protonation of the carbanionic intermediate, followed by elimination of hydrogen chloride to form product olefin, is unlikely because of the high stereospecificity observed for both isomers. Protonation would allow rotation to take place, yielding the most thermodynamically favorable isomer or isomer ratio (eq 8). The alternative possibility of cis addition of nucleophile followed by trans elimination of chloride ion does not appear likely, since both the initial addition and the following elimination would cause eclipsing of the attached groups (eq 9).

$$AR(R)C(Rf)\!=\!CFCl + CH_3O^- \longrightarrow$$
$$AR(R)\bar{C}(Rf)CFClOCH_3 \not\rightarrow AR(R)CHRfCFClOCH_3 \quad (8)$$



(9)

Further, if rotation occurred, the overall reaction would not be so stereospecific as the data indicate, since rotation would allow time for the carbanion to equilibrate (invert); rotation in addition requires the carbanion to be reasonably stable (long-lived), which also does not seem very likely. Indirect proof for this assumption

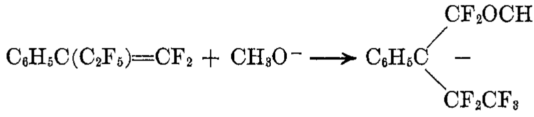
(28) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **17**, 1244 (1961).

(29) J. D. Swalen and C. A. Reily, *J. Chem. Phys.*, **34**, 2122 (1961).

(30) S. J. Cristol and N. L. House, *J. Amer. Chem. Soc.*, **74**, 2193 (1952).

(31) S. J. Cristol and R. P. Argan Bright, *ibid.*, **79**, 3441 (1957).

was provided by reaction of 2-phenylperfluoro-1-butene with methoxide ion (eq 10). If the intermediate carbanion V is reasonably long-lived (stable), the more thermodynamically stable compound VII should be the predominant product; experimentally, the product consisted of 50% VI and 50% VII. This ratio would occur if the intermediate carbanion V was unstable (short-lived) and eliminated fluoride ion in a statistical fashion from the $-CF_2OCH_3$ or $-CF_2CF_3$ group. Product ratios were determined by glpc analysis of the reaction mixture; structures were determined by $^{19}F$ nmr spectroscopy. The observed stereochemistry of the displacement reaction rules out trans addition–trans elimination or cis addition–cis elimination mechanisms.



$$C_6H_5C(C_2F_5){=}CF_2 + CH_3O^- \longrightarrow C_6H_5C\begin{matrix}CF_2OCH_3\\ \\ CF_2CF_3\end{matrix}\ ^{-} \qquad (10)$$

V

$$V \longrightarrow \underset{VI}{C_6H_5C(C_2F_5){=}CFOCH_3} + \underset{VII}{C_6H_5C(CF_2OCH_3){=}CFCF_3}$$

## Experimental Section

**A. Reaction of β-Substituted 1-Chloroperfluoro Olefins with Methoxide Ion.**—Into a 100-ml three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, and pressure-equalized dropping funnel was placed 0.009 mol (*ca.* 2 g) of pure cis or trans olefin and 10 ml of methanol. Stirring was started and a solution of 0.6 g (85% pure) of potassium hydroxide (0.009 mol) in 8 ml of methanol was added dropwise. The resulting mixture was allowed to stir an additional 3 hr at room temperature and then poured into 100 ml of water. The resulting mixture was extracted twice with 30-ml portions of ether, which were combined, washed three times with 25-ml portions of water, and dried over anhydrous magnesium sulfate. Product yields were determined using an external standard of the corresponding methoxy compound employing a 6-ft 10% silicone rubber on Gas-Chrom P analytical column, and cis–trans isomer ratios were determined using a 6-ft 10% Carbowax 20M or Chromosorb P analytical column. Fluorine nmr spectroscopy was used to assign the absolute configuration of products.

**B. Reaction of $C_6H_5C(CF_3){=}CFCl$ (Phenyl and Chlorine Trans) with Potassium Methoxide Generated from Potassium Metal and Methanol.**—In a 50-ml three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, and dropping funnel was placed 3 ml of methanol (dried by distillation from CaO) and 0.5 g (0.0022 mol) of pure $C_6H_5C(CF_3){=}CFCl$ (phenyl and chlorine trans). Into this solution was added dropwise 2 ml of methanol (dried by distillation from CaO), in which 0.087 g (0.0022 g-atom) of potassium metal had been dissolved. The resulting mixture was allowed to stir an additional 3 hr at room temperature and then worked up as in part A. Glpc analysis on the Carbowax 20M column (see part A) demonstrated that 96% of the $C_6H_5C(CF_3)C{=}CFOMe$ formed existed as the isomer bearing the phenyl and methoxy groups trans, while the remaining 4% existed as the corresponding cis isomer. Recovered starting material was unisomerized.

**C. Reaction of $C_6F_5C(C_2F_5){=}CF_2$ with Methoxide Ion.**—Into a 50-ml one-necked flask was placed 10 ml of methanol and 1.2 g (0.005 mol) of $C_6F_5C(C_2F_5){=}CF_2$.[32] To the resulting mixture was added 0.3 g (85% pure, 0.005 mol) of potassium hydroxide. The resulting mixture was stirred an additional 1 hr and then subjected to work-up (see part A). Glpc analysis of the dried ether extract on the silicone rubber column (see part A) showed that the product consisted of a 50:50 mixture of $C_6H_5C(C_2F_5){=}CFOCH_3$ and $C_6H_5C(CF_2OCH_3){=}CFCF_3$. Structural assignments were obtained *via* fluorine nmr spectroscopy. When a similar mixture was allowed to reflux for 6 hr, the corresponding product ratio was 52:48.

**Registry No.**—2-Phenylperfluoro-1-butene, 3315-60-4; methoxide ion, 5300-25-4.

**Acknowledgment.**—This work was supported in part by the Public Health Service (GM 11809).

[32] D. J. Burton and F. E. Herkes, *J. Org. Chem.*, **33**, 1854 (1968).

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# Stable Carbocations. CXX.[1] Preparation of Alkyl (Aryl) Carbenium Ions from Olefins

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*Received December 10, 1970*

Experimental conditions have been found for protonation of olefins in superacids to form stable carbenium ions without concomitant polymerization.

Cationic polymerization generally occurs when treating reactive olefins with strong acids.[2] The first step in cationic polymerization of olefins is assumed to be protonation of the double bond to form a carbenium ion. Intermediate carbenium ions, however, have never been observed in cationic polymerizations. Carbenium ions formed react immediately with excess of monomer olefin in the fast chain propagation reaction. Termination of the polymer chain generally takes place by transfer reaction or elimination. Stable alkyl (aryl) carbenium ions can be generated by ionization of different precursors in strong acids,[3] but protonation of olefins, although proceeding with ease, generally yields complex mixtures. There are qualitative claims in the literature concerning generation of stable carbenium ions by protonation of phenyl- and methyl-substituted olefins.[4-7] However, it has never been shown that these reactions can lead to the clean formation of the

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[1] (a) Part CXIX: G. A. Olah, P. R. Clifford, and Y. Halpern, *J. Amer. Chem. Soc.*, in press. Note change in title of series of publications to "Stable Carbocations," instead of previously used "Stable Carbonium Ions." Carbonium ions, as outlined in part CXVIII, are pentacoordinated ions as contrasted with trivalent carbenium ions. The general naming of carbocations (in accordance with the naming of carbanions) seems to be appropriate. (b) Concerning the definition and naming of carbocations (the generic name for all cations of carbon compounds, as carbanion are the anions), we recently suggested a clear differentiation between trivalent carbenium (and/or carbynium) and penta- and tetracoordinated carbonium ions: G. A. Olah, *ibid.*, in press.

[2] S. Bywater, in "Chemistry of Cationic Polymerization," P. H. Plesch, Ed., Pergamon Press, New York, N. Y. 1963, p. 311.

[3] G. A. Olah and J. A. Olah in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R Schleyer, Ed., Interscience, New York, N. Y., 1970, Chapter 17.

[4] V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

[5] D. G. Farnum, *J. Amer. Chem. Soc.*, **89**, 2970 (1967).

[6] H. C. Den., C. U. Pittman, Jr., and J. O. Turner, *ibid.*, **87**, 2154 (1965).

[7] (a) D. M. Brouwer, *Recl. Trav. Chim. Pay-Bas*, **87**, (3), 210 (1968); (b) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc., London*, 147 (1964).