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A Facile Route to Vinyl- and Arylphosphonates by Vinyl and Aryl Radical Trapping with $(MeO)_3P$

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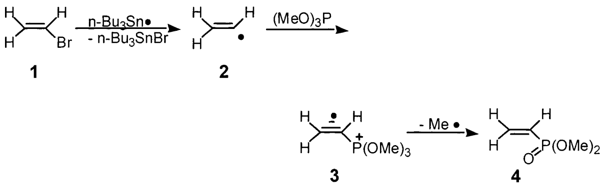
Abstract: The generation of vinyl or aryl radicals under classical, thermal AIBN/*n*-Bu_3SnH conditions at 80 °C in the presence of an excess of $(MeO)_3P$ gives rise to the corresponding vinyl- or arylphosphonates in good yields. This approach complements the photochemical reactions of the same systems previously used. Reactions with the individual stereoisomers of MeCH═CHMeBr (thermal AIBN/*n*-Bu_3SnH conditions) afford a *radical-equilibrated* 96/4 *E*/*Z* ratio of vinylphosphonates. Substitution of $(TMS)_3SiH$ for *n*-Bu_3SnH yields an approximately 1/1 ratio of *separable E and Z* vinylphosphonate diastereomers.

The synthesis and applications of vinyl- and arylphosphonates have attracted a large amount of interest in recent years.[1−5] This is based on the synthetic value of vinylphosphonates[1] as well as the applications of phosphonates as biologically active materials.[6] For example, palladium-catalyzed coupling of nucleoside-based phosphites, ROP(O)HOR′, with vinyl bromides derived from nucleosides affords vinylphosphonate dinucleotides,[3a] and palladium-catalyzed cross-coupling reactions provide a variety of vinylphosphonates.[3b] Platinum-catalyzed hydrophosphinylation of alkynes gives rise to alkenylphosphinates with retention of configuration at phosphorus.[5] Recently, an intermolecular olefin cross-metathesis, using a 1,3-dimesityl-4,5-dihydroimidazol-2-ylideneruthenium alkylidene complex as catalyst, has been successfully employed in the preparation of the vinylphosphonates.[4a] Aryl radicals from the photolysis of aryl halide precursors react with trialkyl phosphites, $(RO)_3P$, to give dialkyl arylphosphonates in high yields.[7] Likewise, UV irradiations of vinyl halides in the presence of trialkyl phosphites afford dialkyl vinylphosphonates.[8]

Recently, we reported that vinyl radicals, formed by the well-known 5-*exo-dig*-cyclization of 5-hexynyl and 3-oxa-5-hexynyl radicals, are trapped by trimethyl phosphite to give dimethyl vinylphosphonates.[4b] A further potential approach to both vinyl- and arylphosphonates is the generation of vinyl and aryl radicals directly from their corresponding vinyl (**1**, eq 2) or aryl halide (eq 3) precursors under standard thermal AIBN/*n*-Bu_3SnH conditions[9] in the presence of excess trimethyl phosphite (eq 1). We report here the usefulness of such reactions to give vinyl- and arylphosphonates in 70−84% isolated yields. We also examined the stereoselectivity with which vinylphosphonates are formed when more than one diastereomer can potentially be generated. Use of $((CH_3)_3Si)_3SiH$ [$(TMS)_3SiH$] rather than *n*-Bu_3SnH allows near-equal amounts of the *separable* individual diasteomers of the product phosphonates to be formed.

The presumed free-radical chain mechanism for these reactions is depicted in eq 1. Vinyl radical **2** is trapped by reaction with trimethyl phosphite. Vinyl (**3**)- and aryl phosphoranyl radicals, formed on oxidative addition of vinyl radicals to phosphites, have been characterized by ESR as π radicals with the odd electron in a Π^* MO orbital centered on the alkene moiety. β scission of radical **3** affords vinylphosphonate **4** and methyl radical. The latter reacts with *n*-Bu_3SnH to regenerate the chain carrying species *n*-$Bu_3Sn\cdot$. In this approach, the possible reduction of intermediate vinyl and aryl radicals by *n*-Bu_3SnH or, alternatively, the sterically hindered silane $(TMS)_3SiH$ must be minimized. We therefore utilized slow syringe pump addition of a benzene solution of the stannane or silane and AIBN to a large excess amount of trimethyl phosphite and the requisite bromide dissolved in benzene and heated at reflux.



(1)

In Table 1 are displayed the results of reaction of a series of vinyl bromides (eq 2). It can be seen that the

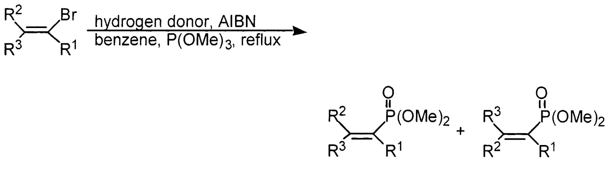


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TABLE 1. Vinylphosphonates from Vinyl Bromides

entry	R^1	R^2	R^3	hydrogen donor	yield[a] (%)	*E*/*Z* ratio[b]
1	CH_3	H	CH_3	Bu_3SnH	83	94/6
2	CH_3	CH_3	H	Bu_3SnH	79	94/6
3	CH_3	H	CH_3	$(TMS)_3SiH$	70	70/30
4	CH_3	CH_3	H	$(TMS)_3SiH$	70	70/30
5	H	CH_3	CH_3	Bu_3SnH	81	
6	H	CH_3	CH_3	$(TMS)_3SiH$	84	
7	H	$Ph(CH_2)_2$	$Ph(CH_2)_2$	Bu_3SnH	81	
8	H	H	Ph	Bu_3SnH	0	
9	Ph	H	H	Bu_3SnH	0	
10	H	4-*tert*-butylcyclohexenyl		Bu_3SnH	83	

[a] Isolated yield. [b] Determined by GC from crude product mixture.

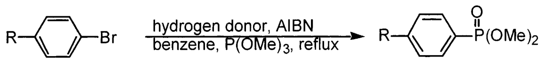
TABLE 2. Preparation of Dimethyl Arylphosphonates[a]

entry	R	hydrogen donor	yield[b] (%)	ref
1	CH_3O	*n*-Bu_3SnH	87	*d*
2[c]	CH_3O	$(TMS)_3SiH$ (*hν* 300)	93	*d*
3	CH_3O	$(TMS)_3SiH$	61	*d*
4[g]	CH_3O	$(TMS)_3SiH$ (toluene)	90	*d*
5	CH_3	*n*-Bu_3SnH	87	*e*
6	H	*n*-Bu_3SnH	91	*f*
7	Cl	*n*-Bu_3SnH	85	*d*
8	CF_3	*n*-Bu_3SnH	65	

[a] At benzene reflux, ca. 80 °C. [b] Isolated material. [c] Under photochemical conditions (300 nm) at room temperature. [d] Phosphonate previously reported.[4] [e] Phosphonate previously reported.[5] [f] Phosphonate previously reported.[6] [g] At toluene reflux.

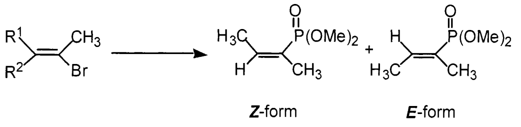
position of substituent R^1, R^2, or R^3 has little effect on the phosphonate yields. However, when R^1 or R^3 is a phenyl group (entries 8 and 9), *no phosphonate* is found even when neat trimethyl phosphite is used as solvent. In these reactions polymer is formed. Presumably, the styryl-type vinyl radical intermediate, or some other radical species, initiates the rapid polymerization of the bromostyrenes which will be much more prone to such a reaction than alkenes with only alkyl substituents on the double bond. The product phosphonates also may be readily polymerized, although there was no GC evidence for a transient formation of phosphonate early on. The implications of the stereochemistry observed (entries 1−4) will be discussed later.

Aryl radicals, generated photochemically from halides or thermally from the less readily available arylazotriphenylmethanes, have been seen to react readily with trialkyl phosphites to generate dialkyl arylphosphonates.[7] Alternatively, aryl radicals, which like vinyl radicals are F species (sp^2 hybridized),[10] can be generated easily from aryl bromide precursors under standard thermal AIBN/*n*-Bu_3SnH conditions. As seen in Table 2, their trapping by trimethyl phosphite gives dimethyl arylphosphonates in good to excellent yields (eq 3). Use of tris(trimethylsilyl) silane, (TMS)SiH, in the thermal-AIBN approach appears to be more effective at the higher temperature (toluene at reflux, ca. 110 °C).[11] Interestingly, with UV initiation the AIBN/$(TMS)_3SiH$ system works well at room temperature (entry 2). The yields in Table 2 are comparable to those seen in the photochemical generation of arylphosphonates reported earlier.[7]



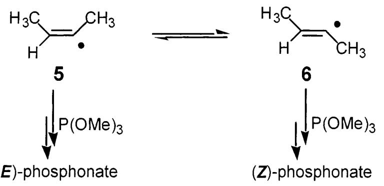
(3)

The stereochemistries of the reactions of the individual 2-bromobutene diastereomers with trimethyl phosphite (eq 4) are revealed in Table 1 under thermal *n*-Bu_3SnH/AIBN conditions. The same mixture of 96% *E* and 4% *Z* dimethyl 1-methyl-1-propenylphosphonate, determined by GC analysis of the reaction product mixture, was obtained *after 6 h of reaction* in about 80% *isolated* yield from the reaction of either the (*E*)- or (*Z*)-2-bromo-2-butene with *n*-Bu_3SnH as the hydrogen atom transfer agent (eq 4). Under the same conditions, but with $(TMS)_3SiH$ in place of *n*-Bu_3SnH, Table 3 shows that a 70/30 *E*/*Z* ratio of the same phosphonates is formed in about 70% isolated yield over the same reaction time period. The individual phosphonate diastereomers were readily separated by flash column chromatography. This suggests that *use of $(TMS)_3SiH$ at short reaction times (Table 3) will allow them to be readily prepared in this way.*



(4)

A possible explanation for the loss of phosphonate stereochemistry is that the 2-butenyl vinyl radical (**5** and **6**, eq 5) is isomerized much more rapidly than it reacts with $(MeO)_3P$. Under such a Curtin−Hammett-governed control of product formation, the *E*/*Z* ratio would be the same from either bromide diastereomer.



(5)

An alternative rationale is that regardless of the *initial* *E*/*Z* ratio of phosphonates formed, the reversible addition of tri-*n*-butyltin radicals to the product phosphonates catalyses their cis−trans (*E*−*Z*) equilibration. Over the 6-h time period of the reaction, the 96/4 *equilibrium* mixtures (*E*/*Z*) encountered (Table 1) are slowly formed. The results of Table 3 are consistent with this view. Thus, an initially observed phosphonate *E*/*Z* ratio of 81/19 from the *E* bromide (0.5 h) is slowly changed to 94/6 in 6 h. The same is seen for the initial *E*/*Z* phosphonate ratio of 76/24 from the *Z* bromide. The diastereomers observed at 0.5 h quite possibly have already undergone partial *E*−*Z* equilibration.

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TABLE 3. Stereochemistry of Phosphonate Formation

R^1	R^2	H[a] donor	E/Z[b] (m/int)[c] 0.5 h	E/Z (m/int) 1 h	E/Z (m/int) 2 h	E/Z (m/int) 3 h	E/Z (m/int) 4 h	E/Z (m/int) 6 h
CH_3	H	A	81/19	78/22	83/17 (21/79)	87/13 (22/78)	91/9 (23/77)	96/4 (23/77)
H	CH_3	A	76/24	77/23	94/6 (17/83)	96/4 (20/80)	96/4 (22/78)	96/4 (23/77)
CH_3	H	B	51/49	59/41	65/35 (11/89)	67/33 (14/86)	67/33 (16/84)	70/30 (22/78)
H	CH_3	B			64/36 (12/88)	66/34 (14/86)		70/30 (22/78)

[a] A = Bu_3SnH, B = $(Me_3Si)_3SiH$. [b] Determined by GC from crude product mixture. [c] m = mixture of E and Z of the products; int = internal standard. The ratio m/int was obtained on the reaction mixture before purification.

Use of an internal standard allowed the *total* area of the E and Z diastereomers to be compared to the area of internal standard over the time of the reaction before purification. The near-constancy of the m/int values of Table 3 obtained shows that the changes in E/Z during the 6-h reaction period are not the result of the selective consumption of one of the phosphonate diastereomers.

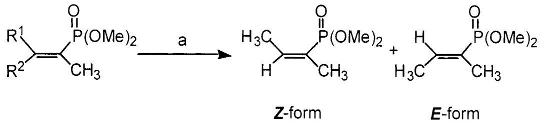
As noted earlier, the sterically hindered hydrogen atom transfer agent $(Me_3Si)_3SiH$ also was employed (Tables 1 and 3) in molar concentrations the same as those of n-Bu_3SnH in the previous reactions. The initially observed E/Z ratio (0.5, 2, 3 h) is now closer to 50/50. Significantly, the product phosphonates undergo relatively *slow equilibration* that does not proceed in 6 h beyond a 70/30 E/Z ratio. Obviously, the sterically hindered radical $(Me_3Si)_3Si^\bullet$ is much less readily added to the double bond of product phosphonate than is n-$Bu_3Sn^\bullet$ so that full equilibration has not yet occurred in 6 h. The ratio 51/49 from the E bromide after 0.5 h reaction may be close to the initial kinetic product ratio, perhaps formed under Curtin–Hammett conditions. (The equilibration of **5** with **6** for the example **2** occurs very rapidly: $k = 4 \times 10^{10}\ s^{-1}$; $E_a = 3$ kcal/mol.[16]) The close to 50/50 E/Z ratio of phosphonates from the E-bromide (eq 4, Table 3) suggests that the transition states for formation of the E and Z phosphoranyl radicals are nearly equal in energy. This is consistent with a C–P distance in the transition state for the predictably very rapid and *exothermic* formation[17] of the phosphoranyl radical (see eq 1) that is relatively great, thus minimizing steric interactions.

Furthermore, subjection of either of the pure phosphonate diastereomers, E or Z, of Table 3 to the thermal AIBN/n-Bu_3SnH conditions of the reaction for their preparation brought about (Table 4) their equilibration (eq 6) to a 96/4 E/Z ratio (GC). As in Table 3, the m/int ratio was unchanged throughout the 6-h control period. Consistent with the above findings on the stereochemistry of phosphonate formation are the cis–trans equilibrations we demonstrated previously for the diastereomeric five-membered ring vinylphosphonates formed by the cyclization/phosphite trapping route (thermal AIBN/n-Bu_3SnH conditions).[4]

TABLE 4. Radical Equilibration of Phosphonate Diastereomers

R^1	R^2	hydrogen donor	E/Z[a] (m/int)[b] 0 h	E/Z 2 h	E/Z 4 h	E/Z 6 h
CH_3	H	Bu_3SnH	0/100 (51/49)[c]	95/5	96/4	96/4
H	CH_3	Bu_3SnH	100/0 (24/76)[d]	94/6	96/4	96/4

[a] Determined by GC from crude product mixture. [b] m = mixture of E and Z of the products, int = internal standard, ratio of m/int was obtained by GC from the crude reaction mixture. [c] The m/int ratio averaged 51 ± 0.5/49 ± 0.5 during equilibration (2–8 h). [d] The m/int ratio averaged 24 ± 0.5/76 ± 0.5 during equilibration (2–8 h).



(6)

We were unable to monitor the cis/trans ratios of the starting bromides of Table 3 over the reaction time because of their inseparability under the GC conditions. Significantly, an earlier study[13] of the stereochemistry of reduction of $CH_3CH{=}C(CH_3)Br$ by AIBN/n-Bu_3SnH showed that the configurations of the starting bromides were not equilibrated under reaction conditions which were similar to those used in the present study. Bromide equilibration is therefore eliminated as a pathway for loss of stereochemistry in the above systems.

Conclusions

Thermal n-Bu_3SnH/AIBN radical initiation conditions in refluxing benzene bring about the conversion of vinyl bromides in the presence of $(MeO)_3P$ to the corresponding vinylphosphonates in good yields. The same conditions effect the conversion of aryl bromides to arylphosphonates. The E or Z stereochemistry of the starting bromides is lost in the product vinylphosphonates. This is seen to be accounted for by radical-induced cis–trans isomerization of the phosphonates. The sterically hindered H-transfer agent $(TMS)_3SiH$ can be substituted for the tin hydride to give good yields of both vinyl- and arylphosphonates. The individual diastereomers of 2-bromo-2-butene give a considerably higher E/Z ratio of phosphonates which are only slowly equilibrated. Evidently, the sterically bulky radical $(TMS)_3Si^\bullet$ adds to the C–C double bond with reduced efficiency compared to the tin species and is therefore a less efficient catalyst of isomerization. Since the two diastereomers are readily separated, the use of $(TMS)_3SiH$ allows a *useful preparation* of the individual phosphonate isomers.

Experimental Section

NMR spectra were recorded on Varian Unity 300 MHz and VXR 500 MHz instruments ($CDCl_3$ solvent): ^1H spectra at 300 or 500 MHz and ^{13}C at 75 or 125 MHz; chemical shifts (δ_{ppm}) downfield from tetramethylsilane as internal standard; ^{31}P NMR

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spectra at 121 MHz with chemical shifts in δ_{ppm} referenced to external 85% phosphoric acid. For ^{1}H NMR data; *J* values record proton−proton splittings unless otherwise indicated. High-resolution mass spectra (HRMS) by EI and FAB methods were recorded on an instrument with GC inlet. Microanalyses were performed by Midwest Microanalytical Laboratories, Indianapolis, IN. Solvents were dried and distilled. Dimethyl 1-methyl-1-propenylphosphonate was reported previously as a mixture of *E* and *Z* isomers.[14] Dimethyl 2-methyl-1-propenylphosphonate[15] and dimethyl 4-methoxyphenyphsphonate[17] also were previously known. The individual *E* and *Z* isomers of 2-bromo-2-butene were commercially available.

1-*tert*-Butyl-4-bromomethylenecyclohexane. To a solution of triphenylbromomethylphosphonium bromide (7.86 g, 18.8 mmol) in THF (80 mL) at −80 °C was added all at once potassium *tert*-butoxide (2.0 g, 18 mmol). The resulting mixture was stirred at −78 °C for 1.5 h. 4-*tert*-Butylcyclohexanone (2.40 g, 15.6 mmol) in THF (10 mL) was slowly added. The reaction temperature was allowed to arise to −40 °C over a 1 h period after which time the reaction mixture was stirred at room temperature for 2.5 h. Water (40 mL) was added. The solution was extracted with hexanes (40 mL × 3), and the combined organic layers were dried with $MgSO_4$. After the solvent was evaporated, the residue was distilled under reduced pressure to give the title compound as a colorless oil (bp 117−119 °C/10 mmHg, 2.20 g, 61% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (s, 9 H), 1.10 (m, 3 H), 1.88 (m, 4 H), 2.41 (m, 1 H), 2.93 (m, 1 H), 5.82 (t, $J = 1.9$ Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.65, 27.79, 28.74, 31.22, 32.60, 35.60, 48.06, 97.42, 145.28. Anal. Calcd for $C_{11}H_{19}Br$: C, 57.15; H, 8.28. Found: C, 57.23; H, 8.20.

1-*tert*-Butyl-4-dimethylphosphonomethylenecyclohexane. The following general procedure for preparation of vinylphosphonates was used (Tables 1 and 2). All preparations were done in benzene (8 mL) on the same molar scale of vinyl bromide (1.0 mmolar) and phosphite (15 mmolar). For example, a solution of 1-*tert*-butyl-4-bromomethylenecyclohexane (0.231 g, 1.00 mmol) and trimethyl phosphite (1.86 g, 15.0 mmol) in benzene (8 mL) was purged with a stream of argon for 3−4 min. The reaction mixture was heated at reflux with stirring under Ar. A solution of tri-*n*-butyltin hydride (0.35 g, 1.2 mmol) and AIBN (25 mg, 0.15 mmol) in argon purged benzene (5 mL) was added dropwise with a motor-drive syringe pump over 4 h. Reflux was maintained for a further 2 h before the solvent was evaporated under vacuum to give a residue, which was purified by silica gel column (eluent, ethyl acetate) to afford the product as a colorless oil (0.217 g, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.83 (s, 9 H), 1.15 (m, 3 H), 1.92 (m, 3 H), 2.18 (m, 1 H), 2.33 (m, 1 H), 3.31 (m, 1 H), 3.67 (d, $J_{PH} = 11.2$ Hz, 3 H), 3.68 (d, $J_{PH} = 11.2$ Hz, 3 H), 5.25 (dm, $J_{PH} = 20.0$ Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.70, 28.86 (d, $J_{PC} = 1.2$ Hz), 29.32, 32.03 (d, $J_{PC} = 7.0$ Hz), 32.55, 39.11 (d, $J_{PC} = 23.6$ Hz), 47.61, 52.04 (d, $J_{PC} = 5.5$ Hz), 52.09 (d, $J_{PC} = 5.5$ Hz), 107.06 (d, $J_{PC} = 188.3$ Hz), 168.13 (d, $J_{PC} = 6.4$ Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.6. GC/MS (EI): *m/z* 260 (M^+, 100), 245 (79), 203 (82), 176 (90), 81 (66). Anal. Calcd for $C_{13}H_{25}O_3P$: C, 59.98; H, 9.68. Found: C, 59.86; H, 9.73.

Dimethyl 2-(2′-Phenylethyl)-4-phenylbutylphosphonate. To a solution of triphenylbromomethylphosphonium bromide (4.2 g, 9.7 mmol) in THF (60 mL) was added potassium *tert*-butoxide (1.08 g, 9.65 mmol) at −78 °C over a 1.5 h period. 1,5-Diphenyl-3-pentanone (2.00 g, 8.39 mmol) in THF (10 mL) was added to the solution at −78 °C. The mixture was stirred at −78 °C for 40 min. The temperature was raised to −20 °C for 1.5 h and then to room temperature for another 1.5 h. Water (40 mL) was added, and the mixture was extracted with hexane (30 mL × 3). The organic layer was dried with $MgSO_4$, filtered, and concentrated to give a residue, which after chromatography on silica gel (eluent, hexane/dichloromethane, 9/1) gave 1-bromo-2-(2′-phenylethyl)-4-phenylbutene as a colorless oil (0.90 g, 35% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.46 (m, 2 H), 2.65 (m, 2 H), 2.84 (m, 4 H), 6.03 (t, $J = 1.3$ Hz, 1 H), 7.21−7.42 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.52, 34.35, 35.24, 38.36, 102.91, 126.25, 126.29, 128.47, 128.56, 128.59, 128.63, 141.31, 141.60, 144.45.

The above vinyl bromide (0.303 g, 1.00 mmol) and trimethyl phosphite (1.86 g, 15.0 mmol) were dissolved in benzene (8.0 mL). A stream of Ar was passed through the solution for several minutes. The reaction mixture was brought to reflux under argon and treated dropwise (syringe pump) with a solution of tri-*n*-butyltin hydride (0.340 g, 1.20 mmol) and AIBN (25 mg, 0.15 mmol) in benzene (5 mL) over 4 h. Reflux was maintained for a further 2 h before the solvent was removed under vacuum, and the residue was purified on a silica gel column (eluent, ethyl acetate/hexane, 1/1) to give the title compound as a colorless oil (0.28 g, 81% yield). ^{1}H NMR (300 MHz,$CDCl_3$): δ 2.52 (m, 2 H), 2.79 (m, 6 H), 3.64 (d, $J_{PH} = 11.2$ Hz, 6 H), 5.38 (dt, $J_{PH} = 17.5$ Hz, $J = 1.3$ Hz, 1 H), 7.14−7.31 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.89, 35.27 (d, $J_{PC} = 2.1$ Hz), 36.14 (d, $J_{PC} = 7.0$ Hz), 40.29 (d, $J_{PC} = 22.6$ Hz), 52.06 (d, $J_{PC} = 5.5$ Hz), 111.15 (d, $J_{PC} = 188.9$ Hz), 126.18, 126.31, 128.43, 128.54, 128.59, 128.61, 140.84, 141.37, 166.33 (d, $J_{PC} = 7.0$ Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.1. GC/MS (EI): *m/z* 344 (M^+, 99), 253 (38), 239 (19), 143 (81), 129 (52), 91 (100). Anal. Calcd for $C_{20}H_{25}O_3P$: C, 69.88; H, 7.32. Found: C, 70.04; H, 7.41.

Dimethyl 4-Methoxyphenylphosphonate.[17] Photochemical Approach (Table 2, Entry 2). 4-Bromoanisole (0.187 g, 1.0 mmol) and trimethyl phosphite (1.86 g, 15.0 mmol) were dissolved in benzene (8 mL), and the solution was purged with argon for several minutes. The flask was placed in a Rayonet Photoreactor (300 nm). Its stirred contents under argon were irradiated at room temperature while a solution of tris(trimethylsilyl)silane (0.298 g, 1.20 mmol) and AIBN (25.0 mg, 0.15 mmol) in benzene (5 mL) was added dropwise via a motor-driven syringe pump over 4 h. Irradiation was continued at room temperature overnight. The solvent was removed under vacuum. The residue was purified on silica gel (eluent, hexanes/ ethyl acetate, 1/1) to give the title compound as a colorless oil (0.201 mg, 93% yield). A parallel thermal reaction at 80 °C with the tin and silyl hydrides gave good to excellent yields of the phosphonate (Table 2).

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Supporting Information Available: Syntheses and spectral data for dimethyl (*E*)-1-methyl-1-propenylphosphonate,. Dimethyl (*Z*)-1-methyl-1-propenylphosphonate, dimethyl 2-methyl-1-propenylphosphonate, and dimethyl 4-trifluoromethylphenylphosphonate. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The *E* and *Z* geometries are readily determined by the relative sizes of the well-studied $^3J_{CP}$ (Duncan, M.; Gallagher, J. M. *J. Org. Magn. Reson.* **1981**, *15*, 37) and were used in the present paper.