Since the radical anion  $(A^{-})$  is identical with the known species generated in the initial step of Na-NH<sub>3</sub> (liquid),<sup>13</sup> Na-naphthalene,<sup>14</sup> and electrochemical reductions<sup>15</sup> 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 NaBH<sub>4</sub> 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 NaBH<sub>4</sub>, were recovered unchanged. (2) When an ethanol solution of 3(10 mM) and 18(5 mM) in the presence of NaBH<sub>4</sub>(50 mM) was irradiated with light above 300 nm, toluenesulfinic 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 NaBH<sub>4</sub>, 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 toluenesulfinic 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 Ntosylmethylamine.10

$$ArSO_2NRR'^{-} \cdot (A^{-} \cdot) \rightarrow RR'N^{-} + ArSO_2 \cdot (1)$$

$$RR'N^{-} + ArSO_{2} \cdot \xrightarrow[H_{2}O]{NaBH_{4}} RR'NH + ArSO_{2}H^{-} \cdot (2)$$

$$ArSO_2H^- + D^+ \rightarrow ArSO_2H + D$$
 (3)

$$RR'N^{-} + ArSO_{2} \cdot \xrightarrow{H_{2}O} RR'NH + ArSO_{3}H^{-} \cdot$$
(4)

$$ArSO_{3}H^{-} + D^{+} \rightarrow ArSO_{3}H + D$$
 (5)

The  $\epsilon$ -N-tosyl group has been used as the most stable sidechain protection of lysine in peptide synthesis,<sup>16</sup> and the reduction with Na–NH<sub>3</sub> (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.<sup>13b,17</sup> 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–NH<sub>3</sub> 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  $\epsilon$ -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 NaBH<sub>4</sub> and 0.3–1 equiv of a water-soluble donor (**21**). The isolated yields of detosylated



peptides from the corresponding  $\epsilon$ -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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 $\Delta G$  (kcal/mol)

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Although the equation was originally valid in acetonitrile, it can be successfully applied to the estimation of  $\Delta G$  values in ethanol when oxidation and reduction potentials in ethanol are used. The half-wave reduction potentials of *p*-toluenesulfonamide in ethanol is -2.36 V.<sup>o</sup> For oxidation potentials, the data in acetonitrile were used because they are little affected by atteration of solvents:<sup>4,6</sup> (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 Liebigs 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. Eberson 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,<sup>1</sup> nucleophilic addition-elimination reactions of fluoro olefins by Grignard or lithium reagents,<sup>2</sup> or alkylation of fluoro olefins with phosphonium ylides<sup>3</sup> (followed by hydrolysis) permits chain extension of the F-alkene within a limited framework. Insertion

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## Communications to the Editor

of difluorocarbene can also be potentially viewed as a homologation conversion,<sup>4</sup> 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 triphenylphosphine<sup>5</sup> or mercury<sup>6</sup> in the presence of 2-phenyl-F-propene<sup>5</sup> (II), the chain-extended phosphonium salt (III) is formed in 70-80% yield.<sup>7,8</sup> 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 3phenyl-3-hydro-F-1-butene (V).9-11 No protonation occurs at the difluoromethylene carbon to give  $CF_2HCF=C(Ph)CF_3$ .

$$[Ph_{3}P^{+}CF_{2}Br]Br^{-} + CF_{2} = O(Ph)CF_{3}$$

$$I \qquad II$$

$$\xrightarrow{Ph_{3}P} (Ph_{3}P^{+}CF_{2}CF = C(Ph)CF_{3}]Br^{-}$$

$$III$$

$$III + H_{2}O \longrightarrow F_{a} (F_{c}) (F_{$$

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<sub>2</sub> 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)<sup>13</sup> gave mainly 3-phenyl-F-1,3-pentadiene (VII).<sup>14</sup> Only traces of the protonation product analogous to

 $I + CF_2 = C(Ph)CF_2CF_3$ 

$$\xrightarrow{Hg} [Ph_{3}\dot{P}CF_{2}CF = C(Ph)CF_{2}CF_{3}]Br^{-}$$

$$VI$$

$$\downarrow H_{2}O$$

$$CF_{2} = CFC(Ph) = CFCF_{3}$$

$$VII, 8:1 E/Z$$

v

$$I + CF_2 = C(Ph)CF_2CF_2CF_3$$

$$\xrightarrow{1. \text{Hg, CH}_3\text{CN}} \text{CF}_2 \longrightarrow \text{CFC(Ph)} \longrightarrow \text{CFCF}_2\text{CF}_3$$

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<sub>2</sub> unit introduction. Similar behavior was observed with 2-phenyl-F-1-pentene.<sup>15</sup>

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

$$VII \xrightarrow{70-100 \circ_{C}} \begin{array}{c} F_{2}C \longrightarrow CFCF_{3} \\ | \\ FC \implies CPh \end{array} \xrightarrow{F^{-}} \begin{array}{c} F_{2}C \longrightarrow CCF_{3} \\ | \\ F_{2}C \longrightarrow CPh \end{array}$$
$$VIII \qquad IX$$

When similar transformations were carried out with 3chloro-2-phenyl-F-propene and excess I, the initial chain extended phosphonium salt reacted a second time. Hydrolysis gave 3-phenyl-3-hydro-F-1,4-pentadiene (X) in 54% isolated yield.<sup>19,20</sup> Thus, chain extension of the initial propene by two  $CF_2$  units was attained.

$$I + CF_{2} = C(Ph)CF_{2}CI \xrightarrow{Ph_{3}P}_{or Hg} [Ph_{3}\dot{P}CF_{2}CF_{2}C(Ph) = CF_{2}]Br^{-}$$

$$I$$

$$I$$

$$I + Ph_{3}P \text{ or } Hg$$

$$[Ph_{3}\dot{P}CF_{2}CF_{2}C(Ph) = CFCF_{2}\dot{P}Ph_{3}]2Br^{-}$$

$$H_{2}O$$

$$(CF_{2} = CF)_{2}CHPh$$

$$V$$

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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- (8) III was obtained as an Z/E mixture. The ratio of Z/E was 1.4-1.9 depending In was obtained as an 2/2 mixture. The ratio of 2/2 was 1.4–1.9 depending on solvent and dehalogenating agent. (2)-III exhibited three sets of signals in the <sup>19</sup>F NMR spectrum at  $\phi^*$  60.6 (d,  $J_{CF_3,F} = 23$  Hz), 93.4 (d, d,  $J_{e_1,C_2}$ = 87,  $J_{CF_2,F} = 19$  Hz), 106.6 ppm (m). (E)-III exhibited three sets of signals in the <sup>19</sup>F NMR spectrum at  $\phi$  55.3 (t, d,  $J_{CF_3,CF_2} = 17$ ,  $J_{CF_3,F} = 12$  Hz), 95.0 (d, m,  $J_{e_1,CF_2} = 78$  Hz), 102.0 ppm (m). IV was usually formed in amounts of <5%. V was formed in yields of 65, 70.6 (based on UID) on a properties scale (60 mmol)

- (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).</li>
  (10) IV: bp 54-57 °C (16 mm); <sup>19</sup>F NMR φ<sup>\*</sup> 98.5 (F<sub>a</sub>, d, d, J<sub>Fa,Fb</sub> = 65.9, J<sub>Fa,Fc</sub> = 32.0 Hz), 113.9 (F<sub>b</sub>, d, d, d, J<sub>Fb,Fc</sub> = 117.8, J<sub>Fb,Fd</sub> = 11.5 Hz), 168.4 (F<sub>c</sub>, d, d, d). 81.5 (F<sub>d</sub>, m), 76.3 ppm (F<sub>a</sub>, m).
  (11) V: bp 68-70 °C (35 mm); <sup>19</sup>F NMR φ<sup>\*</sup> 100.9 (F<sub>a</sub>, d, d, J<sub>Fa,Fb</sub> = 74.5, J<sub>Fa,Fc</sub> = 35.2, J<sub>Fa,H</sub> = 1.5 Hz<sup>12</sup>), 119.5 (F<sub>b</sub>, d, d, d, J<sub>Fb,Fq</sub> = 117.4, J<sub>Fb,H</sub> = 2.6 Hz<sup>12</sup>), 181.3 (F<sub>c</sub>, d, d, d, J<sub>Fa,Fb</sub> = 77.5, J<sub>Fa,CF3</sub> = 7.3 Hz), 68.0 ppm (F<sub>d</sub>, d, d); mass spectrum *m*/e calcd 240.1574, found 240.0373.
  (12) Determined from <sup>1</sup>H NMR Not resolved in the <sup>19</sup>E NMR

- (12) Determined from <sup>1</sup>H NMR. Not resolved in the <sup>19</sup>F NMR.
   (13) Mainly the Z isomer of VI was observed by <sup>19</sup>F NMR.
   (14) <sup>19</sup>F NMR gave a 62% yield of (E)-VII and 8% (Z)-VII. <sup>19</sup>F NMR of (E)-VII: (14)



 $\phi^* \ 98.4 \ (F_a, d, d, J_{F_a,F_b} = 65.2, J_{F_a,F_c} = 32.3 \ Hz), \ 114.2 \ (F_b, d, d, J_{F_b,F_c} = 118.7 \ Hz), \ 167.5 \ (F_c, d, d), \ 69.4 \ (CF_3, m), \ 120.2 \ ppm \ (F_d, m). \ (15) \ \text{Identified only by } ^{19} F \ \text{NMR}. \ \text{Mixture of isomers was at least } 90\% \ E. \ \text{Further}$ 

- confirmation of structure was obtained by thermal cyclization and isolation
- continuation of structure was obtained by thermal cyclication and isolation of the cyclobutene product. (16) VIII: bp 35 °C (6 mm); <sup>19</sup>F NMR  $\phi^*$  74.7 (CF<sub>3</sub>, m), 107.2 (vinyl F, m), 114.4 and 114.8 (J<sub>F,F</sub> = 212 Hz, CF<sub>2</sub>, 177.0 ppm (CF<sub>3</sub>CF, m); mass spectrum *m/e* calcd 270.1493, found 270.0286. (17) The <sup>19</sup>F NMR of IX exhibited three signals at  $\phi^*$  113.3 (CF<sub>2</sub>, m), 115.1 (CF<sub>2</sub>, m), and 61.8 ppm (CF<sub>3</sub>, m). Assignments of the respective CF<sub>2</sub> groups could not be upperfunction and
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   (19) X: bp 41-42 °C (5 mm); <sup>19</sup>F NMR φ\* 102.6 (F<sub>a</sub>, d, d, J<sub>a,Fb</sub> = 77.5, J<sub>a,Fb</sub> = 35.8 Hz), 120.4 (F<sub>b</sub>, d, d, d, J<sub>b,Fc</sub> = 114.4, J<sub>b,H</sub> = 6.3 Hz<sup>12</sup>), 177.9 ppm (F<sub>c</sub>, d, d, d, J<sub>c,H</sub> = 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 I to initial olefin.

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## The Hydronium Ion (H<sub>3</sub>O<sup>+</sup>), 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 <sup>17</sup>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 ~107°. However, it seems that there is strong ab initio theoretical support for a planar geometry<sup>2</sup> and, possibly, some support from infrared spectroscopy.<sup>3</sup>

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  $\angle$ HOH angle being  $\sim 111^{\circ}$ .

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

However, the bond angle for H<sub>2</sub>O is  $\sim 104.5^{\circ}$ ,<sup>5</sup> and, assuming orbital following, which is tacitly assumed in all these arguments, this leads to a  $\sigma$ -orbital hydridization at oxygen of ca. sp<sup>4</sup>, i.e.  $\lambda^2 = 4$ . Using the same argument, that the s character increases by 33% on going from H<sub>2</sub>O to H<sub>3</sub>O<sup>+</sup>, I find that the s character for H<sub>3</sub>O<sub>+</sub> should be ~26.6%, giving  $\lambda^2 =$ 2.76. Then, using Coulson's equation<sup>5</sup> 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(15N-H) data for NH<sub>3</sub> and  $NH_4^{+.6}$  The coupling constant for  $NH_4^{+}$  is 73.7 Hz, and  $\lambda^2$  = 3.0. The coupling for NH<sub>3</sub> of 64 Hz leads to a predicted value for  $\lambda^2$  of 3.6, whereas the experimental bond angle of ~107° leads to  $\lambda^2 = 3.5$ .

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

This value is supported by solid-state studies. Early NMR data suggested that H<sub>3</sub>O<sup>+</sup> 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.<sup>7,8</sup> Thus for p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>--</sup>

 $H_3O^+$ , the mean bond angle is 110.4° (110.7, 111.2, 109.2°) while for  $F_3CSO_3^-H_3O^+$  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<sub>2</sub>, 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<sub>3</sub> (107°) to H<sub>3</sub>O<sup>+</sup> (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 •AlH<sub>3</sub><sup>-</sup>, •SiH<sub>3</sub>, and •PH<sub>3</sub>+.<sup>10</sup>

I conclude that the important new <sup>17</sup>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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# Stabilization of Carbanions by Silicon. **Restricted Arvl Rotation in the** 4-Methyl-4'-trimethylsilyldiphenylmethyl Anion

Sir:

It is well known that groups containing silicon (e.g., SiMe<sub>3</sub>) stabilize negative charge on an *adjacent* carbon atom.<sup>1</sup> Much current research centers on identification of the origin of this stabilization.<sup>2</sup> This report concerns dynamic NMR (DNMR) studies of restricted aryl rotation in the lithium salt of the 4methyl-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 <sup>1</sup>H DNMR spectrum (270 MHz) of the aryl rings of 1 (0.4 M in 20% toluene-d<sub>8</sub>/80% THF, v/v) at 320 K consists

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