106 *Bull. Korean Chem. Soc., Vol. 12, No. 1, 1991*
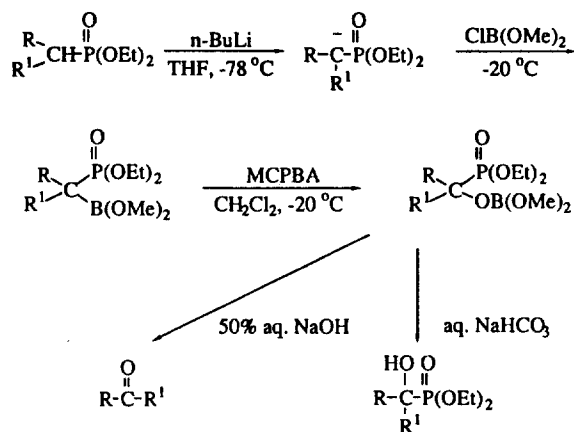
Notes

4. Application Guide for Chiral Column Selection, Daicel Chemical Industries, Ltd., 1989.

5. (a) W. H. Pirkle and M. H. Hyun, *J. Org. Chem.*, **49**, 3043 (1984); (b) W. H. Pirkle, M. H. Hyun, and B. Bank, *J. Chromatogr.*, **316**, 585 (1984); (c) M. H. Hyun, Y. -W. Park and I. -K. Baik, *Tetra. Lett.*, **29**, 4735 (1988); (d) M. H. Hyun, I. -K. Baik, and Y. -W. Park, *J. Liq. Chromatogr.*, **11**, 1249 (1988); (e) M. H. Hyun and C. -S. Min, *Bull. Kor. Chem. Soc.*, **10**, 328 (1989).

6. W. H. Pirkle, G. S. Mahler, and M. H. Hyun, *J. Liq. Chromatogr.*, **9**, 443 (1986).

7. (a) J. Sinnreich and D. Elad, *Tetrahedron*, **24**, 4509 (1968); (b) A. I. Zoltai, G. Dombi, and J. A. Szabo, *Acta. Physio. Chem.*, **27**, 74 (1981); (c) A. I. Meyers, S. Helling, and W. T. Hoeve, *Tetra. Lett.*, **22**, 5115 (1981).

# Oxidative Conversion of Organophosphonates to Carbonyl Compounds via α-Hydroxyorganophosphonates

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In connection with our ongoing research, an efficient method for conversion of organophosphonates into aldehydes or ketones is needed. In this regard, organophosphonates can be regarded as acyl anion equivalents. An α-anion of organophosphonates, which is more nucleophilic than phosphorus yields, is known to react with a variety of electrophiles.[1] Conversion to the ketones may be accomplished by anion formation followed by oxidation with various reagents. They may include molecular oxygen,[2] MoOPH,[3] bis (trimethylsilyl) peroxide,[4] and halodimethylborate / m-chloroperoxybenzoic acid(MCPBA).[5]
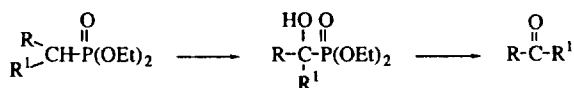
In order to test the effectiveness of these reagents, an α-anion of an organophosphonate ($R = n\text{-}C_8H_{17}$, $R^1 = CH_3$), which was generated by treatment with n-buthyllithium in tetrahydrofuran at $-78°C$, was reacted with molecular oxygen, MoOPH, and chlorodimethylborate / MCPBA,[6,7] respectively and the resulting α-hydroxyorganophosphonate was treated with 50% aqueous sodium hydroxide to produce 2-decanone. Oxidation with MoOPH gave 2-decanone in 66% yield along with the recovery of 16% of the starting material, whereas the reaction with molecular oxygen afforded the desired product in 76% yield.[8] The reaction with chlorodimethylborate / MCPBA gave the best result, yielding 80% of 2-decanone. Also, it is noteworty that α-hydroxyorganophos-

Scheme 1.

Table 1. Oxidation of Organophosphonates Using ClB(OMe)₂ / MCPBA

$\begin{array}{c}R\\ \diagdown\\ \diagup\\ R^1\end{array}$ $\overset{O}{\underset{}{CH\text{-}P(OEt)_2}}$	$R\text{-}\overset{HO}{\underset{R^1}{\underset{\vert}{C}}}\text{-}\overset{O}{\underset{}{P(OEt)_2}}$, %[a]	$R\text{-}\overset{O}{\underset{}{C}}\text{-}R^1$, %[b]
$\begin{array}{c}Ph\\ \diagdown\\ \diagup\\ H\end{array}$ $\overset{O}{\underset{}{CH\ P(OEt)_2}}$	78	62
$\begin{array}{c}Ph\\ \diagdown\\ \diagup\\ C_2H_5\end{array}$ $\overset{O}{\underset{}{CH\text{-}P(OEt)_2}}$	70	70
$\begin{array}{c}n\text{-}C_8H_{17}\\ \diagdown\\ \diagup\\ H\end{array}$ $\overset{O}{\underset{}{CH\text{-}P(OEt)_2}}$	78	50(28)[c]
$\begin{array}{c}n\text{-}C_8H_{17}\\ \diagdown\\ \diagup\\ CH_3\end{array}$ $\overset{O}{\underset{}{CH\text{-}P(OEt)_2}}$	83	80
$\begin{array}{c}PhO(CH_2)_4\\ \diagdown\\ \diagup\\ CH_3\end{array}$ $\overset{O}{\underset{}{CH\text{-}P(OEt)_2}}$	90	74
$\begin{array}{c}PhCH(CH_3)\\ \diagdown\\ \diagup\\ CH_3\end{array}$ $\overset{O}{\underset{}{CH\text{-}P(OEt)_2}}$	92	64

[a]Isolated yields using Method A. [b]Isolated yields using Method B. [c]The number in parenthesis indicates the yield of the aldol product ($n\text{-}C_7H_{15}\text{-}C(CHO)=CH\text{-}C_8H_{17}$).

phonates can be isolated by quenching the reaction mixture with aqueous sodium bicarbonate. When α-anion of diethyl benzylphosphonate with fluorodimethylborate and NaOH / H_2O_2 or MCPBA, diethyl α-hydroxybenzylphosphonate was obtained in 34% and 66% yield, respectively. However, chlorodimethylborate / MCPBA procedure gave diethyl α-hydroxybenzylphosphonate in 78% yield. Therefore, remaining reactions were carried out with chlorodimethylborate / MCPBA, as shown in Scheme 1.

Table 1 summarizes some experimental results and illustrates the efficiency and the scope of the present method. Several structurally different α-hydroxyphosphonates were isolated in high yields by quenching with aqueous sodium bicarbonate. In the direct conversion of organophosphonates

Notes

Bull. Korean Chem. Soc., Vol. 12, No. 1, 1991 107

into the corresponding aldehydes or ketones, the present method works well with diethyl secondary alkylphosphonates, yielding the corresponding ketones in good yields. However, in the case of a diethyl primary alkylphosphonate, conversion of an α-hydroxyphosphonate into the aldehyde causes trouble due to the strongly basic condition and an aldol product was obtained as a byproduct.

Experimental

A Typical Procedure for the Oxidation of Diethyl benzyl-phosphonate (Method A); To a stirred solution of diethyl benzylphosphonate (228 mg, 1 mmol) in tetrahydrofuran (4 m*l*) at $-78^{\circ}C$ was added 0.7 m*l* of 1.5 M n-buthyllithium. After being stirred at $-78^{\circ}C$ for 1 h, chlorodimethylborate (220 μ*l*, 2 mmol) was added to the reaction mixture at $-20^{\circ}C$. After 0.25 h at $-20^{\circ}C$ and 1 h at room temperature, the solvent was evaporated in vacuo. The residue was dissolved in dichloromethane (4 m*l*) under nitrogen and added to a solution of m-chloroperoxybenzoic acid (258 mg, 1.5 mmol) in dichloromethane (4 m*l*) at $-20^{\circ}C$. After being stirred 1 h, the resulting solution was quenched with aqueous sodium bicarbonate (4 m*l*). The extractive workup and chromatographic separation gave diethyl α-hydroxy benzylphosphonate (190 mg, 78%). Its spectral data were in accord with the reported data.[9] (Method B); The reaction mixture obtained by the MCPBA oxidation procedure outlined above was quenched with 50% aqueous sodium hydroxide solution (4 m*l*) and methanol (4 m*l*). The resulting solution was stirred for 50 min. The extractive workup and chromatographic separation gave benzaldehyde (66 mg, 62%).

References

1. J. Boutagy and R. Thomas, *Chemical Review*, **74**, 87 (1974).
2. (a) H. J. Bestmann and O. Kratzer, *Chem. Ber.*, **96**, 1899 (1963); (b) S. S. Kulp and M. J. Mcgee, *J. Org. Chem.*, **48**, 4097 (1983).
3. (a) E. Vedejs, D. A. Enger, and J. E. Telschow, *J. Org. Chem.*, **43**, 188 (1978); (b) R. D. Little and S. O. Myong, *Tetrahedron Lett.*, **21**, 3339 (1980); (c) M. R. Galobardes and H. W. Pinnick, *Ibid.*, **22**, 5235 (1981).
4. J. R. Hwu, *J. Org. Chem.*, **48**, 4433 (1983).
5. D. S. Metteson, *Synthesis*, 147 (1974).
6. K. Fujita and M. Schlosser, *Helv. Chem. Acta.*, **65**, 1258 (1982).
7. J. B. Baudin, M. Julia, and C. Rolando, *Tetrahedron Lett.*, **26**, 2333 (1985).
8. Molecular oxygen gave inferior results for other substrates, as compared with chlorodimethylborate / MCPBA.
9. F. T. Boullet and A. Foucard, *J. Chem. Soc. Chem. Comm.*, 165 (1982).

Synthesis and Structure of Bis[hydrotris(1-py razolyl)borato]iron(III) Nitrate

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Tris(1-pyrazolyl)borate(HB(pz)$_3^-$) ligand has been used in the syntheses of a variety of metal complexes.[1] The ligand is often considered as a cyclopentadienyl analogue as both ligands occupy effectively three coordination sites around a metal center and are both 6 electron donors. In recent years this ligand has received much attention in bioinorganic chemistry since the N$_3$ ligand coordination mimics the multi-imidazole coordination found often in the active site of metal-loenzymes.[2,3] One of the earlier types of complexes studied was the form M(HB(pz)$_3$)$_2$, where M is a divalent metal ion. Crystal structures of two of these complexes, Co(HB(pz)$_3$)$_2$[4] and Fe(HB(pz)$_3$)$_2$[5], have appeared. Although the structure of Fe(HB(pz)$_3$)$_2^+$ was mentioned ref. 3a,[6] the details of synthesis and crystal structure of the compound still remain unpublished. In an attempt to prepare new μ-oxodiiron(III) complexes containing HB(pz)$_3^-$ ligands we accidentally obtained [Fe (HB(pz)$_3$)$_2$](NO$_3$)[7] as a major product. We report here the synthesis and X-ray structure of the compound.

Experimental

All reagents were used as received. KHB(pz)$_3$ was synthesized by the literature methods.[8] UV-Vis and IR spectra were recorded on a Hewlett-Packard 8452A UV-Vis spectrophotometer and a Perkin Elmer 843 IR spectrophotometer, respectively. Elemental analysis was performed in the Korea Research Institute of Chemical Technology. Solid state magnetic susceptibilities were measured with a magnetic susceptibility balance(Johnson Matthey). Solution susceptibilities were determined by the NMR method[9] with a Brucker AM-300 MHz spectrometer.

[Fe(HB(pz)$_3$)$_2$](NO$_3$). A solution of 0.126 g (0.50 mmol) of KHB(pz)$_3$ in 2 m*l* of H$_2$O was added dropwise to a clear orange brown solution containing 0.200 g (0.50 mmol) of Fe (NO$_3$)$_3$ · 9H$_2$O, 0.042 g (0.50 mmol) of NaHCO$_3$ and 5 m*l* of H$_2$O with vigorous stirring. A brown solid precipitated immediately; however, with stirring the suspension took on a deep red appearance. After 12 h the mixture was filtered and the solid was dried under vacuum to afford 0.117 g of a red solid (yield 70%). When the procedure was repeated with 0.075 g (0.18 mmol) of Fe(NO$_3$)$_3$ · 9H$_2$O and 0.093 g (0.36 mmol) of KHB(pz)$_3$ without adding NaHCO$_3$ to the solution the same product was obtained in higher yield(0.085 g, 85%). UV-Vis (MeCN): λ_{max}(ε) 242(sh, 9600), 272(sh, 3900), 442 (5200), 520(sh, 1400) nm. IR(KBr, cm^{-1}): 3120, 3100, 2540 (BH), 1490, 1400, 1370, 1350, 1310, 1210, 1190, 1120, 1070, 1050, 990, 770, 710, 660, 620, 460, 330. Anal. Calcd for C$_{18}$H$_{20}$-N$_{13}$O$_3$B$_2$Fe · H$_2$O: C, 38.47; H, 3.95, N, 32.40. Found: C, 38.54; H, 3.56; N, 32.41.

X-ray Crystal Structure Determination. Dark red crystals of [Fe(HB(pz)$_3$)$_2$](NO$_3$) suitable for an X-ray analysis were grown by slow diffusion of ether into a CH$_2$Cl$_2$ solution of the compound. A crystal having approximate dimensions of