It should be pointed out that one or more of the conformations listed in Table I may be excluded due to steric overlap between atoms separated by *several* peptide units.[4,8] We therefore inspected space-filling models of these forms for possible conflicts of this type.

Conformation I represents a right-handed helix that is approximately threefold; its energy, -0.85 kcal mole^{-1}, is the lowest of the four observed minima. Conformation II is very similar to the left-handed α-helix, for which $\varphi = 228°$ and $\psi = 237°$.[11] It is impossible to build a model of this conformation, however, because of extremely strong steric repulsions between oxygen atoms and N-methyl hydrogen atoms separated from them by three peptide units. The third conformation represents a left-handed helix strikingly similar to the poly-L-proline II helix.[12] Conformation IV represents a right-handed helix with approximately five peptide units per turn.

This analysis and published spectral data[1] strongly suggest that poly-N-methyl-L-alanine is helical, even though it cannot form intramolecular hydrogen bonds and does not contain pyrrolidine rings. On the basis of the relative conformational energies, the right-handed helix I seems to represent the most stable conformation for this acyclic polypeptide.

Through additional experiments and calculations we hope to extend our knowledge of some of the forces leading to helicity in polypeptides in general.[13]

(12) P. M. Cowan and S. McGavin, *Nature*, **176**, 501 (1955).

(13) NOTE ADDED IN PROOF. After submission of our paper, A. M. Liquori and P. De Santis (University of Rome) kindly placed at our disposal their calculations of conformational energies of longer sequences of N-methyl-L-alanine residues. Their results confirm in essentials the conclusions presented here.

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Stable Carbonium Ions. XXXVII.[1]
Alkyl- and Arylalkylfluorocarbonium Ions.
The Dimethyl- and Phenylmethylfluorocarbonium Ion

Sir:

Recently we have reported[2] the observation of the first fluorocarbonium ions: the phenyl- and diphenylfluorocarbonium ions (I and II).
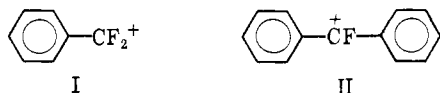

We wish to report now the first examples of stable alkyl- and arylalkylfluorocarbonium ions.

Dimethylfluorocarbonium ion (III) was obtained when 2,2-difluoropropane (prepared from acetone and sulfur tetrafluoride[3]) was dissolved in SbF$_5$-SO$_2$ solution at $-60°$. Ion III was also obtained by protona-
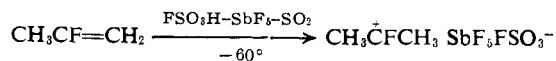
(1) Part XXXVI: G. A. Olah and D. H. O'Brien, *J. Am. Chem. Soc.*, in press.

(2) G. A. Olah, M. B. Comisarow, and C. A. Cupas, *ibid.*, **88**, 362 (1966).

(3) W. R. Hasek, W. C. Smith, and V. A. Englehardt, *ibid.*, **82**, 543 (1960).
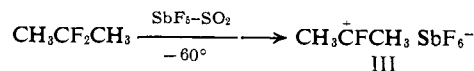

tion of 2-fluoropropene with FSO$_3$H-SbF$_5$.


The pmr spectrum of III (Figure 1) shows the methyl protons as a doublet at -3.93 ppm ($J_{HF} = 26$ Hz) substantially deshielded from their position in the covalent starting material at -1.36 ppm ($J_{HF} = 19$ Hz). The ^{19}F nmr spectrum of III (Figure 2) shows the fluorine atom of III as an extremely deshielded septuplet at -182.0 ppm as compared with the position of the fluorine resonance in the covalent 2,2-difluoropropane ($+81.5$ ppm). The deshielding in ion III thus is -263.5 ppm, clearly indicating the presence of the dimethylfluorocarbonium ion. The coupling constant (J_{HF}) increases from 19 to 26 Hz upon ionization.

Phenylmethylfluorocarbonium ion (α-fluorostyryl cation) (IV) was obtained when α,α-difluoroethylbenzene was dissolved[4] in SbF$_5$-SO$_2$ at $-60°$.
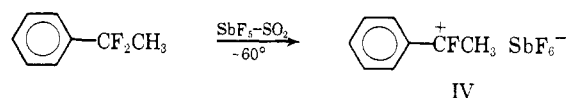
The ^{1}H and ^{19}F resonance spectra of ion IV were obtained (Figures 3 and 4). The pmr spectrum shows the methyl doublet at -3.70 ppm ($J_{HF} = 23$ Hz), compared with -1.65 ppm ($J_{HF} = 17.6$ Hz) in the covalent starting material. The ring protons are also highly deshielded and show a characteristic phenylcarbonium ion pattern. The ^{19}F resonance of ion IV shows the fluorine atom as a highly deshielded quadruplet at -51.3 ppm, as compared with the fluorine resonance of the covalent α,α-difluoroethylbenzene ($+89.2$ ppm).

The phenylmethylcarbonium ion (styryl cation) is extremely difficult to observe in acidic solution as a stable species. It loses a proton easily (at least in equilibrium), and the styrene formed undergoes extremely rapid secondary reaction (alkylation, polymerization, etc.). In contrast, the α-fluorostyryl cation IV is quite stable, despite the fact that proton elimination still could yield α-fluorostyrene and subsequent side reactions. Ion IV as well ion III are tertiary carbonium ions, where the α-fluorine atoms through backdonation of its unshared electron pairs into the vacant sp^2-carbon orbital help stabilize the carbonium ions. Resonance forms like
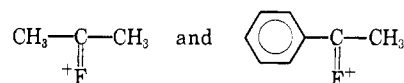
must contribute to stabilization. The considerable fluorine deshielding effects directly substantiate this suggestion.

Attempts to prepare CH$_3$CHF$^+$ (V) or CH$_3$CF$_2^+$ (VII) either by protonation of vinyl or vinylidene fluoride with FSO$_3$H-SbF$_5$ or from CH$_3$CHFCl or CH$_3$CF$_2$Cl with SbF$_5$ were unsuccessful.

Protonation of vinyl fluoride gave a product whose pmr spectrum shows a low-field doublet of quartets at -6.5 ppm ($J_{HH} = 5$ Hz; $J_{HF gem} = 5.65$ Hz) and an up-

(4) K. Matsuda, J. A. Dedlak, J. S. Noland, and E. C. Glecker, *J. Org. Chem.*, **27**, 4018 (1962). A procedural change suggested in ref 27 of this paper was followed, and resulted in a yield o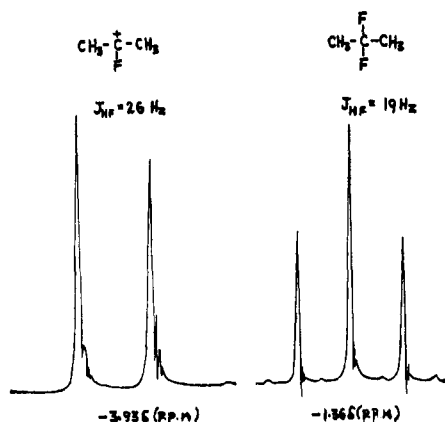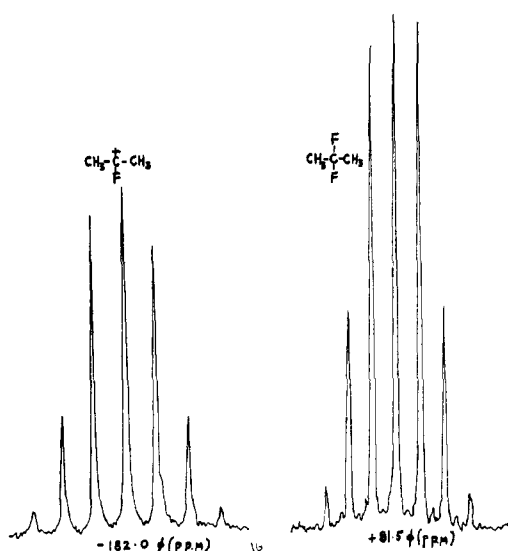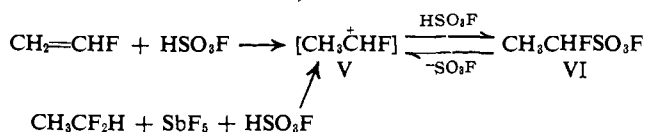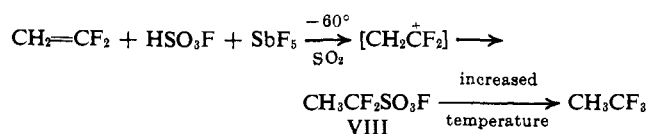f 24% rather than the 18% reported.