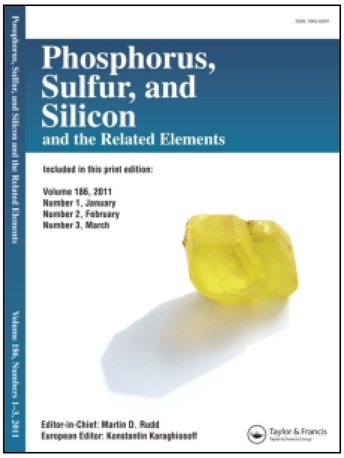

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Communication

TANDEM PETERSON-MICHAEL REACTION USING α-SILYLALKYLPHOSPHINE CHALCOGENIDES AND HORNER-EMMONS REACTION

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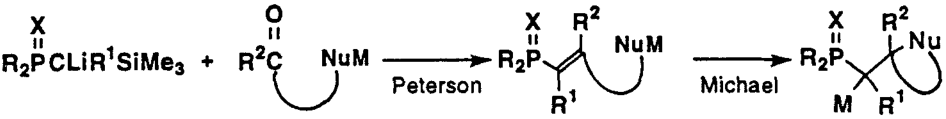
The title tandem reaction was achieved by using 1-(trimethylsilyl)alkylphosphine chalcogenides and the lithio derivative of 2-hydroxytetrahydropyran. The Horner-Emmons reaction of the tandem product was accomplished by in-situ generation and trapping of the α-lithio derivative, followed by Warren's method of olefination.

Key words: Tandem Peterson-Michael; silylalkylphosphine chalcogenides; 2-hydroxytetrahydropyran; lithium tetramethylpiperidide; Horner-Emmons reaction.

INTRODUCTION

The tandem Michael addition-intramolecular Wittig reaction using vinylphosphonium salts or vinylphosphine oxides has been utilized as one useful method for the synthesis of cyclic and heterocyclic ene compounds.[1] The title tandem reaction can be expected in the reaction of α-silyl-α-phosphoryl carbanions[2] with carbonyl compounds having a nucleophilic moiety, giving cyclic compounds functionalized at the side chain. In this paper we wish to report on this tandem reaction and the Horner-Emmons reaction of the products.



RESULTS AND DISCUSSION

The sequential reactions of α-trimethylsilylalkylphosphine chalcogenides (**1**) (a: $R^1 = H$, $X = O$; b: $R^1 = H$, $X = S$; c: $R^1 = Me$, $X = O$; d: $R^1 = Me$, $X = S$) with n-BuLi and then 2-lithio-oxytetrahydropyran (**2**) in THF gave the tandem Peterson-Michael product **3**, the Peterson products (**4**), and their allylic isomers (**5**) (Table I).

TABLE I

Tandem Peterson-Michael reaction of the lithio derivatives of **1** with **2**

							Yield$^{a,b)}$/%			
Run	**1**	R	R^1	X	T/^{o}C	Time/h	**3**	Z-**4**	E-**4**	**5**
1	**1a**	Ph	H	O	0	0.5	-	-	14	72
2	**1a**	Ph	H	O	r.t.	48	94	-	-	-
3	**1b**	Ph	H	S	0	3	13	6	44	36
4	**1b**	Ph	H	S	r.t.	73	36	4	27	32
5	**1b**	Ph	H	S	reflux	24	70	1	5	22
6	**1c**	Ph	Me	O	r.t.	24	50	-	50	-
7	**1d**	Ph	Me	S	r.t.	48	-	-	59	40
8	**1d**	Ph	Me	S	reflux	16	-	-	50	50

a) Yields based on **1** were obtained by glc. b) Satisfactory spectra were obtained for all new compounds.

TABLE II

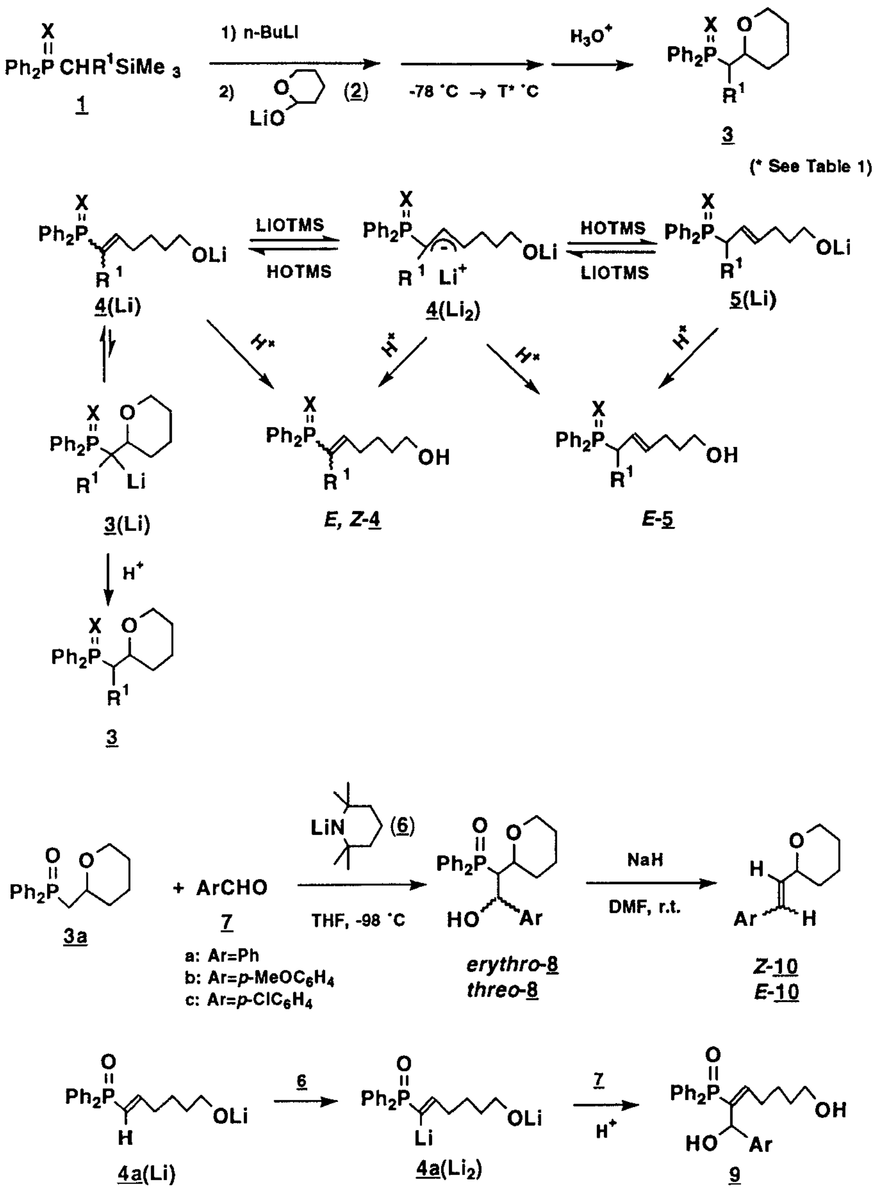
The Horner-Emmons Reaction of **3a**

	Yields$^{a,b)}$/%				Yields$^{b,c)}$/%	
Ar	**4a**	erythro-**8**	threo-**8**	**9**	Z-**10**	E-**10**
Ph	-	51	22	14	54	64
p-MeOC$_6$H$_4$	-	35	22	19	87	67
p-ClC$_6$H$_4$	11	25	49	11	65	57

a) Isolated yields based on **3a**. b) Satisfactory spectra were obtained for all new compounds. c) Isolated yields based on erythro- or threo-**8**.

The data in Table I, together with the results[3] observed when hexanal is used in place of **2**, suggest that LiOSiMe$_3$, which was formed together with **4**(Li) by the Peterson reaction, is a strong enough base to catalyze the relatively rapid equilibration of **4**(Li) and **5**(Li). In addition, **4**(Li) is also in equilibrium with **3**(Li). The latter equilibrium lies much toward **4**(Li), as clarified from the results of the deprotonation of **3** (see below). Therefore, an irreversible protonation of **3**(Li) seems to be a driving force for the formation of **3**.[4] Stirring at room temperature was enough to produce **3a**, whereas reflux conditions were necessary to obtain **3b** in good yield (Table I). To our knowledge, this is the first example of a tandem Peterson-Michael reaction.

The deprotonation of **3** with alkyllithium reagents resulted in β-elimination with ring opening (→E-**4**) as normally expected for a carbanion bearing a good leaving group at the β-position, though there are cases where such elimination does not



Scheme

occur.[5] Therefore, in-situ generation and trapping of the α-lithio derivative of **3** seemed to offer the best chance for bringing about the Horner-Emmons reaction. Thus, the reaction of **3a** with lithium 2,2,6,6-tetramethylpiperidide (**6**), a well-known hindered base, in the presence of aromatic aldehydes (**7a–c**) gave mainly a mixture of diastereomers (erythro and threo) of **8a–c**, together with β-elimination products **4a** and **9a–c**, which were formed by abstraction of a vinyl proton (R^1) of **4a**, followed by the reaction with **7a–c** (Table II).[6]

Erythro- and threo-**8a–c** were readily separated by chromatography, and treated with NaH in dimethylformamide (DMF) at room temperature to give the corresponding Z- and E-olefins (**10**) in fairly good yields, respectively (Table II).[7]

This in-situ generation and trapping reaction may provide one useful method for the Horner-Emmons reaction using various phosphoryl compounds having a leaving group at the β-position to the phosphorus atom.

EXPERIMENTAL

General procedure; Tandem Peterson-Michael reaction of **1**: Compound **1**[8] (ca. 1 mmol) was allowed to react with 1.1 equiv. of n-BuLi at −78°C in tetrahydrofuran (THF) (20 ml) and then with the lithio derivative **2** prepared from 2-hydroxytetrahydropyran (1.3 equiv.) and n-BuLi (1.3 equiv.). After 30 min the reaction mixture was warmed (see Table I), then quenched with aq. NH_4Cl after stirring for the appropriate time. After usual workup the yields of the products (**3**, **4** and **5**) were obtained by GLC. These products were isolated by dry column chromatography (SiO_2, AcOEt), PTLC, or Kugelrohr distillation.

3a: mp 128.0–128.5°C. Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05. Found: C, 71.75; H, 7.03. ^1H NMR($CDCl_3$): δ 1.12–1.79 (m, 6 H, $OCH_2(C\underline{H}_2)_3$), 2.35–2.66 (m, 2 H, $PC\underline{H}_2$), 3.06–3.86 (m, 3 H, $—C\underline{H}O—C\underline{H}_2—$), and 7.26–7.83 (m, 10 H, 2 × $C_6\underline{H}_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C 23.3 (s), 25.5 (s), 33.5 (d, J = 7.1 Hz), 37.3 (d, J = 71.0 Hz), 68.3 (s), 72.6 (d, J = 3.7 Hz), 128.4 (d, J = 12.1 Hz), 128.5 (d, J = 11.7 Hz), 130.6 (d, J = 9.3 Hz), 130.9 (d, J = 9.5 Hz), 131.5 (d, J = 2.6 Hz), 131.6 (d, J = 2.6 Hz), 133.0 (d, J = 100.1 Hz), and 133.9 (d, J = 99.7 Hz). ^{31}P NMR ($CDCl_3$): δ_P 29.5.

Horner-Emmons reaction of **3a**: A mixture of **3a** (ca. 0.1 mmol) and 8 equiv. of aromatic adehyde (**7**) in THF (5 ml) was treated with freshly prepared LiTMP (6 equiv.) at −96°C. After stirring for an additional 30 min at −96°C, the reaction was quenched with aq. NH_4Cl. The reaction mixture was chromatographed (PTLC or liquid chromatography) to afford **4a** and erythro- and threo-**8** and **9**. The olefin synthesis from **8** was carried out as reported previously.[7]

erythro-**8a**: mp 166.0–167.5°C. ^1H NMR ($CDCl_3$): δ 0.76–2.02 (m, 6 H, $OCHH'\ (C\underline{H}_2)_3$), 2.80–3.13 (m, 2 H, $PC\underline{H}-$, $OC\underline{H}H'$), 3.43–3.90 (m, 2 H, $C\underline{H}OCH\underline{H'}$), 4.97–5.14 (bs, 1 H, $O\underline{H}$), 5.22–5.38 (m, 1 H, $C\underline{H}PhOH$), 7.27 (s, 5 H, CPh), 7.37–7.39 (m, 6 H, m, p—H of PPh), and 7.83–8.11 (m, 4 H, o—H of PPh). ^{31}P NMR ($CDCl_3$): δ_P 36.6. HRMS (70 eV): Calcd for $C_{25}H_{27}O_3P$: 406.1697. Found: 406.1697.

Z-**10a**: viscous oil. ^1H NMR ($CDCl_3$): δ 1.32–1.95 (m, 6 H, $OCH_2(C\underline{H}_2)_3$), 3.31–3.66 (m, 1 H, $OC\underline{H}H'$), 3.90–4.34 (m, 2 H, $C\underline{H}OCH\underline{H'}$), 5.65 (dd, J = 11.4 Hz, J = 8.5 Hz, 1 H, $PhCH{=}C\underline{H}$), 6.55 (d, J = 11.4 Hz, 1 H, $PhC\underline{H}{=}CH$), and 7.30–7.31 (m, 5 H, Ph). HRMS (70 eV): Calcd for $C_{13}H_{16}O$: 188.1201. Found: 188.1205.

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