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Surprising Synthesis and Reactivity of an Acidic Hydroxyphosphorane

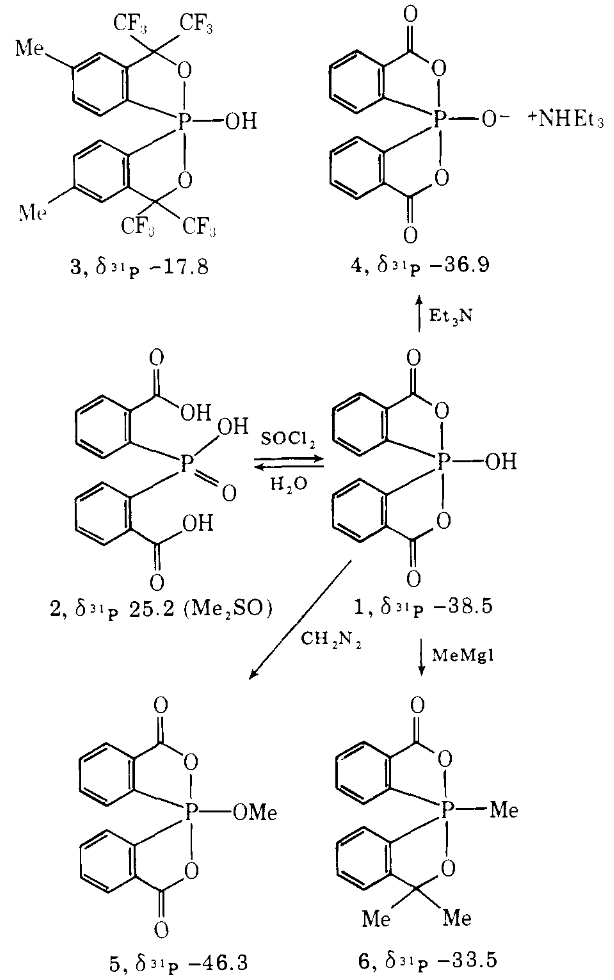
Sir:

Pentacoordinate hydroxyphosphoranes, such as **1**, are usually suggested as intermediates or transition states in nucleophilic substitution at tetracoordinate phosphorus compounds possessing P=O bonds,[1] such as **2**. While a variety of isolable oxyphosphoranes are well known,[2] only very recently have we isolated the first stable hydroxyphosphorane.[3] The chemistry of this new class of pentacoordinate phosphorus hydroxy acids is practically unknown. Acidities of hydroxyphosphoranes have been estimated in the pK_a range of 10–11, 5–6,[3c] or even as "strong acids".[4] We now report a surprising synthesis of the thermally stable and acidic hydroxyphosphorane **1**,[3a] and some of its unexpected reactions.

Trifluoroacetic acid (TFA) induced cyclodehydration of **2** yields a stable crystalline 1:1 complex of **1** with TFA.[3a] We now find that pure **1**, mp 266–269 °C, is obtained upon mixing **2** and thionyl chloride or bromide followed by evaporation of excess of the reagent. Moreover, **1** does not react with $SOCl_2$ or $SOBr_2$ even after 2 h at 60 °C to give a halophosphorane. This lack of reactivity, noted[3c] also for **3**, is very surprising. The acidity of **1** could not be directly determined, because it is decomposed by water. Also, the sodium phosphoranoxide produced from **1** and sodium hydride in tetrahydrofuran (THF) is practically insoluble in common organic solvents, thus preventing protonation experiments.[3c] However, the following observations suggest that **1** is more acidic than **3**, for which a pK_a = 5.3 ± 0.2 has been estimated.[3c]

The chemical shift value for the CH_2 protons of Et_3N (δ 2.45 ppm) is shifted to 3.15 in $Et_3NH^+Cl^-$. The smaller chemical shift change to δ 2.77 ppm for the crystalline complex obtained from **3** and Et_3N indeed suggests that **3** is a weaker acid than acetic acid (pK_a = 4.75, δ_{CH_2} for Et_3NH^+ ^-OAc 2.97). Salt **4**, obtained from **1** and Et_3N,[5] shows δ_{CH_2} 3.09 indicating that **1** is a stronger acid than **3**, or even acetic acid. This is further supported by the observation that **4** does not react with methyl iodide, while the latter and the complex from **3** and Et_3N give methyltriethylammonium iodide and **3**.[3c]

Scheme I



3, $\delta_{^{31}P}$ −17.8

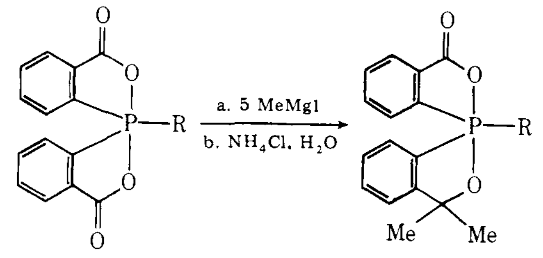
4, $\delta_{^{31}P}$ −36.9

2, $\delta_{^{31}P}$ 25.2 (Me_2SO)

1, $\delta_{^{31}P}$ −38.5

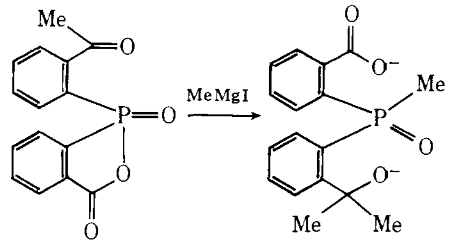
5, $\delta_{^{31}P}$ −46.3

6, $\delta_{^{31}P}$ −33.5



7, R = Me, $\delta_{^{31}P}$ −51.0
8, R = 2-Bu, $\delta_{^{31}P}$ −44.8, −45.0

6, R = Me
9, R = 2-Bu, $\delta_{^{31}P}$ −19.7



11

10

Methoxyphosphorane **5** was prepared from **1** and diazomethane[6] and characterized spectroscopically, but it could not be completely purified because of its facile hydrolysis by traces of water. In spite of the instant hydrolysis of **1** by water to give **2** (Scheme I), it does not react with dry methanol or ethanol even at reflux. More intriguing is the reaction of **1** with a sixfold excess of methylmagnesium iodide. Phosphorane **6** is obtained after refluxing the reagents for 5 h in benzene-THF (4:1), cooling, and quenching with aqueous ammonium chloride. Phosphorane **6** is also prepared from **7** and a fivefold excess of MeMgI. Phosphoranes **7** and **8** were prepared in procedures analogous to that described earlier.[3a] A crystalline precipitate was observed in the Grignard reactions of **1** and **7**, but it was too insoluble to allow recording of its ^{31}P NMR spectrum. However, the analogous reaction mixture from phosphorane **8** and MeMgI exhibited a low-field $\delta_{^{31}P}$ 57.8 prior to, and a high-field $\delta_{^{31}P}$ −19.7 after, the aqueous NH_4Cl quenching. This observation is consistent with intermediates such as **10**, which upon protonation would spontaneously be cyclodehydrated to the product phosphoranes **6** and **9**. Similar facile conversions of phosphine oxide to phosphoranes have recently been observed.[8] The surprising C–P bond formation 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**.

References and Notes

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(5) Phosphorane **4**, mp 118–120 °C, ^1H NMR δ 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 δ 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 δ 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).
(8) I. Granoth and J. C. Martin, *J. Am. Chem. Soc.*, submitted for publication; D. Hellwinkel and W. Krapp, *Chem. Ber.*, **111,** 13 (1978).

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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, α = 81.67 (3)°, β = 83.85 (3)°, γ = 59.76 (2)°, z = 2, ρ_{calcd} = 1.353 g cm^{-3}, ρ_{obsd} = 1.357 g cm^{-3}. X-ray diffraction data were collected by θ–2θ scans with a 2θ maximum of 50°, using Mo Kα radiation.[17] The unweighted and weighted R factors are 6.08 and 6.32%, respectively.

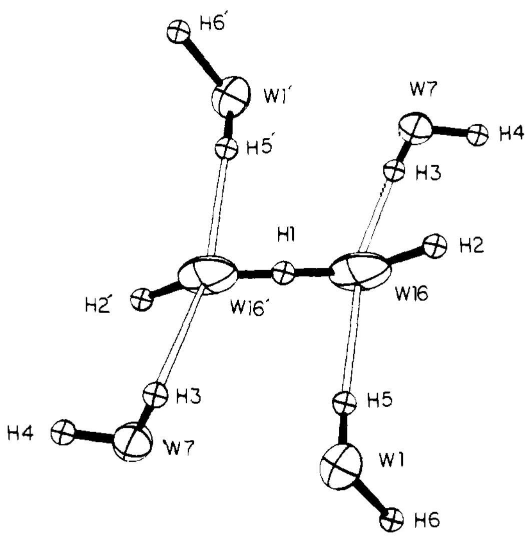

Figure 1. A perspective view of the structure of the $H_3O_2^-$ anion and the weak hydrogen bonding formed between it and adjacent waters of crystallization. Hydrogen atoms 2, 3, 4, and 6 have been located from the difference Fourier. Hydrogen atoms 1 and 5 were not seen in the electron density maps.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