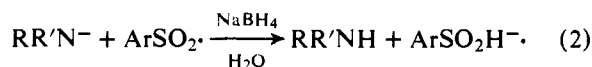
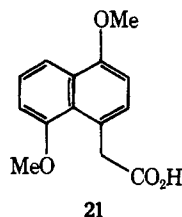


Since the radical anion ($A^{\cdot-}$) is identical with the known species generated in the initial step of Na-NH₃ (liquid),¹³ Na-naphthalene,¹⁴ and electrochemical reductions¹⁵ of sulfonamides, the first step of its decomposition can be described as shown in eq 1. Equations 2-5 presumably show further principal processes in the photohydrolysis in the presence (eq 2, 3) and absence (eq 4, 5) of NaBH₄ on the basis of the following evidence, though a more detailed description of the mechanism must await further work. (1) Most of the donors in these photoreactions, especially in the presence of NaBH₄, were recovered unchanged. (2) When an ethanol solution of **3** (10 mM) and **18** (5 mM) in the presence of NaBH₄ (50 mM) was irradiated with light above 300 nm, toluenesulfonic acid (71%), as its methyl and ethyl esters, as well as the amine (**5**, 89%) and the recovered donor (**18**, 95%), were readily isolated. (3) On irradiation in the presence of NaOEt (6 mM) instead of NaBH₄, an ethanol solution of **3** (7 mM) and **18** (5 mM) gave **5** (62%), **18** (77%), and ethyl toluenesulfonate (45%). There was no detectable formation of toluenesulfonic acid and its ester. (4) When an anhydrous acetonitrile solution of **3** and **18** was irradiated under argon, no reaction occurred, though the fluorescence of **3** was quite efficiently quenched by *N*-tosylmethylamine.¹⁰



The ϵ -*N*-tosyl group has been used as the most stable side-chain protection of lysine in peptide synthesis,¹⁶ and the reduction with Na-NH₃ (liquid) is practically the only useful method for removing the tosyl group. However, a number of serious side reactions such as the reductive fission of proline peptides have been reported.^{13b,17} The photohydrolysis of tosylamides presented here can be expected to be a selective method for the detosylation of lysine peptides since it avoids the side reactions which occur in Na-NH₃ reductions, because only the *N*-tosyl group in usual protected peptides can form an ion pair with an excited electron donor. As preliminary experiments some model ϵ -*N*-tosyl lysine peptides in water or 50% DMF were irradiated with a 100-W lamp (Pyrex filter) in the presence of a large excess of NaBH₄ and 0.3-1 equiv of a water-soluble donor (**21**). The isolated yields of detosylated



peptides from the corresponding ϵ -*N*-tosyl-protected compounds are as follows: Z-Lys (90%), Z-Gly-His-Lys (68%), Z-Gly-Pro-Lys (76%), and Z-Gly-Lys-Gly (81%). No cleavage of the peptide bonds was observed. Experiments to determine further applications are now in progress.

Acknowledgment. We thank Professor H. Kokubun (Tohoku University) for helpful discussions and fluorescence lifetime measurements.

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- $$\Delta G (\text{kcal/mol}) = 23.06 [E(D/D^+)_{\nu} - E(A/A^{\cdot-})_{\nu} - e^2/\epsilon R] - E_{0-0} (\text{kcal/mol})$$
- Although the equation was originally valid in acetonitrile, it can be successfully applied to the estimation of ΔG values in ethanol when oxidation and reduction potentials in ethanol are used. The half-wave reduction potential of *p*-toluenesulfonamide in ethanol is -2.36 V.^c For oxidation potentials, the data in acetonitrile were used because they are little affected by alteration of solvents.^{d,e} (a) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970); (b) Y. Taniguchi, Y. Nishida, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **45**, 764 (1972); (c) L. Horner and R. J. Singer, *Justus Liebig's Ann. Chem.*, **723**, 1 (1969); (d) N. L. Weinberg, D. H. Marr, and C. N. Wu, *J. Am. Chem. Soc.*, **97**, 1499 (1975); (e) L. Ebersson and K. Nyberg, *ibid.*, **88**, 1686 (1966).
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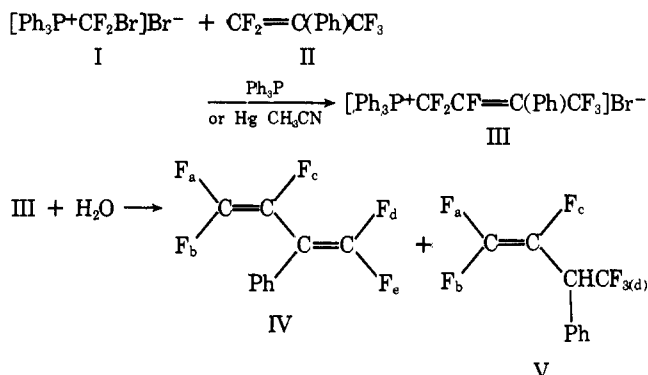
Difluoromethylene Chain-Extension Reactions. Preparation of Fluorinated Alkenes and Alkadienes from Olefin Precursors

Sir:

Chain-extension or homologation reactions are well documented in many areas of organic synthesis. In the field of organofluorine chemistry, however, a notable lack of effort and success for similar conversions has been achieved. Alkylation of fluoro olefins via *F*-alkyl carbanions,¹ nucleophilic addition-elimination reactions of fluoro olefins by Grignard or lithium reagents,² or alkylation of fluoro olefins with phosphonium ylides³ (followed by hydrolysis) permits chain extension of the *F*-alkene within a limited framework. Insertion

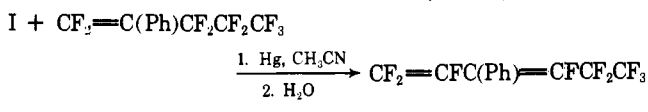
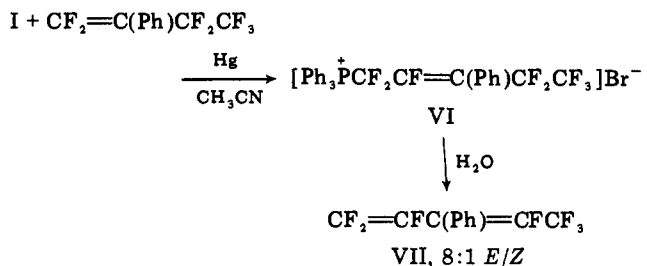
of difluorocarbene can also be potentially viewed as a homologation conversion,⁴ but again no generality of this type of sequence has been achieved.

We now report the first example of a difluoromethylene (CF_2) chain-extension reaction that occurs with retention of precursor functionality. When bromodifluoromethyltriphenylphosphonium bromide (I) is treated with triphenylphosphine⁵ or mercury⁶ in the presence of 2-phenyl-*F*-propene⁵ (II), the chain-extended phosphonium salt (III) is formed in 70–80% yield.^{7,8} Formation of III presumably occurs via reaction of the difluoromethylene ylide with II. Subsequent hydrolysis of III gives a mixture of 2-phenyl-*F*-1,3-butadiene (IV) and 3-phenyl-3-hydro-*F*-1-butene (V).^{9–11} No protonation occurs at the difluoromethylene carbon to give $\text{CF}_2\text{HCF}=\text{C}(\text{Ph})\text{CF}_3$.



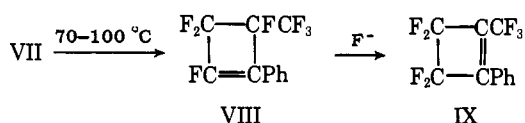
Thus, the overall net result of this reaction is the conversion of a fluorinated propene into a fluorinated 1-butene. The carbon chain has been extended by the introduction of a CF_2 unit, and the olefinic functionality has been retained. Similar results were obtained with 2-benzyl-*F*-propene and 2-butyl-*F*-propene and I, followed by hydrolysis.

When a similar sequence of reactions was carried out with 2-phenyl-*F*-1-butene, hydrolysis of the chain-extended phosphonium salt (VI)¹³ gave mainly 3-phenyl-*F*-1,3-pentadiene (VII).¹⁴ Only traces of the protonation product analogous to



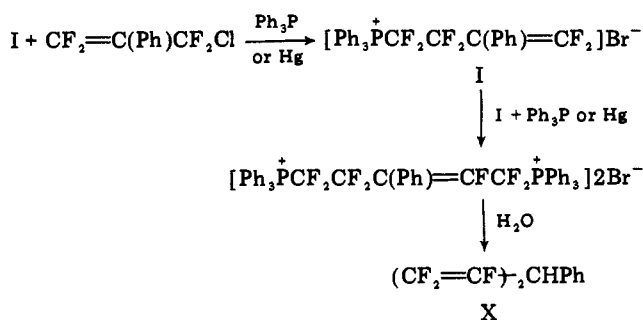
V was observed. Thus, in this case, the net reaction is the conversion of a fluorinated 1-butene into the fluorinated conjugated pentadiene by a CF_2 unit introduction. Similar behavior was observed with 2-phenyl-*F*-1-pentene.¹⁵

The dienes undergo facile thermal cyclization to give the respective cyclobutene derivative.¹⁶ Fluoride ion isomerization provides the thermodynamic cyclobutene isomer.¹⁷ Thermal ring opening of IX can potentially give a pentadiene isomeric with VII.¹⁸



When similar transformations were carried out with 3-chloro-2-phenyl-*F*-propene and excess I, the initial chain ex-

tended phosphonium salt reacted a second time. Hydrolysis gave 3-phenyl-3-hydro-*F*-1,4-pentadiene (X) in 54% isolated yield.^{19,20} Thus, chain extension of the initial propene by two CF_2 units was attained.

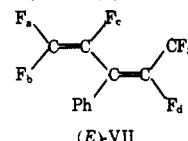


This synthetic sequence provides the fluorocarbon chemist with a useful tool for difluoromethylene homologation-type reactions. Chain-extended olefins and dienes can be prepared by the appropriate choice of olefin to be reacted with the difluoromethylene ylide. The resultant dienes also provide an entry to the cyclobutene derivatives and to isomeric cyclobutenes and dienes by additional synthetic elaboration. Our work continues to explore the scope of these novel chain extension reactions and additional utility of the fluorinated ylides.

Acknowledgment. We are indebted to the National Science Foundation and the Office of Army Research for financial support of this work.

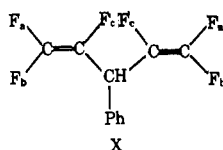
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- (7) Triglyme and CH_2Cl_2 are also suitable solvents for this conversion. Best results were obtained with excess I; otherwise incomplete consumption of II occurred.
- (8) III was obtained as an *Z/E* mixture. The ratio of *Z/E* was 1.4–1.9 depending on solvent and dehalogenating agent. (*Z*)-III exhibited three sets of signals in the ^{19}F NMR spectrum at ϕ 60.6 (d, $J_{\text{CF}_3\text{F}} = 23$ Hz), 93.4 (d, d, $J_{\text{F}_2\text{CF}_2} = 87$, $J_{\text{CF}_2\text{F}} = 19$ Hz), 106.6 ppm (m). (*E*)-III exhibited three sets of signals in the ^{19}F NMR spectrum at ϕ 55.3 (t, d, $J_{\text{CF}_3\text{CF}_2} = 17$, $J_{\text{CF}_3\text{F}} = 12$ Hz), 95.0 (d, m, $J_{\text{F}_2\text{CF}_2} = 78$ Hz), 102.0 ppm (m).
- (9) IV was usually formed in amounts of <5%. V was formed in yields of 65–70% [based on (II)] on a preparative scale (60 mmol).
- (10) IV: bp 54–57 °C (16 mm); ^{19}F NMR ϕ 98.5 (F_a, d, d, $J_{\text{F}_a\text{F}_b} = 65.9$, $J_{\text{F}_a\text{F}_c} = 32.0$ Hz), 113.9 (F_b, d, d, d, $J_{\text{F}_b\text{F}_c} = 117.8$, $J_{\text{F}_b\text{F}_d} = 115.5$ Hz), 168.4 (F_c, d, d, d, 81.5 (F_d, m), 76.3 ppm (F_a, m).
- (11) V: bp 68–70 °C (35 mm); ^{19}F NMR ϕ 100.9 (F_a, d, d, d, $J_{\text{F}_a\text{F}_b} = 74.5$, $J_{\text{F}_a\text{F}_c} = 35.2$, $J_{\text{F}_b\text{H}} = 1.5$ Hz¹²), 119.5 (F_b, d, d, d, $J_{\text{F}_b\text{F}_c} = 117.4$, $J_{\text{F}_b\text{H}} = 2.6$ Hz¹²), 181.3 (F_c, d, d, d, q, $J_{\text{F}_c\text{H}} = 27.5$, $J_{\text{F}_c\text{CF}_3} = 7.3$ Hz), 68.0 ppm (F_d, d); mass spectrum *m/e* calcd 240.1574, found 240.0373.
- (12) Determined from ^1H NMR. Not resolved in the ^{19}F NMR.
- (13) Mainly the *Z* isomer of VI was observed by ^{19}F NMR.
- (14) ^{19}F NMR gave a 62% yield of (*E*)-VII and 8% (*Z*)-VII. ^{19}F NMR of (*E*)-VII:



- ϕ 98.4 (F_a, d, d, $J_{\text{F}_a\text{F}_b} = 65.2$, $J_{\text{F}_a\text{F}_c} = 32.3$ Hz), 114.2 (F_b, d, d, $J_{\text{F}_b\text{F}_c} = 118.7$ Hz), 167.5 (F_c, d, d), 69.4 (CF₃, m), 120.2 ppm (F_d, m).
- (15) Identified only by ^{19}F NMR. Mixture of isomers was at least 90% *E*. Further confirmation of structure was obtained by thermal cyclization and isolation of the cyclobutene product.
 - (16) VIII: bp 35 °C (6 mm); ^{19}F NMR ϕ 74.7 (CF₃, m), 107.2 (vinyl F, m), 114.4 and 114.8 ($J_{\text{F}_2\text{F}} = 212$ Hz, CF₂, 177.0 ppm (CF₃CF, m); mass spectrum *m/e* calcd 270.1493, found 270.0286.
 - (17) The ^{19}F NMR of IX exhibited three signals at ϕ 113.3 (CF₂, m), 115.1 (CF₂, m), and 61.8 ppm (CF₃, m). Assignments of the respective CF_2 groups could not be unambiguously made.

- (18) R. D. Chambers, C. G. P. Jones, and G. Taylor, *J. Chem. Soc., Chem. Commun.*, 964 (1979), and references therein.
 (19) X: bp 41–42 °C (5 mm); ^{19}F NMR ϕ° 102.6 (F_a , d, d, $J_{F_a, F_b} = 77.5$, $J_{F_a, F_c} = 35.8$ Hz), 120.4 (F_b , d, d, d, $J_{F_b, F_c} = 114.4$, $J_{F_b, H} = 6.3$ Hz 12), 177.9 ppm (F_c , d, d, d, $J_{F_c, H} = 25.0$ Hz); mass spectrum m/e calcd 252.1684, found 252.0373.



- (20) Mixtures of the mono- and diphosphonium salt were obtained with less than a 2:1 ratio of 1 to initial olefin.

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The Hydronium Ion (H_3O^+), Pyramidal or Planar?

Sir:

The ion H_3O^+ is a simple species of fundamental importance in chemistry. It is, therefore, a matter of great importance that, as a result of a most interesting ^{17}O NMR study, the conclusion was drawn that this cation is "practically planar".¹ This is certainly an unexpected result, since the isoelectronic molecule, NH_3 , has a bond angle of $\sim 107^\circ$. However, it seems that there is strong ab initio theoretical support for a planar geometry² and, possibly, some support from infrared spectroscopy.³

I therefore wish to examine the NMR evidence for this contention and then to turn to other arguments which, I believe, show that a pyramidal structure for H_3O^+ is most probable, the mean $\angle\text{HOH}$ angle being $\sim 111^\circ$.

The argument in favor of planarity is as follows:¹ H_2O is sp^3 hybridized and has $J_{\text{O-H}} = 79.9$ Hz; H_3O has $J_{\text{O-H}} = 106$ Hz, which is an increase of 33%. On the reasonable assumption that there is a linear relation between $J_{\text{O-H}}$ and the s character of the oxygen σ orbitals,⁴ this requires ca. sp^2 hybridization for H_3O^+ , which suggests that it is planar.

However, the bond angle for H_2O is $\sim 104.5^\circ$,⁵ and, assuming orbital following, which is tacitly assumed in all these arguments, this leads to a σ -orbital hybridization at oxygen of ca. sp^4 , i.e. $\lambda^2 = 4$. Using the same argument, that the s character increases by 33% on going from H_2O to H_3O^+ , I find that the s character for H_3O^+ should be $\sim 26.6\%$, giving $\lambda^2 = 2.76$. Then, using Coulson's equation⁵ relating bond angle to hybridization (eq 1), I find the bond angle to be $\phi = 111.3^\circ$. This line of reasoning is supported by $J(^{15}\text{N-H})$ data for NH_3 and NH_4^+ .⁶ The coupling constant for NH_4^+ is 73.7 Hz, and $\lambda^2 = 3.0$. The coupling for NH_3 of 64 Hz leads to a predicted value for λ^2 of 3.6, whereas the experimental bond angle of $\sim 107^\circ$ leads to $\lambda^2 = 3.5$.

$$\phi = \cos^{-1} \left[\frac{1.5}{2\lambda^2 + 3} - \frac{1}{2} \right] \quad (1)$$

This value is supported by solid-state studies. Early NMR data suggested that H_3O^+ was nearly planar, but subsequent X-ray diffraction studies on a wide range of salts containing H_3O^+ ⁷ gave an average bond angle between the central oxygen and three hydrogen-bonded neighbor atoms of $109.3 \pm 5^\circ$. Since strong hydrogen bonds are usually nearly linear, this strongly supports the concept that, in the solid-state, H_3O^+ is pyramidal. Indeed, if it were to be planar, it would be a quite extraordinary coincidence that the neighboring anions should always adopt this pyramidal arrangement. More recent neutron diffraction studies confirm conclusively that H_3O^+ is pyramidal in the solid state.^{7,8} Thus for $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$

H_3O^+ , the mean bond angle is 110.4° (110.7, 111.2, 109.2°) while for $\text{F}_3\text{CSO}_3^- \text{H}_3\text{O}^+$ it is 112.7° (111.1, 115.5, 111.6°). These angles are very close to those formed with the hydrogen bond acceptor atoms, showing that the hydrogen bonds are nearly linear.

These values are remarkably close to that deduced from the NMR data. This is an important result since it establishes that the constraints imposed by the crystal packing do not exert a major influence on the structure of H_3O^+ . Furthermore, since the liquid-phase studies were for H_3O^+ in liquid SO_2 , which is only weakly basic, they show that the bond angle is not strongly dependent upon the extent of hydrogen bonding.

It is interesting to note that there is an increase in average bond angle on going from NH_3 (107°) to H_3O^+ (111.3°). This may result in part from hydrogen bonding, but probably largely reflects the change in electronegativity.⁹ The same trend is observed, for example, for the isoelectronic hydrides $\cdot\text{AlH}_3^-$, $\cdot\text{SiH}_3$, and $\cdot\text{PH}_3^+$.¹⁰

I conclude that the important new ^{17}O NMR data reported by Mateescu and Benedikt suggest that H_3O^+ is pyramidal in solution with a bond angle of $\sim 111.3^\circ$.

Acknowledgment. I thank a referee for helpful comments.

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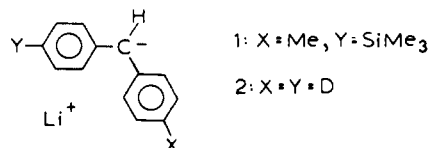
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Stabilization of Carbanions by Silicon. Restricted Aryl Rotation in the 4-Methyl-4'-trimethylsilyldiphenylmethyl Anion

Sir:

It is well known that groups containing silicon (e.g., SiMe_3) stabilize negative charge on an adjacent carbon atom.¹ Much current research centers on identification of the origin of this stabilization.² This report concerns dynamic NMR (DNMR) studies of restricted aryl rotation in the lithium salt of the 4-methyl-4'-trimethylsilyldiphenylmethyl anion (**1**) and extended Hückel calculations for more simple related systems. These results allow a quantitative assessment of the effect of a para trimethylsilyl group on the stability of a diphenylmethyl anion.



The ^1H DNMR spectrum (270 MHz) of the aryl rings of **1** (0.4 M in 20% toluene- d_8 /80% THF, v/v) at 320 K consists