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Synthesis and Thermolysis of Hexacoordinate 1,2-Oxaphosphetanides

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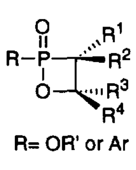
Abstract: β-Hydroxyalkylphosphoranes containing two Martin ligands were prepared by reduction of the corresponding phenylthiomethylphosphorane with lithium naphthalenide, followed by the reaction with carbonyl compounds. Treatment of the β-hydroxyalkylphosphoranes with KH in the presence of 18-crown-6 gave a mixture of stereoisomers of the corresponding hexacoordinate 1,2-oxaphosphetanides stable in solution at room temperature. Upon heating, the adducts of benzophenone derivatives gave the corresponding benzophenones, while a hexafluoroacetone adduct afforded the corresponding olefin.

In the course of our studies[1,2] on diheteracyclobutanes in which a highly coordinate main group element is adjacent to the other heteroatom, we achieved the syntheses of oxetanes with pentacoordinate P,[1a,b,c] Si,[1d] Ge,[1e] Sn,[1f] and tetracoordinate B[1g] centers as well as azetidines with a pentacoordinate P center.[1h] These oxetane compounds correspond to the intermediates of the Wittig,[3a] Peterson-type[3b,c] and boron-Wittig reactions.[3d] We also reported synthesis of tetracoordinate 1,2-oxaphosphetanes by intramolecular dehydration of β-hydroxyalkylphosphonic acid monoesters[4a] and -phosphinic acids.[4b] The results showing that both tetracoordinate and pentacoordinate 1,2-oxaphosphetanes **1** and **2** undergo the Wittig-type reaction to give the corresponding olefins prompted us to examine the reactivity of hexacoordinate 1,2-oxaphosphetanides. Recently, hexacoordinate 1,2-oxaphosphetanides were independently observed by low temperature ^{31}P NMR spectroscopy in the stereoselective condensation reaction of lithium enolates of alkoxycarbonylmethylspirooxyphosphoranes **3** with benzaldehyde.[5] In this paper we wish to report the synthesis and thermolysis of hexacoordinate 1,2-oxaphosphetanides **4**[6] stable in solution at room temperature.



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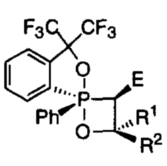

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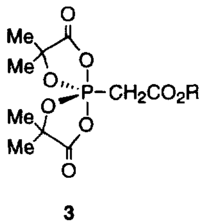

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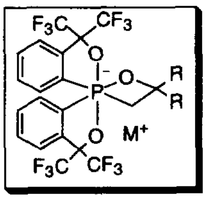

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Sequential treatment of the dilithio derivative[7] (6.6 mmol) of hexafluorocumyl alcohol with PCl_3 (3 mmol), with phenylthiomethyl chloride (4 mmol), and then with aqueous NH_4Cl gave phenylthiomethylphosphorane **5** (37%) after purification by HPLC. Pentacoordinate β-hydroxyalkylphosphoranes **6a-d**[8] were prepared in moderate yields by reduction of **5** with 2 equiv. of lithium naphthalenide (LiNaph) at -72 °C, followed by the reaction with carbonyl compounds (**7**) at -72 °C → 25 °C (Table 1).

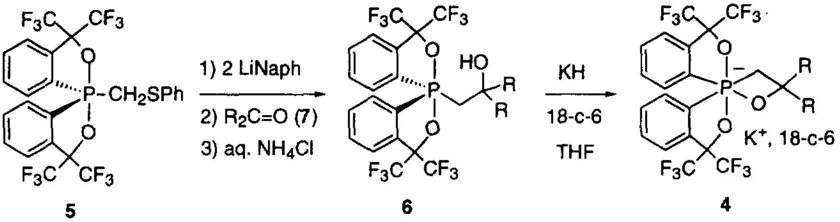
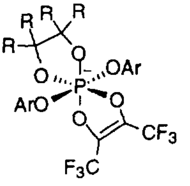
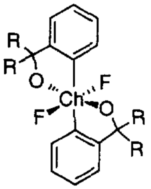


Table 1. Yields and ^{31}P NMR Data of **6**.

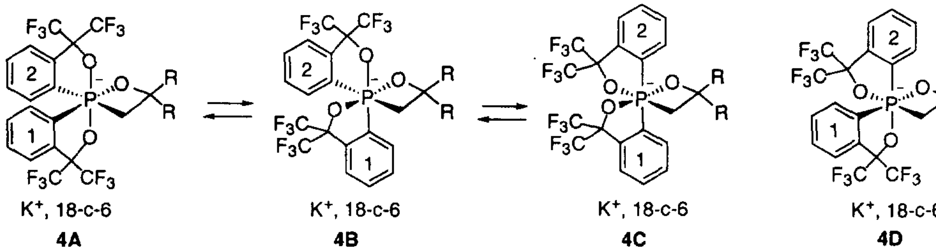
6	R	δ_P	Yields[a]/%
a	CF_3	-21.6	39
b	C_6H_5	-20.6	45
c	p-$MeOC_6H_4$	-21.0	46
d	p-ClC_6H_4	-20.4	49

a) Isolated yields based on **5**.


Ar=p-FC_6H_4
8


9: Ch=S; R=CF_3
10: Ch=Te; R=CF_3

Deprotonation of β-hydroxyalkylphosphoranes **6** with KH in the presence of 18-crown-6 was carried out in THF under argon. After removal of the solvent under reduced pressure, the residue was dissolved in acetone-d_6, and the solution was sealed in an NMR tube. The reaction was monitored by ^{31}P NMR spectroscopy to show quantitative formation of a hexacoordinate 1,2-oxaphosphetanides **4**.[9] Although two signals were observed for each of **4** in the range from δ_P -111 to -114, in an early reaction stage, the up-field signal rapidly disappeared, while the down-field signal slowly decreased to give another signal at δ_P -118 ~ -124.[10] Judging from these chemical shifts the resulting species are considered to have a hexacoordinate phosphorus center. In the ^{19}F NMR spectra two A_3B_3 signals appeared in the early stage and then decreased to give two sets of new unresolved A_3B_3 signals (three A_3B_3 signals for **4a**). The final isomers were stable in solution at room temperature. Among four isomers possible for these hexacoordinate compounds if neglecting their enantiomers, three of them could be observed. In hexacoordinate compounds such as **8**,[11] **9**[12] and **10**[13] similar isomerization under appropriate conditions was reported and in all cases *cis* isomers were found to be thermodynamically more stable than *trans* ones. It has been proposed that an increase in the number of polarized three-center bonds results in stabilization of the system,[13] suggesting that the final isomer is **4D**. In order to elucidate the relationships between Martin ligands 1 and 2 and the methylene group, differential NOE



experiments using **4b** in CD_3CN were carried out to show that the final isomer is not **4Db**, but **4Cb**.[14] Since **4A** can be regarded as kinetically favorable isomer, the signals observed were tentatively assigned to isomers **4B**, **4A**, and **4C**, in the order of going from downfield to upfield. The centered phosphorus nucleus of **4C** is more shielded than those of **4A** and **4B** by the electron-positive group forming the most polarized three-centered bond, thus **4C** resonates at the highest field. The ^{31}P and ^{19}F NMR data of **4C** are summarized in Table 2.

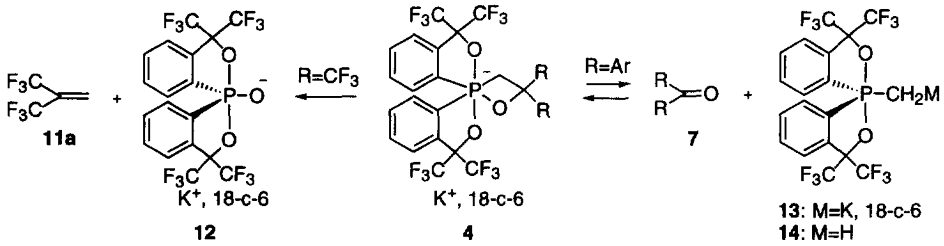
Table 2. ^{31}P and ^{19}F NMR Data of the Most Stable Isomers of **4**.[a)]

	δ_P	δ_F
a	-118.37	-71.60 ~ -71.79 (m, 3F),[b)] -71.88 (q, 12.3, 3F), -72.80 ~ -73.00 (m, 3F), -73.19 (q, 12.3, 3F), -74.4 ~ -74.64 (m, 3F), -74.73 ~ -74.98 (m, 3F)
b	-122.90	-71.45 (q, 8.9, 3F), -73.21 (q, 7.8, 3F), -73.80 ~ -74.35 (m, 6F)
c	-122.76	-71.42 (q, 9.1, 3F), -73.12 (q, 6.1, 3F), -73.91 ~ -74.14 (m, 6F)
d	-124.04	-71.61 (q, 9.2, 3F), -73.29 (q, 6.1, 3F), -74.15 ~ -74.40 (m, 6F)

a) The spectra were measured for an acetone-d_6 solution after standing for an appropriate period.

b) The multiplicity, $^4J_{FF}$ (Hz), and integral values are shown in the parentheses.

Upon heating around 80-100 °C in a mixture of THF and C_6D_6 (5:1) **4b-d** underwent a retroaddition reaction to give almost quantitatively the corresponding benzophenone derivatives and methylphosphorane **14**, formed by protonation of the resulting metallomethylphosphorane **13**, whereas **4a** gave the corresponding olefin **11a** (40%) and hydroxyphosphorane produced by protonation of oxidophosphorane **12**.



The formation of **7** and **14** indicates that an equilibrium between **4** and a mixture of **7** and **13** shifts towards the latter two as the temperature is raised. Potassiomethylphosphorane **13** seems to be highly basic to react with an unidentified proton source to give methylphosphorane **14**. The equilibration in the case of the hexafluoroacetone derivative **4a** is considered to be more inclined toward the hexacoordinate species than in the cases of the benzophenone derivatives **4b-d**, because of the high electrophilicity of hexafluoroacetone, thus allowing **4a** to undergo the Wittig-type olefin formation reaction.

In conclusion, hexacoordinate 1,2-oxaphosphetanides were NMR-spectroscopically characterized and demonstrated to undergo two types of reactions depending on the substituents.

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8. Spectral data of **6b** are shown as a typical example: ^{1}H NMR (500 MHz, $CDCl_3$) δ= 3.58 (dd, $^2J_{HH}$=14.4 Hz, $^2J_{HP}$=16.6 Hz, 1H, PC$\underline{H}$H'), 3.63 (t, $^2J_{HH}$=$^2J_{HP}$=14.4 Hz, 1H, PCH$\underline{H}$'), 4.38 (s, 1H, OH), 6.97-7.00 (m, 3H), 7.13-7.17 (m, 1H), 7.18-7.22 (m, 2H), 7.25-7.27 (m, 2H), 7.28-7.31 (m, 2H), 7.46-7.51 (m, 2H), 7.58-7.62 (m, 4H), 8.03 (dd, $^3J_{HH}$=8.1 Hz, $^3J_{HP}$=11.7 Hz, 2H). ^{19}F NMR (254 MHz, $CDCl_3$) δ= -73.94 (q, $^4J_{FF}$=9.9 Hz), -74.11 (q, $^4J_{FF}$=9.9 Hz). ^{31}P NMR (109 MHz, $CDCl_3$) δ= -20.63. HRMS (70 eV) *m/z* Found: 712.1028. Calcd for $C_{32}H_{21}F_{12}O_3P$: 712.1037.
9. Spectral data of **4b** are shown as typical examples: **4Bb**: ^{1}H NMR (270 MHz, acetone-d_6) δ= 3.32 (t, $^2J_{HH}$=$^2J_{HP}$=10.8 Hz, 1H, PC$\underline{H}$H'), 3.60 (s, 24H, $(OC\underline{H}_2C\underline{H}_2)_6$), 4.25 (dd, $^2J_{HH}$=10.8 Hz, $^2J_{HP}$=21.2 Hz, 1H, PCH$\underline{H}$'), 6.87-6.96 (m, 3H), 6.99-7.05 (m, 4H), 7.08-7.17 (m, 3H), 7.17-7.22 (m, 1H), 7.25-7.30 (m, 1H), 7.30-7.34 (m, 1H), 7.52-7.60 (m, 3H), 7.96-8.06 (br s, 1H), 7.17-8.29 (br s, 1H). ^{31}P NMR (109 MHz, acetone-d_6) δ= -111.61. ^{19}F NMR (254 MHz, acetone-d_6) δ= -69.52 (q, $^4J_{FF}$=9.2 Hz, 3F), -69.68 (q, $^4J_{F}$=12.2 Hz, 3F), -72.31 (q, $^4J_{FF}$=9.2 Hz, 3F), -72.68 (q, $^4J_{FF}$=12.2Hz). **4Cb**: ^{1}H NMR (270 MHz, acetone-d_6) δ= 2.78 (tq, $^2J_{HH}$=$^2J_{HP}$=13.0 Hz, J_{HF}=2.0 Hz, 1H, PC$\underline{H}$H'), 3.60 (s, 24H, $(OC\underline{H}_2C\underline{H}_2)_6$), 4.00 (t, $^2J_{HH}$=$^2J_{HP}$=13.0 Hz, 1H, PCH$\underline{H}$'), 6.56-6.62 (m, 1H), 6.65-6.70 (m, 1H), 6.71-6.78 (m, 2H), 6.80-6.86 (m, 1H), 6.89-6.96 (m, 2H), 6.98-7.03 (m, 1H), 7.03-7.10 (m, 5H), 7.28-7.32 (m, 1H), 7.32-7.37 (m, 1H), 7.38-7.43 (m, 2H), 7.76 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{HP}$=12.5 Hz, 1H). ^{31}P NMR (109 MHz, acetone-d_6) δ= -122.76. ^{19}F NMR (254 MHz, acetone-d_6) δ= -71.45 (q, $^4J_{FF}$=8.9 Hz, 3F), -73.21 (q, $^4J_{FF}$=7.8 Hz, 3F), -73.80 ~ -74.35 (m, 6F).
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14. NOE signals were observed between the protons α to the P atom of Martin ligands 1 and 2 and each of the methylene protons. The multiplet (δ 7.03-7.10) in acetone-d_6 was separated in CD_3CN.

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