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THE REACTIONS OF BIS(TRIMETHYLSILYL) HYPOPHOSPHITE WITH CARBONYL COMPOUNDS[1)]

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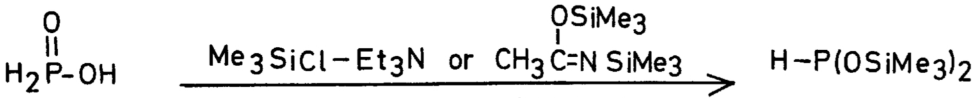
Bis(trimethylsilyl) hypophosphite, generated in situ from hypophosphorous acid and silylating agents such as trimethylsilyl chloride in the presence of triethylamine or bis(trimethylsilyl)-acetamide, reacted with carbonyl compounds to give the carbonyl adducts, which were successfully converted to anilinium salt of the corresponding phosphonous acids by treatment with aniline-containing ethanol.

α-Hydroxyphosphonous acids (1) were synthesized about 90 years ago by the reaction of hypophosphorous acid with carbonyl compounds.2) According to the classical method, rather drastic conditions were required and the yields of 1 were unsatisfactory.2,3) Improved method for the synthesis of 1 has not been described to date at all.

On the other hand, we have recently developed the method of trimethylsilylation of phosphorous acid. By this method, an isolable quite reactive tervalent compound, tris(trimethylsilyl) phosphite,1) can be generated. This silylation procedure can be extended to other oxyphosphorus acids with lower oxidation state.

Bis(trimethylsilyl) hypophosphite (2) was first described by Voronkov and his co-workers.4) They described its physical properties and two kinds of reactions with acrylonitrile and vinylsilane at 150°C. But, no report has appeared on its chemical reactivities toward other electrophiles since their report.

In connection with our interest in P-C containing oxyphosphorus acids,1g) we now wish to report the reaction of 2 with carbonyl compounds which provides an improved synthetic method of 1.



$$H_2\overset{O}{\overset{\|}{P}}\text{-OH} \xrightarrow[\text{(BSA)}]{Me_3SiCl-Et_3N \text{ or } CH_3\overset{OSiMe_3}{C}=N\,SiMe_3} H-P(OSiMe_3)_2$$

(2)

The compound 2 could be prepared by the reaction of hypophosphorous acid and trimethylsilyl chloride in the presence of triethylamine and it was isolated by distillation under argon atmosphere. However, it was inflammable when it was exposed to air. Therefore, 2 was used always in situ in order to avoid the accident. Hypophosphorous acid was treated with trimethylsilyl chloride and triethylamine in dry THF. Without isolation of 2, benzaldehyde was added and the mixture was stirred at room temperature for 3 hr. The precipitate of triethylamine hydrochloride was filtered off. The reaction mixture was poured into aniline-containing ethanol. Mono-anilinium salt of 1-hydroxy-benzylphosphonous acid (1a) was obtained in 42% yield. The structure of 1a was confirmed by its ir and nmr spectra and elemental analysis (see experimental section). In a similar manner, several α-hydroxyphosphonous acids (1b-1h) were obtained as shown in Table.

A neutral silylating agent, bis(trimethylsilyl)acetamide (BSA),[5)] was found to be effective in these reactions in place of trimethylsilyl chloride-triethylamine.

When aliphatic aldehydes were employed, the yields of the corresponding phosphonous acids were relatively low. It seems to be due to the side reaction yielding silyl enolethers with elimination of α-hydrogen from the aldehydes.

The typical procedure for the reaction of 2 with carbonyl compounds is described as follows.

Preparation of mono-anilinium salt of 1-hydroxy-benzylphosphonous acid (1a)

Pyridinium salt of hypophosphorous acid (10 mmol) was rendered anhydrous by repeated evaporation with excess dry pyridine and dissolved in dry THF (20 ml). To the solution benzaldehyde (10 mmol) was added at room temperature. The reaction mixture was stirred for 3 hr. Precipitate was removed by filtration. The filtrate was concentrated to dryness. The residue was dissolved in ethanol (20 ml) and aniline (30 mmol) was added. Then ether (150 ml) was added. White crystals of 1a separated was collected by filtration and dried over P_2O_5: mp 158-160°, ir(KBr):3190, 2300(P-H),1590,1540,1484 cm^{-1}; nmr(d-DMSO): 4.72(d,1H,J_{P-H}=9.5H z,HCP),6.75(d,1H, J_{P-H}=528.6Hz,HP),6.63(d,2H,J_{H-H}=6.5Hz,o-ArH of $H_3\overset{+}{N}C_6H_5$); Anal. Calcd for $C_{13}H_{16}O_3NP$: C,59.06;H,6.10;N,5.30. Found:C,58.91;H,6.00;N,5.20.

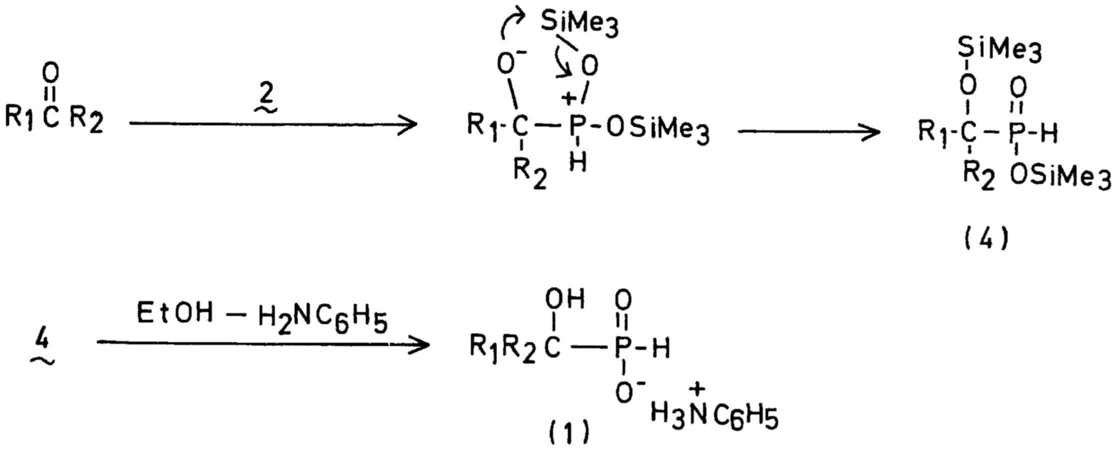


Table Synthesis of α-hydroxyphosphonous acids

	Carbonyl Compound (R_1COR_2) R_1	R_2	Molar ratio of $RCHO/H_3PO_2$	Silylating agents	(equiv. to R_1COR_2)	Yield of 1 (%)	Mp (°C)
a	C_6H_5	H	1.0	$Me_3SiCl-Et_3N$	2.2	25	158-160
	C_6H_5	H	1.0	BSA	1.5	59	
	C_6H_5	H	1.2	$Me_3SiCl-Et_3N$	3.3	42	
b	p-MeO-C_6H_4	H	1.2	$Me_3SiCl-Et_3N$	3.3	97	162-163
c	p-Me_2N-C_6H_4	H	1.0	$Me_3SiCl-Et_3N$	2.2	72	220
d	C_2H_5	H	1.2	$Me_3SiCl-Et_3N$	3.3	17	119-121
e	$(CH_3)_2CH$	H	1.2	$Me_3SiCl-Et_3N$	3.3	19	183-184
f	C_4H_9	H	1.2	$Me_3SiCl-Et_3N$	3.3	22	143-145
g	C_6H_5	CH_3	1.0	$Me_3SiCl-Et_3N$	2.0	18	164-165
	C_6H_5	CH_3	1.2	$Me_3SiCl-Et_3N$	3.3	48	
	C_6H_5	CH_3	1.0	BSA	1.5	67	
h	p-Cl-C_6H_4	CH_3	1.0	$Me_3SiCl-Et_3N$	3.3	25	170-172
	p-Cl-C_6H_4	CH_3	1.2	$Me_3SiCl-Et_3N$	3.3	62	
	p-Cl-C_6H_4	CH_3	1.0	BSA	1.5	79	
	p-Cl-C_6H_4	CH_3	1.2	BSA	1.5	88	

References

1) This paper participates as Part IX in the series of Silyl Phosphites. Part VI, Part VII, and Part VIII are now in preparation. For the related reactions see the following: (a) T. Hata and M. Sekine, J. Am. Chem. Soc., 96, 7363 (1974); (b) T. Hata and M. Sekine, Tetrahedron Lett., 3943 (1974); (c) M. Sekine and T. Hata, ibid., 1711 (1975); (d) T. Hata, M. Sekine, and N. Kagawa, Chem. Lett., 635 (1975); (e) T. Hata, M. Sekine, and N. Ishikawa, ibid., 645 (1975); (f) T. Hata, M. Sekine, and I. Yamamoto, ibid., 601 (1976); (g) M. Sekine, I. Yamamoto, A. Hashizume, and T. Hata, ibid., 485 (1977).

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