was redissolved in methanol, precipitated by addition of ether, and isolated by centrifugation. Air drying gave 77 mg (43%) of (-)-**5** as a white powder that retained traces of solvent but was >95% pure by ^1H NMR: mp 191-193 °C dec; $[\alpha]^{25}_D$ -220° (*c* 3.00, CH_3OH); IR (KBr) 3600-3000, 1685 cm^{-1}; ^1H NMR (methanol-d_4) δ 6.57 (1 H, dd, J = 4.8, 1.8 Hz, H_2), 5.21 (1 H, d, J = 1.3 Hz, $=CH_2$), 4.53 (1 H, d, J = 1.3 Hz, $=CH_2$), 4.37 (1 H, t, J = 4.6 Hz, H_3), 4.27 (1 H, dt, J = 9.4, 5.6 Hz, H_5), 3.80 (1 H, dd, J = 9.5, 4.3 Hz, H_4), 3.21 (1 H, dd, J = 18.1, 5.6 Hz, H_{6eq}), 2.12 (1 H, ddd, J = 18.1, 9.5, 1.8 Hz, H_{6ax}).

Acknowledgment. We are grateful to the National Institutes of Health, Grant GM 19103, for financial support.

Synthesis of Alkenes with *P*-(α-Lithioalkyl)phosphinothioic Amides

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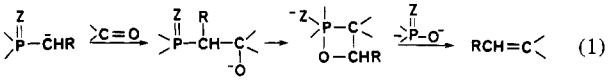
Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received February 12, 1982*

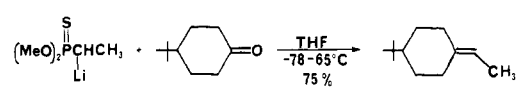
Abstract: *N,N,P*-Trimethyl-*P*-phenylphosphinothioic amide (**1**) was prepared from phenylphosphonothioic dichloride by sequential treatment with methylmagnesium halide, sulfuryl chloride, and dimethylamine. Treatment of **1** in tetrahydrofuran with butyllithium afforded *P*-(lithiomethyl)-*N,N*-dimethyl-*P*-phenylphosphinothioic amide (**2**). Aldehydes and ketones upon treatment with **2** provided stable β-hydroxy adducts, which upon treatment with methyl iodide and pyridine in acetone underwent smooth decomposition to yield alkenes. Alkylation of **2** provided higher homologues of **1** that were demonstrated to be useful in the production of tri- and tetrasubstituted alkenes. Pure (*E*)- and (*Z*)-alkenes were prepared by chromatographic separation of appropriate β-hydroxy adducts prior to treatment with methyl iodide and pyridine.

Relatively few reactions discovered in the last 30 years have had the impact on synthetic organic chemistry as has the Wittig reaction.[1,2] In many systems the reaction is problem free. In other cases difficulties can arise from threee sources—problems occur in separation of the triphenylphosphine oxide from the alkene, difficultly separable mixtures of (*E*)- and (*Z*)-alkenes are often formed, and low or neglible yields can result due to the moderate reactivity of phosphonium ylides. A number of phosphorus-stabilized carbanionic reagents also have been used in carbonyl alkylidenation reactions; the names of Horner, Wittig, Wadsworth, and Emmons are associated with these reactions.[2-4] The cycloelimination of alkenes from the oxyanion formed by addition of the carbanion to the carbonyl groups occurs readily in those cases where the alkene is conjugated to another π system (C=C, Ar, C=O, C=N, etc.). The elimination is presumed to occur via the intermediacy of a cyclic phosphorane (eq 1). In



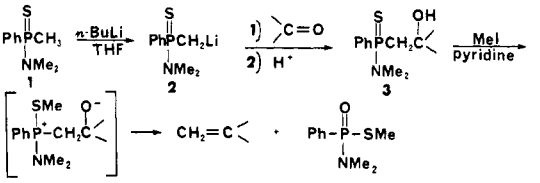
(1)

the P=O class of stabilized carbanions, the majority of the work has been done with phosphonates, most of which are readily available through Arbuzov reactions, but phosphine oxide carbanions have received some attention.[2] There are surprisingly few reports on the chemistry of P=S stabilized carbanions.[2] The most cogent study is that of Corey and Kwiatkowski who examined the production of alkenes from aldehydes and ketones and dimethyl (1-lithioalkyl)phosphonothionates (e.g., eq 2).[5]

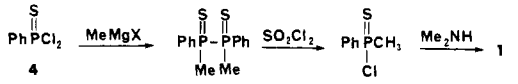


(2)

Scheme I



Scheme II



In this paper we describe a new phosphorus-based method for the alkylidenation of ketones and selected aldehydes that we believe will find considerable utility, especially in those cases that are inert or sluggish in their reactions with phosphonium ylides. Our method is outlined in Scheme I. The synthesis of the parent reagent, *N,N,P*-trimethyl-*P*-phenylphosphinothioic amide (**1**) (bp 110 °C (0.1 mm)),[5] is shown in Scheme II. The starting phenylphosphonothioic dichloride (**4**) is commercially available[6] and quite inexpensive.[7]

The choice of (dimethylamino)phenylphosphinothioyl carbanions as reagents was based on the premises that the carbanions would be considerably more nucleophilic than phosphonium ylides and that activation of the phosphorus centers toward nucleophilic additions of the oxyanions to form the necessary phosphoranes for cycloelimination of the alkenes could be achieved by facile alkylations of the initial adducts **3** at sulfur.[8,9]

(1) Maercker, A. *Org. React.* (*N.Y*) **1965**, *14*, 270.
(2) Cadogan, J. I. G., Ed. "Organophosphorus Reagents in Organic Synthesis"; Academic Press: New York, 1979.
(3) Wadsworth, W. S., Jr. *Org. React.* (*N.Y*) **1977**, *25*, 73.
(4) Sulfur- and silicon-based reagents have also proven to be of considerable utility in carbonyl alkylidenation reactions. For leading references for sulfur-based reagents, see: Johnson, C. R.; Kirchhoff, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 3602. For a recent review of silicon-based olefinations, see: Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London, 1981.
(5) Corey, E. J.; Kwiatowski, G. T. *J. Am. Chem. Soc.* **1966**, *88*, 5654.
(6) Aldrich Chemical Company, Inc. Milwaukee, Wi.
(7) The preparation of *P*-methyl-*P*-phenylphosphinothioic chloride by the method shown in Scheme II has been described. For example, see: Maier, L. *Chem. Ber.* **1961**, *94*, 3034, 3051. Schlor, H.; Schrader, G. German Patent 1 067 021, 1961; *Chem. Abstr.* **1962**, *56*, 10191f.
(8) The P=S functionality is well-known to undergo alkylation at sulfur; for a recent example, see: Omelanczulk, J.; Perkokowska, W.; Mikolajczyk, M. *J. Chem. Soc., Chem. Commun.* **1980**, 24.
(9) Electrophilic activation of a P=S group toward addition of a β-oxygen function has been achieved by Corey and Kwiatkowski (ref 5) using silver ion.

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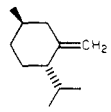
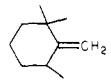
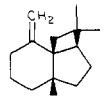
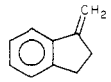
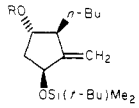
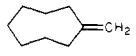
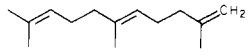
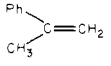
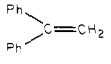
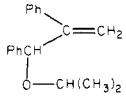
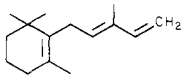
Table I. Methylenation of Ketones and Aldehydes with Reagent 1

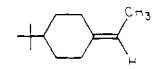
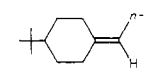
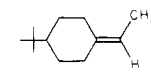
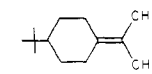
entry	product alkene	yield,[a] %	spectral characteristics
1		99	^{13}C NMR ($CDCl_3$) δ 151.1, 106.2, 49.5, 44.5, 34.1, 33.5, 27.5, 27.2, 22.2, 21.4, 19.0
2		50	^{13}C NMR ($CDCl_3$) δ 161.0, 102.2, 41.9, 37.6, 37.0, 33.5, 30.0, 26.7, 22.5, 19.3
3		59	^{13}C NMR ($CDCl_3$) δ 152.3, 108.4, 52.8, 52.7, 45.6. 41.1, 36.1, 35.7, 33.9, 30.6, 25.1, 24.8, 22.4, 18.3, 14.0
4		72	^{1}H NMR ($CDCl_3$) δ 6.9-7.5 (m, 4 H), 5.4 (s, 1 H), 4.98 (s, 1 H), 2.5-3.0 (b, 4 H)
5		~78[b]	^{13}C NMR ($CDCl_3$) δ 156.7, 143.1, 129.2, 127.9, 126.8, 126.1, 101.9, 74.3, 40.5, 29.6, 27.0, 25.9, 22.7, 18.3, 14.0, 0.97, −4.55, −4.68
6		80	
7		94	^{1}H NMR ($CDCl_3$) δ 5.0-5.4 (b, 2 H), 4.71 (s, 2 H), 1.8-2.2 (b, 8 H), 1.4-1.8 (b, 12 H)
8		77	*c*
9		96	*c*
10		99	^{13}C NMR ($CDCl_3$) δ 149.1, 141.3, 140.0, 128.1, 127.4, 115.1, 80.8, 69.4, 22.42, 22.16
11	$CH_3(CH_2)_8CH{=}CH_2$	13	^{1}H NMR (CCl_4) δ 5.4-6.0 (b, 1 H), 5.18 (d, 1 H, J = 4 Hz), 4.78 (d, 1 H, J = 9 Hz), 1.8-2.3 (b, 2 H), 0.6-1.6 (b, 19 H)
12		93	^{13}C NMR ($CDCl_3$) δ 141.8, 136.4, 134.4, 132.5, 128.1, 109.8, 40.0, 35.0, 33.0, 28.4, 27.7, 19.7, 11.7

[a] Isolated yields of alkenes based on carbonyl compound. [b] The R group in the starting ketone was $PhC(CH_3)_2$. The group was partially lost during reaction or workup. The alkene obtained was a mixture of R=H and R=$PhC(CH_3)_2$ (~3:2). [c] Spectral properties identical with those of authentic samples.

For methylenation of ketones with **1**, the following general procedure was utilized. Lithium reagent **2** was generated by the addition of 1 equiv of butyllithium to a solution of **1** in tetrahydrofuran (THF) cooled to −78 °C. One equivalent of ketone in THF was added to reagent **2**. The crude adduct was dissolved in acetone and 2 equiv of pyridine and 1.5 equiv of iodomethane were added. The mixture was stirred overnight, and the product was obtained by flash chromatography on silica gel using pentane as eluent. As can be seen in the summary of ketone methylenation reactions shown in Table I, the yields obtained by this method are exceptionally good.

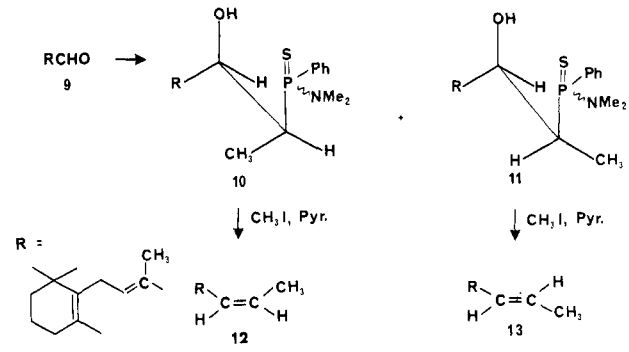
Lithium reagent **2** has been found to undergo smooth alkylation (>90% yields) with methyl iodide, *n*-butyl bromide, and benzyl bromide. Compound **8** was obtained by methylation of the lithium reagent derived from **5**. The results of straightforward alkylidenation reactions with compounds **5**–**8** in the manner described above for reagent **1** are given in Table II.

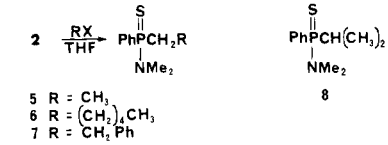
Table II. Production of Higher Substituted Alkenes

entry	reagent	alkene	yield, %	spectral characteristics
1	5		89	^{1}H NMR ($CDCl_3$) δ 5.17 (q, 1 H, J = 6 Hz), 1.6 (d, 3 H, J = 6 Hz), 0.86 (s, 9 H), 0.8-2.9 (b, 9 H); ^{13}C NMR ($CDCl_3$) δ 140.0, 114.7, 48.7, 37.0, 32.5, 29.2, 28.3, 27.7, 12.67
2	6		77	^{1}H NMR ($CDCl_3$) δ 5.07 (t, 1 H, J = 7 Hz), 0.87 (s, 9 H), 0.8-2.9 (b, 18 H); ^{13}C NMR ($CDCl_3$) δ 139.3, 121.2, 48.7, 37.2, 32.6, 29.4, 28.6, 27.7, 27.0, 22.4, 14.1
3	7		93	^{1}H NMR ($CDCl_3$) δ 7.24 (s, 5 H), 5.29 (t, 1 H, J = 7 Hz), 3.35 (d, 2 H, J = 7 Hz), 0.85 (s, 9 H), 0.8-3.0 (b, 9 H); ^{13}C NMR ($CDCl_3$) δ 142.0, 140.3, 128.4, 125.7, 119.6, 48.6, 37.1, 33.6, 32.5, 29.3, 28.6, 27.7
4	8		72	^{1}H NMR ($CDCl_3$) δ 1.7 (s, 9 H), 0.8-2.9 (b, 9 H); ^{13}C NMR ($CDCl_3$) δ 132.0, 119.9, 48.5, 32.5, 30.3, 28.7, 27.7, 20.0; IR (neat, NaCl) 2940, 1445, 1368, 1244, 1182, 1115, 983, 920 cm^{-1}
5	5	$CH_3(CH_2)_5CH{=}CH{\sim\sim}CH_3$ 3:2 trans:cis	53	^{13}H NMR ($CDCl_3$) δ 131.8,[a] 131.0, 124.6,[a] 123.6, 32.7, 31.8, 29.7, 29.0, 26.9, 22.8, 17.9, 14.2, 12.7

[a] Peak due to major isomer.

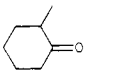
Scheme III





The addition of a racemic reagent such as **5** to a prochiral carbonyl substrate results in adducts with three asymmetric centers which are obtained as a mixture of four *d,l* diastereomers (e.g., Scheme III). The chromatographic retention of the diastereomers on silica gel is more sensitive to the relative configuration at the

Table III. Production of Diastereomerically Pure Alkenes Utilizing Reagent **5**

carbonyl compd	adducts 3, yield,[a] %	alkenes	yield,[b] %
8	33	**12**	92
	59	**13**	99
PhCHO	26	$PhCH{=}CHCH_3$, cis	78
	50	trans	97
	86		78[c]
	6		
			84[c]

[a] Yields of isolated adducts as pairs of *d,l* diastereomers (epimeric at phosphorus). [b] Yield based on adducts **3**. [c] Assignments based on ^{13}C NMR. The upper compound exhibited resonance for the vinyl methyl at δ 12.22 and ring methyl at 17.9. For the lower compound the two resonances appeared at 12.60 and 18.7. The ring methyl of 2-(methylmethylene)cyclohexane appears at 19.8 and the vinyl methyl of 4-(*tert*-butylethylidene)cyclohexane appears at 12.67.

two carbon centers than at phosphorus. For example, the two diastereomers represented by **10** (Scheme III) have retention times (silica gel HPLC, 10% EtOAc in hexane) of 3.4 and 3.5 min whereas the second pair of diastereomers **11** have retention times of 5.0 and 5.4 min. Preparative medium-pressure chromatography was effective for the separation of diastereomeric pair **10** from pair **11** with a combined recovery of 92% based on aldehyde **9**. Treatment of **10** with methyl iodide/pyridine resulted in pure *cis*-alkene **12** in 92% yield; similarly **11** gave the *trans*-alkene **13** in 99% yield. Other examples of the production of diastereomerically pure alkenes are given in Table III.[10]

The cycloelimination reaction is apparently quite sensitive to the nature of the alkene that is produced. As noted in the introductory remarks, alkylidenation of carbonyl compounds with phosphoryl-stabilized carbanions is most successful when the alkene is conjugated (as in the case of Horner–Wadsworth–Emmons reactions). Corey and Kwiatkowski note that "Although carbonyl adducts were easily obtained from aldehydes and the lithio derivatives of dimethyl methylphosphonothioate... these did not afford olefins under normal or even drastic conditions....". With our method we have found that simple monosubstituted alkenes are obtained in poor yield from aliphatic aldehydes (e.g., dodecanal to 1-tridecane, 13%), whereas aldehyde reactions that produce conjugated or higher-substituted alkenes proceed in higher yields (e.g., heptanal to 2-nonenes, 58%; benzaldehyde to 1-phenylpropenes, 71%). We have also noticed a considerable kinetic difference in the cycloelimination reactions of diastereomers leading to diastereomeric alkenes favoring more rapid formation of the more stable alkene. When a mixture of adducts of **5** and benzaldehyde was subjected to treatment with methyl iodide and pyridine for a shortened period of time, pure *trans*-1-phenylpropene (27%) was obtained.

In summary, we believe this new variant of Wittig chemistry offers considerable synthetic promise in overcoming the typical disadvantages often encountered in the use of phosphonium ylides. For example, treatment of the substrates utilized in entries 3[11] and 5[12] in Table I with methylenetriphenylphosphorane does not result in production of the desired exocyclic methylene compound.[11,12]

(10) The production of diastereomerically pure alkenes from purified β-hydroxy phosphonic amides (Corey, E. J.; Kwiatkowski, G. T. *J. Am. Chem. Soc.* **1966**, *88*, 5653) and β-hydroxy phosphine oxides (Earnshaw, C.; Wallis, C. J.; Warren, S. *J. Chem. Soc., Chem. Commun.* **1977**, 314. Clough, J. M.; Pattenden, G. *Tetrahedron* **1981**, *37*, 3911) has been achieved.

(11) McMurry, J. E; Choy, W. *Tetrahedron Lett.* **1980**, 2477. see also: Johnson, C. R.; Meanwell, N. A. *J. Am. Chem. Soc.* **1981**, *103*, 7667. We thank Dr. N. A. Meanwell of our laboratory for a gift of the ketone utilized in entry 3, Table I.

(12) G. L., Larson, personal communication. We thank Professor Larson for a gift of the ketone utilized in entry 5, Table I.

Experimental Section

Dimethyldiphenyldiphosphine Disulfide. Phenylphosphonothioic dichloride (475 g, 2.25 mol (Aldrich) dissolved in 300 mL of diethyl ether was added dropwise to a solution of methylmagnesium bromide (4.75 mol) in 2 L of diethyl ether cooled in a CCL_4/CO_2 bath. The addition rate was controlled such that the reaction temperature never rose above 5 °C. After the addition was complete the reaction mixture was allowed to warm to ambient temperature, refluxed for 30 min, and quenched with 3 N HCl. A white solid formed during the acid quench; this was filtered and dried to yield the meso biphosphine disulfide (251 g, 72%), mp 207–210 °C (lit.[13] mp 206–208 °C). The organic layer was separated, dried, and removed to yield the *d,l*-biphosphine disulfide (31.1 g, 9%), mp 145 °C (lit.[13] mp 145–146 °C).

Methylphenylphosphinothioic Chloride. A mixture of the above meso and *d,l* products (222.6 g, 0.717 mol) was suspended in 1.2 L of toluene in a 2-L round-bottomed flask and the mixture was placed in an ice bath. To this was added freshly distilled sulfuryl chloride (96.8 g, 0.717 mol) at such a rate that the reaction temperature never rose above 10 °C. After the addition was complete the reaction mixture was stirred at 23 °C for 1.5 h, then at 60 °C for 1 h. The reaction was filtered and the solvent removed to yield, after distillation, 231 g (85%) of a light yellow liquid, bp 93 °C (0.3 torr) (lit.[14] bp 106 °C (0.1 torr)); ^1H NMR ($CDCl_3$) δ 7.2–8.2 (m, 5 H); 2.43 (d, 3 H, J_{PH} = 13 Hz).

***N,N,P*-Trimethyl-*P*-phenylphosphinothioic Amide (1).** Methylphenylphosphinothioic chloride (36.8 g, 0.193 mol) was dissolved in 100 mL of THF and was cooled to 0 °C. From a jacketed addition funnel (dry ice/acetone) was added dropwise, over the course of 20 min, a solution of dimethylamine (16.6 mL, 0.25 mol) and triethylamine (39.07 g, 0.386 mol) in 100 mL of THF. The reaction was stirred with a mechanical stirrer. After the addition was complete, the reaction mixture was stirred for 12 h at room temperature and was then filtered to remove triethylamine hydrochloride. The filtrate was collected and extracted twice with water. The organic layer was dried over Na_2SO_4 and concentrated to yield, after distillation, a light yellow liquid (37.8 g, 98%): bp 110 °C (0.1 torr); ^{13}C NMR ($CDCl_3$) δ 136.45, 131.77, 131.05, 129.75, 128.91, 128.06, 37.04, 22.48 (d, J_{PC} = 76.2 Hz); ^{31}P NMR ($CDCl_3$) δ 70.72; IR (neat, NaCl) 2880, 1440, 1112, 962, 895, 750, 700 cm^{-1}; mass spectrum, *m/e* 199 (M^+). Anal. Calcd for $C_9H_{14}NPS$: C, 54.25; H, 7.08. Found: C, 54.47; H, 7.13.

***P*-Ethyl-*N,N*-dimethyl-*P*-phenylphosphinothioic Amide (5).** Compound **1** (11.96 g, 60 mmol) was dissolved in 400 mL of THF at −78 °C and butyllithium (60 mmol) in hexane was added. The mixture was stirred at −78 °C for 30 min prior to the addition of iodomethane (10.0 g, 70 mmol) dissolved in 20 mL of THF. The reaction mixture was stirred at −78 °C for 30 min and then at room temperature for 30 min. The reaction mixture was poured into water and shaken; the THF layer was washed with water and dried over Na_2SO_4. The solvent was removed to yield, after distillation, a clear liquid (12.17 g, 95% yield): bp 116 °C (0.05 torr); ^{13}C NMR ($CDCl_3$) δ 134.6, 132.1, 131.8, 131.4, 128.8, 128.1, 128.0, 37.2, 26.8 (d, J_{PC} = 73.2 Hz), 7.0 (d, J_{PC} = 2.9 Hz); ^{31}P NMR ($CDCl_3$) δ 79.84; IR (neat, NACl) 2920, 1110, 1055, 1035, 960 cm^{-1}. Anal. Calcd for $C_{10}H_{16}NPS$: C, 56.32;, H, 7.56. Found: C, 56.50; H, 7.68.

***N,N*-Dimethyl-*P*-phenylphosphionothioic Amide (6).** Compound **1** (2.01 g, 10.08 mmol) was dissolved in 80 mL of THF and cooled to −78 °C and butyllithium (10.08 mmol) in hexane was added. The mixture was stirred for 30 min at −78 °C prior to the addition of 1-bromobutane (1.51 g, 11 mmol) dissolved in 5 mL of THF. The mixture was stirred at −78 °C for 1 h and then at room temperature for 1 h. After workup and distillation, a clear liquid was obtained (2.32 g, 90% yield): bp 137 °C (0.05 torr); ^1H NMR ($CDCl_3$) δ 7.3–8.0 (m, 5 H), 2.5 (d, 6 H, J_{PH} = 14 Hz), 2.2 (m, 2 H), 1.3 (br s, 6 H), 0.8 (br s 3 H). Anal. Calcd for $C_{13}H_{22}NPS$: C, 61.15; H, 8.68. Found: C, 61.31; H, 8.77.

***N,N*-Dimethyl-*P*-phenyl-*P*-(2-phenylethyl)phosphinothioic amide (7),** prepared from **1** and benzyl bromide with the method described above for **6**, was obtained as a clear liquid (2.65 g, 90% yield): bp 186 °C (0.05 torr); ^1H NMR ($CDCl_3$) δ 7.4–8.2 (m, 5 H), 7.2 (br s, 5 H), 2.6 (d, 6 H, J_{PC} =14 Hz), 2.0–3.1 (m, 4 H). Anal. Calcd. fr $C_{16}H_{20}NPS$: C, 66.41, H, 6.97. Found: C, 66.18; H, 7.11.

***P*-Isopropyl-*N,N*-dimethyl-*P*-phenylphosphinothioic Amide (8).** Compound **5** (1.84 g, 8.6 mmol) was dissolved in 45 mL of THF and cooled to −78 °C. Butyllithium (8.6 mmol) in hexane was added and the mixture was stirred at −78 °C for 30 min prior to the addition of iodomethane (0.84 mL, 9.0 mmol). This mixture was stirred at −78 °C for 30 min and then at room temperature for 1 h. The reaction mixture was poured into water and diethyl ether and shaken, the organic layer was

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dried over $NaSO_4$, and the solvent was removed to yield, after distillation, a clear liquid (1.87 g, 95% yield): bp 111 °C (0.05 torr); ^1H NMR ($CDCl_3$) δ 7.3–8.2 (m, 5 H), 2.42 (d, 6 H, J_{PH} = 13 Hz), 2.4 (m, 1 H, 1.0 (ddd, 6 H, J_{PH} = 20, 6, 3 Hz); ^{13}C NMR ($CDCl_3$) δ 132.9, 132.4, 131.6, 128.6, 127.8, 126.4, 37.4, 30.3 (d, J_{PC} = 70.3 Hz), 16.6 (d, J_{PC} = 7.8 Hz); IR (neat, NaCl) 2930, 1440, 1107, 960, 885, 752, 725 cm^{-1}. Anal. Calcd. for $C_{11}H_{18}NPS$: C, 58.12; H, 7.98. Found: C, 58.06; H, 8.13.

General Procedure for the Production of Alkenes. The *P*-alkyl-*N*,*N*-dimethyl-*P*-phenylphosphinothioic amide (3.00 mmol), dissolved in 30 mL of THF and cooled to −78 °C, was reacted with butyllithium (3.00 mmol) in hexane. The mixture was stirred at −78 °C for 30 min prior to the addition of the carbonyl compound (3.00 mmol) dissolved in 2 mL of THF. This mixture was stirred at −78 °C for 2 h and then allowed to warm to 0 °C at which point the reaction was quenched with saturated aqueous NH_4Cl. The mixture was poured into diethyl ether and water in a separatory funnel and shaken. The organic layer was dried over Na_2SO_4 then the solvent was removed to yield the carbonyl adduct. With no further purification, the adduct was dissolved in a sufficient amount of acetone to give a 0.2 M solution, and the pyridine (2.0 equiv) and iodomethane (1.5 equiv) were added. The reaction mixture was allowed to stir at room temperature for 16 h and then was filtered. The filtrate was collected and concentrated to yield the crude alkene which was placed on a small flash column. The alkene was eluted with pentane, then the pentane was removed to yield the product. The weight of the alkene obtained was used to determine the overall yield of the transformation.

***cis*- and *trans*-1-Phenylpropene.** Compound **5** (1.263 g, 5.92 mmol) was dissolved in 60 mL of THF and cooled to −78 °Cl. Butyllithium (5.92 mmol) in hexane was added, and the mixture was stirred for 30 min at −78 °C prior to the addition of benzaldehyde (0.628 g, 5.92 mmol). After stirring the mixture at −78 °C for 2 h, the reaction was quenched at −78 °C with saturated aqueous NH_4Cl. The mixture was poured into a diethyl ether/water mixture and shaken, and the organic layer was dried over Na_2SO_4 and then concentrated to yield a viscous liquid. By HPLC (9:1 hexane/EtOAc) five compounds could be seen with retention times of 5.5 min (compound **5**, 14%) and (adducts) at 5.8 (31%), 6.0 (14%), 8.4 (35%), and 9.2 min (6%). The reaction mixture was placed on a large MPLC column (20:1 hexane/EtOAc), the compounds eluting at times 5.5, 5.8, and 6.0 min were collected as one fraction (0.750 g, ca. 65 mol % adduct) (fraction one), and the compounds eluting at 8.4 and 9.2 min were collected as a second fraction (0.937 g) (fraction two).

Fraction one was calculated to contain 1.76 mmol (30%) of the aldehyde adducts. The entire fraction was dissolved in 15 mL of acetone, and to this was added iodomethane (0.31 mL, 3.39 mmol) and pyridine (0.37 mL, 4.51 mmol). The mixture was stirred at room temperature for 18 h. At this point the reaction mixture was examined by TLC and the starting adduct could still be seen; additional iodomethane (0.3 mL, 3.39 mmol) and pyridine (0.37 mL, 4.51 mmol) were added to the reaction mixture and the reaction temperature was brought to 65 °C for 32 h. The reaction mixture was then filtered, and the filtrate was reduced to yield a yellow liquid which was placed on a small flash column and was developed with pentane to yield, after removal of the solvent, a clear liquid (0.162 g, 78%) that was identified as *cis*-1-phenylpropene. This was spectroscopically identical with that reported;[15] ^{13}C NMR ($CDCl_3$) δ 137.7, 130.0, 128.9, 128.1, 126.8, 126.4, 14.6.

Fraction two, (0.937 g, 2.93 mmol, 50%), was dissolved in 20 mL of acetone, and to this was added iodomethane (0.39 mL, 4.15 mmol) and pyridine (0.45 mL, 5.54 mmol), the mixture was stirred at room temperature for 8 h and then filtered, and the filtrate was concentrated to yield a yellow liquid which was placed on a small flash column and chromatogra phed (hexane) to yield, after removal of the solvent, a clear liquid (0.337 g, 97% yield) that had spectroscopic properties identical with those reported for *trans*-1-phenylpropene;[15] ^{13}C NMR ($CDCl_3$) δ 138.1, 131.2, 128.5, 126.8, 125.9, 125.3, 18.29.

Reaction of 5 with (2*E*)-4-(2,6,6-Trimethyl-1-cyclohexenyl)-2-methyl-2-butenal. Compound **5** (1.268 g, 5.95 mmol), dissoved in 60 mL of THF and cooled to −78 °C, was treated with butyllithium (5.95 mmol). After 30 min, the aldehyde (1.227 g, 5.95 mmol) dissolved in 5 mL of THF was added; the mixture was stirred and maintained at −78 °C for 2 h and then warmed to 0 °C. The reaction was quenched with saturated aqueous NH_4Cl, and the reaction mixture was poured into diethyl ether and water and shaken. The organic layer was dried over Na_2SO_4 and concentrated to yield a clear liquid. By HPLC (9:1 hexane/EtOAc) four products could be detected with retention times of 3.4 min (20%), 3.5 min (22%), 5.0 min (48%), and 5.4 min (10%). This mixture was placed on a large MPLC column (20:1 hexane/EtOAc) and the adducts corresponding to those at 3.4 and 3.5 min, by HPLC, were collected as one fraction (0.815 g, 33%). The remaining adducts were collected as a second fraction (1.467 g, 59%). The combined diastereomers from the first fraction (0.543 g, 1.29 mmol), iodomethane (0.18 mL, 1.9 mmol), and pyridine (0.21 mL, 1.26 mmol) were dissolved in 10 mL of acetone, and the mixture was stirred at room temperature for 18 h. Progress of the reaction was monitored by TLC. After 18 h, the starting adduct could still be seen, so additional quantities of iodomethane (0.18 mL, 1.94 mmol) and pyridine (0.21 mL, 2.6 mmol) were added and the reaction mixture was warmed and maintained at 65 °C for 28 h. The reaction mixture was filtered and the volume of the filtrate reduced, this was placed on a small flash column and the alkene was eluted with pentane to yield, after removal of the solvent, a clear liquid identified as (2*Z*,4*E*)-6-(2,6,6-trimethyl-1-cyclohexenyl)-4-methyl-2,4-hexadiene (0.260 g, 61%): ^{13}C NMR ($CDCl_3$) δ 136.6, 133.9, 131.8, 130.9, 127.8, 122.9, 39.8, 35.0, 32.9, 28.3, 27.4, 19.6, 16.8, 14.6; IR (neat, NaCl) 2930, 1362, 1116, 1034, 863, 711 cm^{-1}. The second fraction of collected diastereomers (1.384 g, 3.30 mmol), iodomethane (0.46 mL, 5.0 mmol), and pyridine (0.53 mL, 6.6 mmol) was dissolved in 20 mL of acetone and stirred at room temperature for 5 h. The alkene, isolated as above, was identified as (2*E*,4*E*)-6-(2,6,6-trimethyl-1-clcylohexenyl)-4-methyl-2,4-hexadiene, (0.713 g, 99% yield): ^{13}C NMR ($CDCl_3$) δ 136.6, 136.4, 132.0, 131.4, 127.9, 121.2, 40.0, 35.0, 33.0, 28.4, 27.6, 19.8, 18.2, 12.5; IR (neat, NaCl) 2930, 1450, 1384, 1362, 1115, 968 (strong), 767 cm^{-1}.

Reaction of 5 with 2-Methylcyclohexanone. Compound **5** (1.277 g, 5.99 mmol) was dissolved in 60 mL of THF and the solution was cooled to −78 °C. Butyllithium (5.99 mmol) was added and the mixture was stirred for 30 min prior to the addition of 2-methylcyclohexanone (0.672 g, 5.99 mmol). After stirring at −78 °C for 2 h, the reaction mixture was warmed to 0 °C and saturated aqueous NH_4C was added. The mixture was poured into diethyl ether/water and shaken, and the organic layer was dried over Na_2SO_4 and then concentrated to yield a clear liquid. HPLC indicated three products [3.4 min (90%), 8.4 min (7%), 9.0 min (3%)]. The product mixture was placed on a large MPLC column (20:1 hexane/EtOAc) and the major adduct was collected as fraction one (1.554 g, 80%)). The two minor adducts were collected as fraction two (0.127 g, 7%).

The major adduct (1.466 g, 4.50 mmol), iodomethane (0.63 mL, 6.8 mmol), and pyridine (0.73 mL, 9.0 mmol) were dissolved in 22 mL of acetone and stirred at room temperature for 24 h. The reaction mixture was then filtered and the filtrate concentrated to yield a yellow liquid. This was placed on a small flask column and developed with pentane to yield a clear liquid that was assigned the structure (*E*)-2-(methylethylidene)cyclohexane (0.438 g, 78%) on the basis of the upfield shift of the ^{13}C methyl resonances: ^{13}C NMR ($CDCl_3$) δ 144.2, 112.5, 38.5, 36.8, 28.0, 27.8, 25.7, 18.7, 12.6; IR (neat, NaCl) 2930, 1448, 990, 893, 805, 733 cm^{-1}.

The second fraction, containing the minor diastereomers, (0.106 g, 0.326 mmol), iodomethane (0.05 mL, 0.5 mmol), and the pyridine (0.05 mL, 0.65 mmol), was dissolved in 2 mL of acetone, and the mixture was stirred at room temperature for 24 h and then at 65 °C for 2 h. The alkene, isolated as above, was a clear liquid that was assigned the structure (*Z*)-2-(methylethylidene)cyclohexane (0.034 g, 84% yield); ^{13}C NMR ($CDCl_3$) δ 143.8, 115.1, 33.1, 32.4, 29.7, 28.5, 21.1, 17.9, 12.2.

Kinetically Controlled Production of *trans*-1-Phenylpropene. Compound **5** (1.230 g, 5.77 mmol) was added to benzaldehyde (0.612 g, 5.77 mmol) as described in the previous experiment. The crude mixture of adducts was dissolved in 30 mL of acetone, and to this was added iodomethane (0.31 mL, 3.3 mmol) and pyridine (0.36 mL, 4.5 mmol). This mixture was stirred at room temperature for 5.5 h. The reaction mixture was then filtered, and the filtrate was reduced to yield a yellow liquid which was placed on a small flash column. The column was developed with pentane to yield, after removal of the solvent, a clear liquid that by ^1H NMR and ^{13}C NMR was identified as pure *trans*-1-phenylpropene (0.183 g, 27% yield).

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