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# Tandem addition of nucleophilic and electrophilic reagents to vinyl phosphinates: the stereoselective formation of organophosphorus compounds with congested tertiary carbons†

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Carbon anions formed *via* the addition of Grignard reagents to  $S_P$ -vinyl phosphinates were modified with electrophilic reagents to afford organophosphorus compounds with diverse carbon skeletons. The electrophiles included acids, aldehydes, epoxy groups, chalcogens and alkyl halides. When alkyl halides were used, bis-alkylated products were afforded. Substitution reactions or polymerization occurred when the reaction was applied to vinyl phosphine oxides.

Organophosphorus compounds play important roles in the fields of medicine,<sup>1</sup> biology,<sup>2</sup> materials<sup>3</sup> and synthetic chemistry.<sup>4</sup> Because the performance of these compounds is highly dependent on their carbon skeleton, the construction of C-P bonds is of great significance in modern organic synthesis.<sup>5</sup>

Traditionally, C-P bonds were constructed using various phosphorus sources. For example, P-Cl species react with organometallic reagents to form C-P bonds.<sup>6</sup> Electrophilic organohalides and  $P^{III}$  species undergo rearrangements also affording C-P bonds (Michaelis-Arbusov reactions).<sup>7</sup> The alkylation of P-H bonds with various electrophilic species forms C-P bonds, and these reactions are promoted by bases (Michaelis-Becker reactions)<sup>8</sup> or transition metals.<sup>9</sup> The carbon skeletons of organophosphorus compounds can be diversified *via* these various modifications.<sup>10</sup>

The formation of C-C bonds is an important theme in organic synthesis. One such effective approach, nucleophilic addition to unsaturated C-C bonds (Michael addition), has been extensively studied and utilized.<sup>11</sup> Vinyl phosphorus can also be applied to this addition.<sup>10c-e</sup> However, apart from a few bifunctionalization or carbometallation reactions, the simultaneous or tandem formation of two C-C bonds by means of an addition has been quite limited (Chart 1).<sup>12</sup>

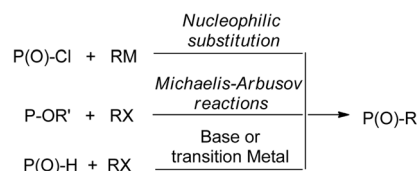
Herein, we present a novel method to construct C-C bonds where nucleophilic and electrophilic alkyl groups are introduced *via* a tandem process onto vinyl phosphorus. The electrophilic reagents include, but are not limited to, alkyl halides.

A carbon anion was proposed as an intermediate, and  $P,C$ -stereogenic phosphinates with congested tertiary carbons were obtained, in many cases in optically pure states.

The research began with  $S_P$ -menthyl phenylphosphinate ( $S_P$ -3), a compound with a vinyl link on a chiral phosphorus atom.  $S_P$ -3 was obtained from epimeric menthyl phosphinate 1 and acetophenone. Two of four possible diastereomers of 2 were obtained *via* recrystallization, which were converted to  $S_P$ -3a and  $S_P$ -3b *via* chlorination and elimination (Scheme 1).

When the reaction of  $S_P$ -3a with ethyl magnesium bromide 4b was quenched with acetic acid 5, two major signals at 40.0 and 38.6 ppm were observed in the  $^{31}P$  NMR spectrum, in a ratio of 38 : 62 (run 1 of Scheme 2). The two signals were assigned as the two diastereomers 6ba/6ba', respectively, as derived from the chiral  $\alpha$ -carbon.  $^1H$  NMR spectrum of isolated 6ba confirmed the structure. The menthoxy group of  $S_P$ -3a was not replaced by the Grignard reagent.<sup>13</sup>

## 1) Traditional formation of C-P bonds:



## 2) Formation of C-C bonds via Michael addition:



## 3) Our Current Work: Tandem bis-alkylation of vinyl phosphorus:

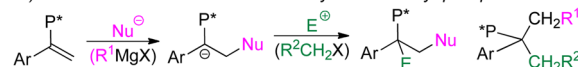
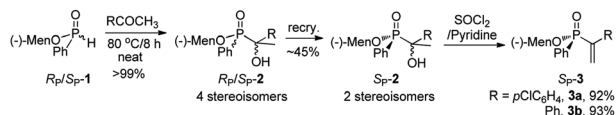
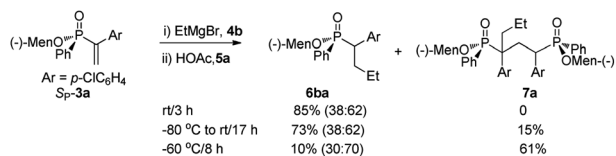


Chart 1 Comparison of reported reactions to our current work.

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Scheme 1 The preparation of optically pure  $S_P$ -3.Scheme 2 Examination of the addition of ethyl magnesium bromide to  $S_P$ -3a.

Addition of **4b** at  $-80\text{ }^\circ\text{C}$  did not improve the ratio of **6ba**/**6ba'**, and led to the observation of multiple signals in the range 43 to 39 ppm (run 2). The signals were ascribed to **7a** a species that has two indefinite chiral carbon atoms, and hence theoretically gives four diastereomers and eight P-signals (Scheme 2). The integration on the  $^1\text{H}$  NMR spectrum supported the structure of **7a**. When the reaction was carried out at  $-60\text{ }^\circ\text{C}$  for 8 hours, **7a** was detected as the major product (run 3).

The formation of **7a** demonstrated that  $\alpha$ -carbon anion **8** was generated as an intermediate (*vide infra*, Scheme 5), and was converted to **6ba** when quenched with **5a**. It was supposed that the addition of **4a** to  $S_P$ -3a became slow at low temperature, and unconsumed  $S_P$ -3a reacted with **8** to afford **7a** (run 3).

The formation of **6** and **7** inspired us to modify **8** with various electrophilic reagents (El), such as aldehydes, epoxy groups, and chalcogen compounds (Table 1). When paraformaldehyde (**5b**) was added to the mixture of  $S_P$ -3a and **4b**, hydroxyl-substituted **6bb** was obtained in a 95% yield and 56 : 44 dr (entry 2 of Table 1). Isolated **6bb**/**6bb'** (in 64 : 36 dr) resulted in a distinct  $^{31}\text{P}$  NMR spectrum whilst integration of the  $^1\text{H}$  NMR spectrum supported the structures of the two diastereomers. The existence of a stereogenic P-atom led to a complicated  $^{13}\text{C}$  NMR spectrum.

When racemic 2-methyloxirane (**5c**) was used, four diastereomers of **6bc** were generated, with an isolated P-signal at 46.0 ppm (entry 3). The diastereomeric ratio of **6** could be improved after isolation.<sup>14</sup> Sulfur could be introduced on the  $\alpha$ -carbon by means of dimethyl disulfide (**5d**) and diphenyl disulfide (**5e**), affording **6bd** and **6be**, respectively, in excellent yields (entries 4 and 5).

Secondary alkyl Grignard reagent **4c** was also added to  $S_P$ -3a. When quenched with **5a**, **6ca** was afforded in a 93% yield and 49 : 51 dr (entry 6). Alkylthio-substituted **6cd** and **6ce** were formed from **5d** or **5e**, respectively (entries 7 and 8). When phenyl magnesium bromide **4d** was used, the modifications with **5a**–**e** afforded **6da**–**de** (entries 9–13). The reaction with 2-methyl-oxirane afforded four diastereomers that were not separated.

The structures of  $S_{\alpha\text{-C}}$ -**6db** and  $S_{\alpha\text{-C}}$ -**6ca** were confirmed using X-ray diffraction (Fig. 1). Given that  $S_{\alpha\text{-C}}$ -**6ca** resulted in the

Table 1 The addition of Grignard reagents to  $S_P$ -3a and the subsequent modification of **8**

Entry	R	El, 5	Yield of 6% <sup>a</sup> (dr)	Isolated 6 yield % <sup>a</sup> (dr)
1	Et	HOAc	95 (38 : 62)	<b>6ba</b> , 33 (97 : 3) <sup>b</sup> <b>6ba'</b> , 37 (26 : 74) <sup>b</sup>
2		(CH <sub>2</sub> O) <sub>n</sub>	95 (56 : 44)	<b>6bb</b> , 55 (64 : 36)
3		2-Me-oxirane	87 (23 : 31 : 26 : 20)	<b>6bc</b> , 17 (>99 : 1) <sup>b</sup> <b>6bc'</b> , 46 (35 : 65)
4		Me <sub>2</sub> S <sub>2</sub>	89 (54 : 46)	<b>6bd</b> , 62 (48 : 52)
5		Ph <sub>2</sub> S <sub>2</sub>	75 (55 : 45)	<b>6be</b> , 56 (54 : 46)
6	<i>i</i> Pr	HOAc	93 (49 : 51)	<b>6ca</b> , 21 (56 : 44) <sup>b</sup>
7		Me <sub>2</sub> S <sub>2</sub>	73 (61 : 39)	<b>6cd</b> , 50 (48 : 52)
8		Ph <sub>2</sub> S <sub>2</sub>	75 (65 : 35)	<b>6ce</b> , 53 (71 : 29)
9	Ph	HOAc	88 (52 : 48)	<b>6da</b> , 38 (98 : 2) <sup>b</sup> <b>6da'</b> , 35 (20 : 80) <sup>b</sup>
10		(CH <sub>2</sub> O) <sub>n</sub>	89 (42 : 58)	<b>6db</b> , 70 (36 : 64)
11		2-Me-oxirane	95 (6 : 41 : 42 : 11)	<b>6dc</b> , 67 (5 : 81 : 5 : 9)
12		Me <sub>2</sub> S <sub>2</sub>	95 (81 : 19)	<b>6dd</b> , 68 (79 : 21)
13		Ph <sub>2</sub> S <sub>2</sub>	91 (73 : 27)	<b>6de</b> , 68 (75 : 25)

<sup>a</sup> Typical procedure: to a solution of  $S_P$ -3a (80 mg, 0.192 mmol) in THF (1 mL), was added the solution of Grignard reagent (384  $\mu\text{L}$ , 1 M in THF, 0.384 mmol). After stirring at room temperature for 30 min, El (1.5 eq. to  $S_P$ -3a) was added. The reaction was quenched with aqueous ammonium chloride after stirring at r.t. for 3 h. The yield and dr were estimated from the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, and dr was assigned as  $S_P$ -6/ $R_P$ -6'. <sup>b</sup> The stripe of the compounds in the preparative TLC gathered in a narrow range.

upfield signal in the  $^{31}\text{P}$  NMR spectrum (39.0 ppm), the signal located downfield (40.5 ppm) was assigned to  $R_{\alpha\text{-C}}$ -**6ca**. The structures of the two diastereomers of **6** were inferred based on that of **6ca**.

It was interesting that alkyl halides **9** could be used as the El to modify **8**, affording the 1,2-bisalkylated compounds **10**. After  $S_P$ -3a was mixed with **4b**, methyl iodide **9a** was added, and **10aba** was afforded in a 78% yield and 60 : 40 dr, as confirmed from the signals at 43.4 and 40.0 ppm in the  $^{31}\text{P}$  NMR spectrum (entry 2 of Table 2). The former diastereomer was isolated and confirmed using  $^1\text{H}$  NMR spectroscopy when methyl magnesium bromide **4a** was used and the mixture was treated with ethyl bromide **9b**, **10aab**, which has two  $\alpha$ -ethyl groups and a symmetric  $\alpha$ -carbon, was obtained as a single isomer (entry 1).

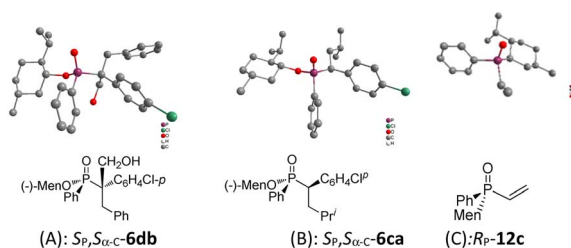
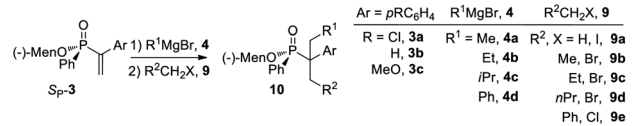
Fig. 1 The structures of X-ray diffraction. (A)  $S_P$ ,  $S_{\alpha\text{-C}}$ -**6db**; (B)  $S_P$ ,  $S_{\alpha\text{-C}}$ -**6ca**; (C)  $R_P$ -**12c**.

Table 2 The tandem addition of Grignard reagents and alkyl halides to *S<sub>P</sub>*-3

						
Entry	R on Ar	R <sup>1</sup>	R <sup>2</sup>	Yield of 10%	dr <sup>a</sup>	Isolated yield of 10% (dr)
1	Cl	Me	Me	63	NA	<b>10aab</b> , 50
2	Cl	Et	H	78	60 : 40	<b>10aba</b> , 58 (99 : 1)
3	Cl	Et	Me	77	56 : 44	<b>10abb</b> , 58 (>99 : 1) <sup>b</sup>
4	Cl	Et	Et	66	NA	<b>10abc</b> , 50
5	Cl	Et	<i>n</i> Pr	47	47 : 53	<b>10abd</b> , 35 (49 : 51)
6	Cl	<i>i</i> Pr	H	87	62 : 38	<b>10aca</b> , 13 (99 : 1) <sup>c</sup>
7	Cl	Ph	H	76	62 : 38	<b>10ada</b> , 60 (>99 : 1)
8	Cl	Ph	Me	57	72 : 28	<b>10adb</b> , 40 (84 : 16)
9	Cl	Ph	Ph	79	NA	<b>10ade</b> , 63 <sup>b</sup>
10	Cl	Ph	Ph	66	NA	<b>10ade</b> <sup>d</sup>
11	H	Me	Me	43	NA	<b>10bab</b> , 33
12	H	Et	H	48	58 : 42	<b>10bba</b> <sup>e</sup>
13	H	Et	Me	94	67 : 33	<b>10bbb</b> , 52 (59 : 41) 23 (88 : 12) <sup>c</sup>
14	H	Et	Et	77	NA	<b>10bbc</b> , 61
15	H	Ph	Ph	68	NA	<b>10bde</b> , 50
16	OMe	Et	H	77	>99 : 1	<b>10cba</b> , 58 (>99 : 1)
17	OMe	Et	Me	23	65 : 35	<b>10cbb</b> , 5 (96 : 4) <sup>c</sup> 13 (67 : 33) <sup>c</sup>
18	OMe	Et	<i>n</i> Pr	42	43 : 57	<b>10cbd</b> , 34 (40 : 60) <sup>c</sup>
19	OMe	Ph	Ph	90	NA	<b>10cde</b> , 80

<sup>a</sup> The yield and dr were estimated from the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, and the dr was determined from the ratio of the two diastereomers with at upfield and downfield signals in the <sup>31</sup>P-NMR spectrum. <sup>b</sup> Alkyl halide **9** and *S<sub>P</sub>*-3 were mixed, then the Grignard reagent was added. <sup>c</sup> The stripe of the compounds in the preparative TLC gathered in a narrow range. <sup>d</sup> PhMgBr was added at 0 °C to a solution of the starting material, then BnCl was added at room temperature. Entry 10 gave a similar result to entry 9 and could not be isolated. <sup>e</sup> The product could not be separated from **6** (direct acidification with acetic acid).

The reaction of *S<sub>P</sub>*-3a with **4b** and several primary alkyl halides (**9b** to **9d**) afforded **10abb** to **10abd** (entries 3 to 5). After isolation, one of the two diastereomers of **10abb** was obtained whilst **10abc** was formed as a single isomer.

The Nu-El pair of **4c/9a** and *S<sub>P</sub>*-3a afforded **10aca** in an 87% yield, and a single diastereomer was also obtained after isolation (entry 6). Phenyl Grignard **4d**, **9a–9b** similarly afforded **10ada–10adb**, respectively (entries 7 and 8). When benzyl chloride **9e** was used, **10ade** was obtained in a similar yield, irrespective of the order of addition (entries 9 and 10).

Similarly to *S<sub>P</sub>*-3a, *S<sub>P</sub>*-3b reacted with the Nu-El pair of **4a/9b**, affording **10bab** as a single isomer (entry 11). The pair of **4b/9a** gave crude **10bba** that contained a by-product of **6** (entry 12). The isolation of **10bbb** gave a different variation of two diastereomers (entry 13). **10bbc** and **10bde**, both with symmetric α-carbons, were smoothly obtained as single isomers (entries 14–15).

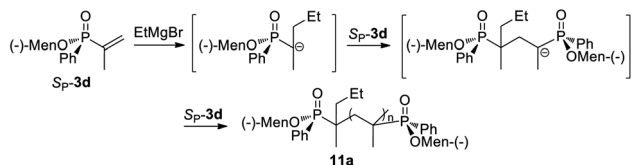
*p*-Methoxyl substituted *S<sub>P</sub>*-3c was obtained *via* chlorination of *S<sub>P</sub>*-2c and elimination with LiH/DMSO (refer to Scheme 1). It was interesting that *S<sub>P</sub>*-3c and the Nu-El pair of **4b/9a** afforded **10cba** in an excellent dr (entry 16). When **9b** and **9d** were used, both **10cbb** and **10cbd** were obtained in unsatisfactory yields (entries 17 and 18). α-Symmetric **10cde** was obtained in a good yield (entry 19).

*S<sub>P</sub>*-3d has a 2-propenyl group and was prepared *via* addition of *R<sub>P</sub>*-1 to acetone, followed by chlorination and elimination (refer to Scheme 1). When *S<sub>P</sub>*-3d was mixed with a Grignard reagent, multiple signals around 45.0 ppm were observed in the <sup>31</sup>P NMR spectrum, which were assigned as dimer **7** or polymer **11** (Scheme 3). The structure of **7** or **11a** was not confirmed. It was supposed that the smaller steric hindrance of the vinyl moiety led to further addition of the carbon anion to *S<sub>P</sub>*-3d, to afford the product with multiple signals at 45.0 ppm.

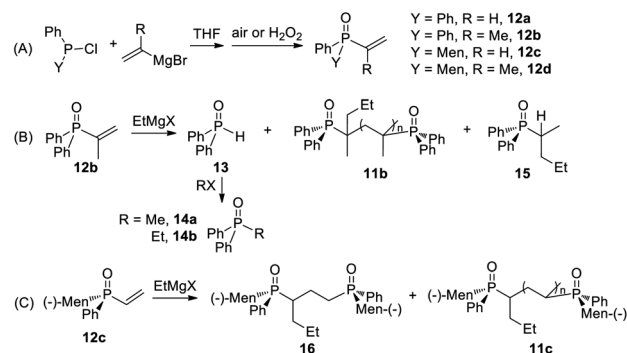
Vinyl phosphine oxide **12** was prepared from the reaction of phosphine chloride with a vinyl Grignard reagent (Scheme 4). Optically pure *R<sub>P</sub>*-12c was obtained *via* recrystallization, and its structure was confirmed using X-ray diffraction (Fig. 1). When **12b** was stirred with **4b** at room temperature, a signal at 21 ppm, accompanied with multiple peaks around 36–38 ppm, were observed in the <sup>31</sup>P NMR spectrum. The signal at 21 ppm was ascribed to diphenyl phosphine oxide **13**. After treatment with methyl iodide, **13** was converted to diphenyl methylphosphine oxide **14a**. The multiple peaks were assigned as polymerized **11b** (Scheme 3, part B of Scheme 4). The reaction of **12a** similarly formed **13** and **14**.

When **12b** was added to a mixture of **4b** and **9b**, the formation of **11b** was suppressed and **14b** was afforded as major

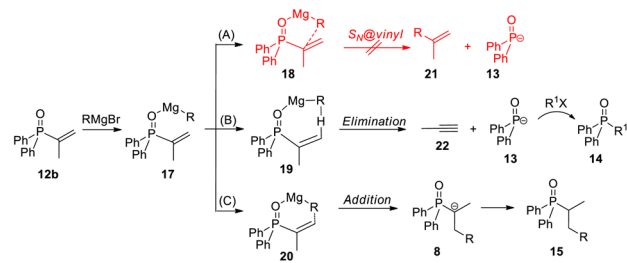




Scheme 3 The polymerization of 2-propenyl phosphinate  $S_P$ -3d with 4b.



Scheme 4 The preparation of **12** and their reactions with Grignard reagents/alkyl halides.



Scheme 5 Proposed reaction of vinyl phosphine oxide **12** with a Grignard reagent.

product. Meanwhile a small signal at 36 ppm was assigned as **15a**, whose molecular ion peak could be observed in the mass spectrum (*vide infra*).

The reaction of **12c** with **4b/9b** also gave multiple signals. After isolation, dimer **16** was obtained as a mixture of diastereomers (part C of Scheme 4). The reaction of **12d** with **4b** did not occur, even at elevated temperature.

The reactivity shown in Scheme 4 is proposed to proceed *via* the coordination of P=O to magnesium to form **17**, which is converted to carbon anion **8** or a P-anion (as **13**) (Scheme 5). When a *p*-tolyl Grignard reagent reacted with **12b**, the vinyl-H signals of **21** were not detected, which rules out the generation of **13** *via* route A. Simultaneously, a yellow alkynyl copper solid was obtained when the reaction mixture was treated with CuI/ammonia, the structure of which was confirmed from the alkynyl signal ( $2254\text{ cm}^{-1}$ ) in the infrared spectrum. The results indicated that the elimination of a  $\beta$ -proton afforded **22**, as well as **13** (route B). Alternatively, addition of a Nu to the  $\beta$ -carbon formed **20**, which was converted to **8** then to **15** (route C). The

molecular ion peak of **15b** ( $R = p\text{-tolyl}$ ) at 334.2 could be observed in the mass spectrum.

## Conclusions

In summary, the addition of Grignard reagents to the vinyl bonds of a series of  $S_P$ -menthyl phenylphosphinates (**3**) formed carbon anion intermediates (**8**), which were modified with various electrophilic reagents (El) to afford organophosphorus compounds with diverse carbon skeletons. In many cases, single stereoisomers were obtained. The El reagents (**5**) included acids, aldehydes, epoxy groups, and chalcogen compounds. When alkyl halide **9** was used as the El, bis-alkylated product **10** was obtained *via* a tandem addition process. Aliphatic and aromatic alkyl groups could be introduced as nucleophiles, whilst primary alkyl and benzyl groups were introduced as the El. For vinyl diphenylphosphine oxides, a replacement of the vinyl group occurred *via* base-promoted elimination. Vinyl menthyl phenylphosphine oxide tended to form polymerized products. This research provides a novel approach to construct organophosphorus compounds with diverse carbon skeletons, which it is hoped will have important applications in the fields of organophosphorus chemistry and asymmetric catalysis.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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