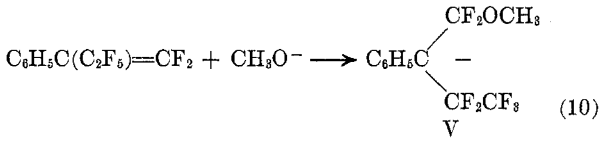
was provided by reaction of 2-phenylperfluoro-1-butene with methoxide ion (eq 10). If the intermediate carbanion V is reasonably long-lived (stable), the more thermodynamically stable compound VII should be the predominant product; experimentally, the product consisted of 50% VI and 50% VII. This ratio 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.



$$C_6H_5C(C_2F_5){=}CF_2 + CH_3O^- \longrightarrow \underset{\mathrm{V}}{C_6H_5\overset{CF_2OCH_3}{\underset{CF_2CF_3}{C^-}}} \qquad (10)$$

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

## 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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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

[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).

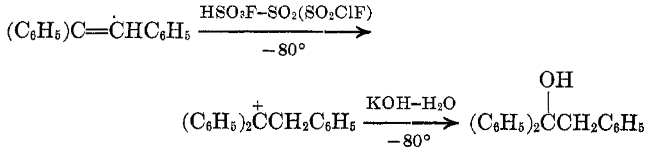
[7] (a) D. M. Brouwer, *Recl. Trav. Chim. Pay-Bas*, **87**, (3), 210 (1968); (b) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc., London*, 147 (1964).

expected cations, without concurrent formation of complex mixtures of cyclized or polymeric cations and other polymeric materials. For years in our laboratory attempts were made to clearly generate stable monomeric carbenium ions by protonation of olefins. It became obvious that one must find proper conditions to minimize the possibility of reaction between the carbenium ion and excess olefin.

We have now succeeded in finding the conditions which allow the formation of stable monomeric carbenium ions as the only or predominant product in high yields of the protonation of olefins in superacids. We should emphasize that there is not a single general procedure which can be applied to any olefin, but specific conditions have to be used in each case. The purpose of this paper is to describe characteristic procedures for the preparation of different types of carbenium ions by protonation of olefins.

## Results and Discussion

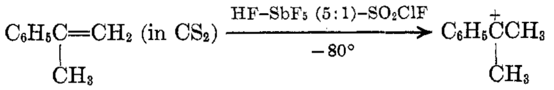
**A. Diphenylbenzylcarbenium Ion** (1).—Attempts to generate ion **1** by protonation of triphenylethylene with $HSO_3F$–$SbF_5$ (either in $SO_2$ or $SO_2ClF$ solution) at low temperatures were unsuccessful. On the other hand, slow addition of an $SO_2$ (or $SO_2ClF$) solution of triphenylethylene to tenfold molar excess of $HSO_3F$ in the same solvent results in the formation of a pale red solution whose pmr spectrum is identical with that previously reported for ion **1**.[8] By quenching cation **1** with $H_2O$–KOH, 1,1,2-triphenylethanol is obtained in about 80% yield.



$$(C_6H_5)C{=}CHC_6H_5 \xrightarrow[-80^\circ]{HSO_3F-SO_2(SO_2ClF)} (C_6H_5)_2\overset{+}{C}CH_2C_6H_5 \xrightarrow[-80^\circ]{KOH-H_2O} (C_6H_5)_2\overset{OH}{\overset{|}{C}}CH_2C_6H_5$$

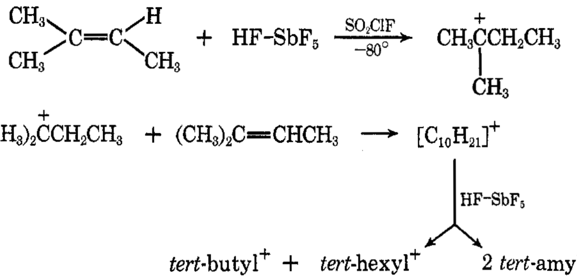
**B. Diphenylmethylcarbenium Ion** (2).—Attempted protonation of 1,1-diphenylethylene by $HSO_3F$–$SbF_5$ (1:1) or HF–$SbF_5$ (1:1) in $SO_2$ or $SO_2ClF$ solution results in dark red somewhat viscose solutions whose pmr spectra show only very broad absorption peaks due to polymeric materials. However, addition of 1,1-diphenylethylene to $HSO_3F$ (in $SO_2$ or $SO_2ClF$), using the same technique as above, gives a clear red solution whose pmr spectrum is identical with that reported previously for ion **2**.[9]

**C. Phenyldimethylcarbenium Ion** (3).—Difficulties arise in producing ion **3** by protonation of $\alpha$-methylstyrene, not because of the instability of the ion but because of the highly nuceophilic character of the olefin[2] causing polymerization. This difficulty is not overcome by the very slow addition of dilute solution of the olefin to the acid at low temperature. On the other hand, by dissolving the olefin in a solvent ($CS_2$) which is immiscible with the acid solution and adding the solution of the olefin to the acid at low temperature reaction occurs only in the contact layer. The protonated olefin so formed is immediately extracted into the acid layer and its chance to react with additional olefin is minimized. By applying this procedure to the protonation of $\alpha$-methylstyrene, using HF–$SbF_5$ (5:1) as the acid, phenyldimethylcarbenium ion **3** is formed and shows an identical spectrum as reported previously.[5,6,9,10]



$$C_6H_5\underset{CH_3}{\underset{|}{C}}{=}CH_2 \text{ (in } CS_2) \xrightarrow[-80^\circ]{HF-SbF_5\ (5:1)-SO_2ClF} C_6H_5\underset{CH_3}{\underset{|}{\overset{+}{C}}}CH_3$$

**D. Dimethylethylcarbenium Ion** (4).—By slow, careful addition of dilute solutions of 2-methyl-2-butene in $SO_2$ or $SO_2ClF$ to various ratios of $HSO_3F$–$SbF_5$ or HF–$SbF_5$ in either $SO_2$ or $SO_2ClF$ at low temperature, almost no polymeric product is formed. The clear solutions obtained exhibit pmr spectra which indicate the presence of three cations: the expected dimethylethylcarbenium ion (**4**) as well as dimethylisopropylcarbenium ion (**5**) and trimethylcarbenium ion (**6**). By varying the relative molar ratio of $HSO_3F$–$SbF_5$ and HF–$SbF_5$, different ratios of the cations are obtained. The highest ratio of *tert*-amyl$^+$–*tert*-hexyl$^+$ (12:1) is obtained by using HF–$SbF_5$ (5:1). The presence of *tert*-hexyl and *tert*-butyl cations in this reaction mixture indicates that some of the *tert*-amyl$^+$ cation reacts with excess isopentene to form a dimeric ion ($C_{10}$ species) which is then cleaved by the strong acid to form *tert*-butyl and *tert*-hexyl cations, or two *tert*-amyl cations.



**E. Dimethylisopropylcarbenium Ion** (5).—A mixture of *tert*-hexyl cations is formed by ionizing hexyl halides or alcohols, or hexane itself with superacids.[7,11,12] The distribution of the three tertiary isomers is temperature dependent. Below −60° the unrearranged *tert*-hexyl cations are formed from the appropriate tertiary isohexane precursors. Raising the temperature results in increasingly converting the slightly less stable isomers (methyldiethyl and dimethyl-*n*-propylcarbenium ions) into the more stable dimethylisopropylcarbenium ion.[12] The expected unrearranged dimethylisopropylcarbenium ion (**5**) is formed only in minor amounts together with a higher yield of *tert*-butyl and *tert*-amyl cations when treating a dilute $SO_2$ (or $SO_2ClF$) solution of 2,3-dimethyl-2-butene with various superacid systems (varying ratios of $HSO_3F$–$SbF_5$ or HF–$SbF_5$ in $SO_2$ or $SO_2ClF$) at −80°. Results show that under these reaction conditions a large portion of the initially formed *tert*-hexyl cation reacts further with excess unprotonated olefin to produce polymeric ions which are cleaved subsequently by the superacid to form the more stable *tert*-butyl and *tert*-amyl cations. On the other hand, addition of a solution of 2,3-dimethyl-2-butene in $SO_2ClF$ to a fivefold molar excess of HF–$SbF_5$ (5:1)–$SO_2ClF$ at −120° results in

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[8] G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 5571 (1966).

[9] G. A. Olah, *ibid.*, **86**, 932 (1964).

[10] D. G. Farnum, *ibid.*, **86**, 934 (1964).

[11] G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

[12] G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

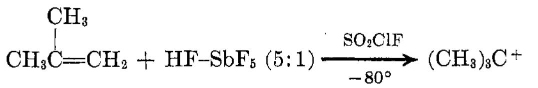
the almost exclusive formation of the dimethylisopropylcarbenium ion. The pmr spectrum of this reaction mixture shows the only impurity to be the *tert*-butyl cation. By adding a dilute $SO_2ClF$ solution of 2,3-dimethyl-2-butene to a fivefold excess of HF in the same solvent at −80°, 2,3-dimethyl-2-fluorobutane is obtained. Addition of excess $SbF_5$ in the same solvent leads to the almost exclusive formation of dimethylisopropylcarbenium ion. Based on these results an addition–elimination mechanism is probable in the reaction at −120°.

$$(CH_3)_2C{=}C(CH_3)_2 + HF \xrightarrow[-80^\circ]{SO_2ClF}$$

$$(CH_3)_2CHCF(CH_3)_2 \xrightarrow[-80^\circ]{SbF_5\text{–}SO_2ClF}$$

$$(CH_3)_2CH\overset{+}{C}(CH_3)_2 \rightleftharpoons (CH_3)_2\overset{+}{C}CH(CH_3)_2$$

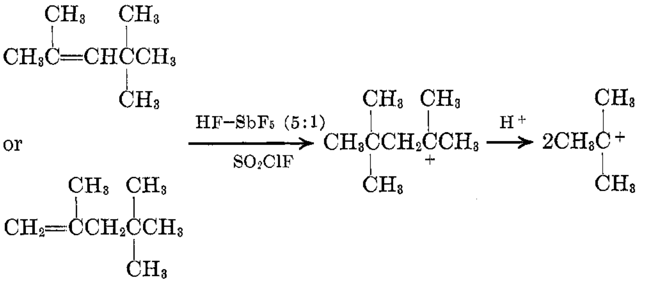
**F. Trimethylcarbenium Ion (6).**—By adding an $SO_2ClF$ solution of isobutylene into a fivefold molar excess of HF–$SbF_5$ (5:1)–$SO_2ClF$ at −80°, a clear, pale yellow solution is obtained whose pmr spectrum shows it to be almost exclusively the trimethylcarbenium ion.



$$CH_3\overset{\overset{CH_3}{|}}{C}{=}CH_2 + HF\text{–}SbF_5\ (5{:}1) \xrightarrow[-80^\circ]{SO_2ClF} (CH_3)_3C^+$$

**G. Dimethyl-*tert*-butylcarbenium Ion (7).**—Protonation of 2,3,3-trimethyl-1-butene by HF–$SbF_5$ (5:1) in $SO_2ClF$ leads to the formation of the expected dimethyl-*tert*-butylcarbenium ion, together with some *tert*-butyl cation as the only impurity. The fact that raising the temperature of the solution of the cations decreases the concentration of the *tert*-heptyl cation while increasing the concentration of the *tert*-butyl cation indicates that the *tert*-heptyl cation is cleaved by the strong acid to the more stable *tert*-butyl cation.

**H.**—In the protonation of 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene, the expected product is the **dimethylneopentylcarbenium ion (8)**. In both cases protonation with HF–$SbF_5$ (5:1) in $SO_2ClF$ results, however, only in the formation of the *tert*-butyl cation. This indicates that either both protonation of the double bond of the olefin and protolysis of the $C_3$–$C_4$ bond in cation **8** occurs[13] or that β cleavage of the dimethylneopentylcarbenium ion is fast.



**I. Methylcarbenium Ion, Ethyl Cation (9).**—Ethyl cation **9** has only recently been indicated to exist in the equilibrating $CH_3CH_2F \rightarrow SbF_5$ system in $SO_2$ solution.[14] When ethylene is treated with $HSO_3F$–$SO_2ClF$ at −80°, a clear solution is obtained which exhibits the pmr spectrum of ethylfluorosulfonate, $CH_3CH_2OSO_2F$, consisting of a quartet at 5.1 ppm ($J$ = 7.5 Hz) and a triplet at 1.7ppm ($J$ = 7.5 Hz) for the methylene and methyl groups, respectively. Performing the reaction in HF–$SbF_5$ (1:1) instead of $HSO_3F$ results in formation of the ethyl fluoride–antimony pentafluoride complex[14] which exhibits a pmr spectrum consisting of a quartet at 5.53 ppm ($J$ = 8 Hz) and a triplet at 2.3 ppm ($J$ = 8 Hz) for the methylene and methyl groups, respectively. This complex is formed together with some *tert*-butyl, *tert*-amyl, and *tert*-hexyl cations. These products may be formed either by reaction of the intermediate ethyl cation **9** (produced either on protonation of ethylene or present in equilibrium in the ethyl fluoride–antimony pentafluoride complex) with ethylene or by polycondensation of the ethyl fluoride complex.[14]

Whereas our previous studies in this field were primarly directed toward the structural study of intermediate, long-lived carbenium ions, present investigations we feel would open up the possibility of preparative work with carbenium ion salts. Olefins are the most convenient precursors to carbenium ions, and, consequently, it was felt that it would be useful to develop practical methods to generate carbenium ions directly from olefins. Having achieved this goal we are carrying out studies in the application of stable carbenium ion complexes in synthetic reactions and will report our results.

## Experimental Section

All the olefins used were commercially available.

**Pmr spectra** were taken using a Varian Model A-56/60A spectrometer, equipped with variable low-temperature probe, operating geneally at −75°.

**Preparation of Cations.**—Dilute solutions (between 5–10% w/w) of olefin in the solvents discussed were added dropwise into the previously prepared acid solution (in $SO_2$ or $SO_2ClF$) at low temperature, −85° (Dry Ice–acetone bath) or −120° (ethanol–liquid $N_2$ bath), according to the specific olefin in question (see Discussion). The reaction mixtures were vigorously stirred during the slow addition of the solutions of olefins to avoid local overheating. The rate of addition is determined by the ability to keep temperatures close to constant during additions.

**Quenching procedures** were identical with those described previously.[8]

**Registry No.**—**1,** 14290-01-8; **2,** 16805-85-9; **3,** 16804-70-9; **4,** 17603-15-5; **5,** 17603-18-8; **6,** 14804-25-2; **7,** 17603-19-9; **8,** 762-82-3; **9,** 14936-94-8.

**Acknowledgment.**—Support of our work by the National Science Foundation and the Petroleum Research Fund is gratefully acknowledged.

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(13) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo., *J. Amer. Chem. Soc.*, **93**, 1251 (1971).

(14) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, in press.