during the synthesis of **6** from **1** may involve the intermediate production of ketophosphinate **11**. Intermediate **11** should react with MeMgI to yield **10**.

Phosphorane **8** contains two chirality centers, one is the phosphorus atom and the other is C-2 of the 2-butyl group. Consequently, a mixture of diastereoisomers of **8** may show two singlets in the H-decoupled $^{31}P$ NMR spectrum, which is indeed the case. Phosphorane **9**, however, shows only one $^{31}P$ NMR signal. This is attributed to coincidence of the $^{31}P$ chemical shift values for diastereoisomers of **9**.

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(5) Phosphorane **4,** mp 118–120 °C, $^1H$ NMR $\delta$ 1.18 (9 H, t, $^3J_{HH}$ = 7 Hz, Me), 3.09 (6 H, q, $^3J_{HH}$ = 7 Hz, $CH_2$), 7.45–7.74 (4 H, m, H–Ar), 7.97–8.10 (2 H, m, H ortho to CO), 8.26–8.46 (2 H, m, H ortho to P), and other new compounds described in this report had C, H, P elemental analysis within 0.4% of calculated values, unless otherwise noted. Unless otherwise noted, chemical shifts for $^{31}P$ and $^1H$ are given in parts per million downfield from 85% $H_3PO_4$ and $Me_4Si$, respectively, in $CDCl_3$ as the solvent.

(6) Methoxyphosphorane **5**, $^1H$ NMR $\delta$ 3.84 (3 H, d, $^3J_{HP}$ = 15 Hz, Me), 7.60–8.47 (8 H, m, H–Ar).

(7) Phosphorane **6**, mp 179–181 °C (cyclohexane), $^1H$ NMR $\delta$ 1.62 (3 H, s, Me), 1.65 (3 H, s, Me), 2.13 (3 H, d, $^2J_{HP}$ = 17 Hz, MeP), 7.25–8.48 (8 H, m, H–Ar).

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## The Bihydroxide ($H_3O_2^-$) Anion. A Very Short, Symmetric Hydrogen Bond

*Sir:*

While a number of crystalline salts of hydrated hydronium ions have been characterized ($H_5O_2^+$,[1-6] $H_7O_3^+$,[7-8] $H_9O_4^+$,[7,9-10] and $H_{13}O_6^+$ [11]), to date there has been no well-determined structural characterization of a corresponding hydrated hydroxide anion, although the tetrahedral $H_6O_4^{2-}$ anion has been proposed on the basis of spectroscopic results.[12-15] We would like to report the first isolation and structural characterization of the simplest such hydroxide hydrate, the $H_3O_2^-$ anion.

As part of a program to characterize the structure and bonding of the complexes of thiohydrax*a*mates and thiohydrox*i*mates, we prepared the tris(thiobenzohydroximato)-chromate(III) trianion in aqueous solutions of sodium hydroxide. The addition of triethylmethylammonium iodide gave crystals of the mixed salt $Na_2[Et_3MeN][Cr(PhC(S){=}N(O))_3]\cdot{}^1\!/\!_2NaH_3O_2\cdot 18H_2O$.[16] This salt contains sodium and triethylmethylammonium cations, and tris(thiohydroximato)chromate(III) and hydroxide anions. The monohydrated hydroxide (or bihydroxide) ion exists as the discrete species $H_3O_2^-$ with an extremely short hydrogen bond. The material crystallizes in the centric triclinic space group $P\bar{1}$, with $a$ = 13.013 (4) Å, $b$ = 13.204 (4) Å, $c$ = 17.081 (6) Å, $\alpha$ = 81.67 (3)°, $\beta$ = 83.85 (3)°, $\gamma$ = 59.76 (2)°, $z$ = 2, $\rho_{calcd}$ = 1.353 g cm$^{-3}$, $\rho_{obsd}$ = 1.357 g cm$^{-3}$. X-ray diffraction data were collected by $\theta$-$2\theta$ scans with a $2\theta$ maximum of 50°, using Mo K$\alpha$ radiation.[17] The unweighted and weighted $R$ factors are 6.08 and 6.32%, respectively.

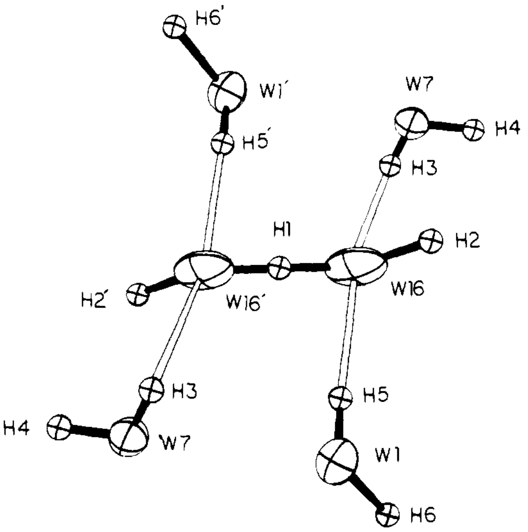

**Figure 1.** A perspective view of the structure of the $H_3O_2^-$ anion and the weak hydrogen bonding formed between it and adjacent waters of crystallization. Hydrogen atoms 2, 3, 4, and 6 have been located from the difference Fourier. Hydrogen atoms 1 and 5 were not seen in the electron density maps. Their positions are deduced from those of the other atoms in the structure.

The crystal structure consists of discrete tris(thiobenzohydroximato)chromate(III) anions, hydrated sodium cations, the $H_3O_2^-$ anions, and waters of crystallization—all linked by hydrogen bonds. The hydrophobic phenyl groups of the chromium complex and the triethylmethylammonium cations are so arranged that they form sheets along the $C$ faces of the structure at $z = {}^1\!/\!_2$. In between these sheets are hydrophilic regions toward which point the hydrophilic NO groups of the hydroximate anions, the sodium ions, the waters of crystallization, and the $H_3O_2^-$ anion. This anion (Figure 1) lies on a crystallographic inversion center with an O-O distance of 2.29 (2) Å. This distance corresponds to a very short hydrogen bond—too short for a water-water interaction. This and the presence of one-half of an hydroxide anion in the stoichiometry of the complex leads us to assign this species as the previously unobserved $H_3O_2^-$ anion, composed of a central proton on or near the inversion center surrounded by two $OH^-$ groups. The anion is then itself linked to the extensive hydrogen bond system of the crystal through weak hydrogen bonds to adjacent water molecules.

The very short hydrogen bond is, to our knowledge, the shortest observed to date for water,[18-20] and would seem to suggest the presence of a symmetric hydrogen bond. In this context, it is interesting to compare the structure of the $H_3O_2^-$ anion with that of the isoelectronic bifluoride ion, $HF_2^-$, especially since $F^-$ and $OH^-$ ions have nearly the same crystal and effective ionic radii (1.15 and 1.28 Å for the fluoride ion, and 1.18 and 1.32 Å for the hydroxide ion, respectively[21]). In the alkali and ammonium salts, the bifluoride ion crystallizes in the symmetric linear form $FHF^-$ with an F-F separation of 2.264 (3), 2.277 (6), and 2.269 (5) Å for the $Na^+$,[22] $K^+$,[23] and $NH_4^+$ salts,[24] respectively. The asymmetric $HF_2^-$ ion in the $p$-toluidinium salt has an F-F separation of 2.260 (4) Å (from both neutron and X-ray diffraction studies[25]). These distances compare well with the O-O separation of 2.29 (2) Å in the $H_3O_2^-$ anion, where a distance of approximately 2.30 to 2.32 Å would be expected from ionic radii comparisons.

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(16) Analyses for the fully hydrated crystals were not possible because of their tendency to lose water. Drying a sample in air overnight gave the following: Anal. Calcd for $Na_2(C_7H_{18}N)[Cr(C_7H_5NOS)_3]\cdot\frac{1}{2}NaH_3O_2\cdot 11H_2O$: C, 37.82; H, 6.40, N, 6.30; S, 10.79. Found: C, 37.8; H, 5.5; N, 6.3; S, 10.1. After drying under high vacuum at room temperature for 12 h, the dried sample gave the following: Anal. Calcd for $Na_2(C_7H_{18}N)[Cr(C_7H_5NOS)_3]\cdot\frac{1}{2}NaH_3O_2\cdot 2H_2O$: C, 46.24; H, 5.34; N, 7.70; S, 13.20; Na, 7.91. Found: C, 45.74; H, 5.05; N, 7.67; S, 12.98; Na, 7.92. In order to establish the formulation as a hemihydroxide double salt, the dried crystals were dissolved in water and potentiometrically titrated with standard HCl solution. The first break in the pH–volume plot occurred at pH 9.7, which corresponds to the end point of the hydroxide content. Equiv wt: calcd, $1.47 \times 10^3$; found, $1.46 \times 10^3$.
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# The Role of α and β Fluorine in Product Determination of Fluoro Olefin–Tertiary Phosphine Reactions. Ylide vs. Vinylphosphorane Formation[1]

*Sir:*

Recent reports have documented the facile conversion of cyclic *F*-alkenes into stable phosphonium and ammonium ylides.[2-4] The stability of these unusual fluorinated carbanions has been attributed to the inductive effect of the difluoromethylene groups adjacent to the carbanionic site[3] (β-fluorine stabilization). Since the structure of these systems did not permit the incorporation of a fluorine atom on the ylidic carbon (carbanion site), it was not possible to assess the role of α fluorine (destabilization)[5] on the fate of the initial addition–elimination product.[6]

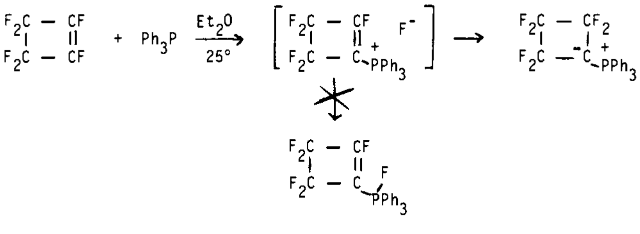


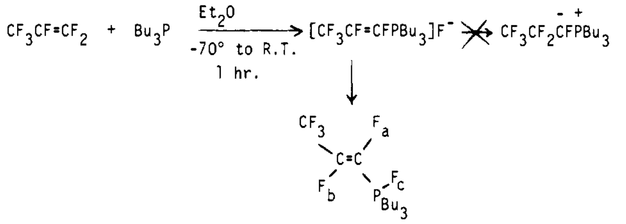
**Table I**

$$F\text{-1-alkene} + Bu_3P \xrightarrow[-70\text{ to RT}]{Et_2O} \text{vinylphosphorane}$$

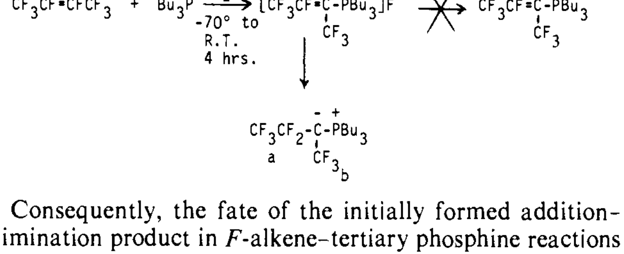
| olefin | vinylphosphorane (%)[a] | *E*/*Z*[a] |
|---|---|---|
| *F*-1-pentene | $CF_3(CF_2)_2CF{=}CFP(F)Bu_3$ (81) | 100% *Z* |
| *F*-1-heptene | $CF_3(CF_2)_4CF{=}CFP(F)Bu_3$ (83) | 100% *Z* |
| 2-phenyl-*F*-1-propene | $CF_3(C_6H_5)C{=}CFP(F)Bu_3$ (84) | 91/9 |
| 2-phenyl-*F*-1-butene | $CF_3CF_2(C_6H_5)C{=}CFP(F)Bu_3$ (87) | 92/8 |

[a] Determined by $^{19}F$ NMR vs. internal $C_6H_5CF_3$.

We now report the first example of the role of α fluorine in the mechanistic course of the reaction of *F*-1-alkenes with tertiary phosphines. When hexafluoropropene (HFP) was allowed to react with *n*-tributylphosphine,[7] no evidence of any stable ylide could be obtained.[8] Instead, the *F*-vinylphosphorane was obtained in nearly quantitative yield—with the *Z* isomer formed stereoselectively.[9-11] Table I summarizes the data for several related systems that behave analogously to HFP. The reactions are facile, clean, and give excellent yields of the vinylphosphoranes. Note, that, with *F*-1-pentene, *F*-1-heptene, and 2-phenyl-*F*-1-butene, that *only* the terminal vinylphosphorane is formed. No isomeric phosphoranes, which could be formed by an $S_N2'$ reaction, were ever observed.



However, when *F*-2-butene was employed under similar conditions in this reaction, *only* the phosphonium ylide was observed; no vinylphosphorane was detected.[12,14] Thus, the *F*-2-butene behavior is analogous to the cyclic *F*-alkenes. Comparison of the potential phosphonium ylides that could be formed from the reaction of *F*-1-alkenes, *F*-2-alkenes, and cyclic *F*-alkenes with tertiary phosphines, and the respective stability of these ylides, illustrates the role of α and β fluorine in the determination of the fate of the reaction course. When only β fluorines are present (*F*-2-butene and cyclic *F*-alkenes), the initial addition-elimination adduct is converted into the phosphonium ylide. However, when both α and β fluorines are present, the ylide is either not formed or exhibits only transient stability, and the vinylphosphorane becomes the stable product.



Consequently, the fate of the initially formed addition–elimination product in *F*-alkene–tertiary phosphine reactions can be confidently predicted by assessment of the α and β fluorines in this intermediate. When no α fluorines are present, conversion into the phosphonium ylide will become the major

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