JOC The Journal of Organic Chemistry

pubs.acs.org/joc Note

Unusual Application for Phosphonium Salts and Phosphoranes: Synthesis of Chalcogenides

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Cite This: J. Org. Chem. 2021, 86, 5954–5964 Read Online

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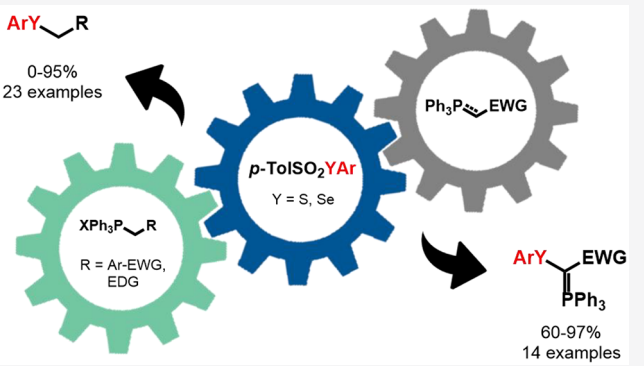
ABSTRACT: A novel strategy for the synthesis of sulfides and selenides from phosphonium salts and thio- or selenesulfonates, commercially available compounds, is described. When phosphoranes were used in the reaction, different products were obtained. The methodology does not require the use of metals, reactive species, or anhydrous conditions to be performed.



Since the discovery of the Wittig reaction,[1] phosphonium salts and phosphoranes have been among the most important chemicals for the stereoselective synthesis of functionalized alkenes.[2] In addition, the applications of these reagents in the preparation of ionic liquids,[3] sensors,[4] and catalysts[5] and in separation processes[6] were also described. The large commercial availability, low cost, chemical stability, and ease of handling also make these reagents interesting in the development of new synthetic strategies.

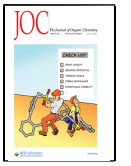
Organosulfides and selenides are important not only from a synthetic point of view, as they can be used as intermediates or reagents for the preparation of molecules of high structural complexity,[7] but also because they can exhibit different properties and biological/pharmacological activities.[8] In addition, these compounds have several applications in materials chemistry[9] and as ligands in asymmetric synthesis.[10]

There are several methods for the synthesis of sulfides and selenides described in the literature. The most common approach is based on the substitution reaction between alkyl halides using thiols or selenols as nucleophiles.[11] This strategy has some inconveniences: thiols are known for their unpleasant odor and difficult handling, while selenols usually need to be generated and used *in situ* due to being prone to autoxidation into the corresponding diselenides.[12] The umpolung equivalents, organoselenium halides (e.g., phenylselenyl bromide or chloride), are stable and commercially available solids; however, the use of phenylsulfenyl chloride has the disadvantage of the need to be stored and manipulated under argon.[13] Other strategies for the synthesis of chalcogenides based on the coupling reaction of aryl halides and chalcogenols[14] or dichalcogenides[15] promoted by different transition metals, desulfurilative sulfonylthiolation of arenes,[16] and the use of iodine and its derivatives[17] have been also described.

Despite several developments such as the use of different catalysts, solvents, and reaction media, until recently, few changes have been made for the use of new starting materials to synthesize chalcogenides.[18] In this context, chalcogenosulfonates appear as an alternative for the use of chalcogenols,[19] since this class of compounds has high stability and some of them are commercially available.

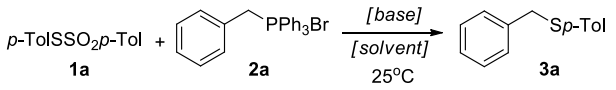
In this work, the synthesis of sulfur and selenium compounds based on the reaction between thio- or selenesulfonates and different phosphonium salts or phosphoranes is described. In the course of developing an optimal set for the reaction conditions, we first examined the best base to promote the reaction. Thus, *S*-(*p*-tolyl) *p*-toluenethiosulfonate,[20] **1a** (0.36 mmol), and benzyltriphenylphosphonium bromide, **2a** (0.43 mmol), both prepared according to the literature procedures, were treated at room temperature using different bases, and the progress of the reaction was monitored by TLC. The results are presented in Table 1.

Received: January 15, 2021
Published: March 31, 2021



https://doi.org/10.1021/acs.joc.1c00114
J. Org. Chem. 2021, 86, 5954–5964

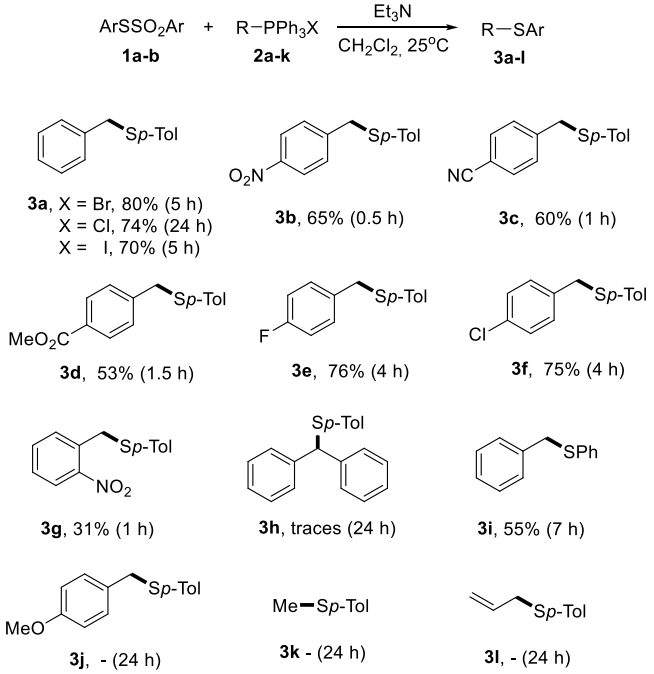
Table 1. Reaction Optimization[a]



entry	base (equiv)	solvent	time (h)	3a (%)[b]
1	K_2CO_3 (2)	CH_2Cl_2	72	44
2	imidazole (2)	CH_2Cl_2	72	0
3	*t*-BuOK (2)	CH_2Cl_2	1	43
4	Et_3N (2)	CH_2Cl_2	72	45
5	Et_3N (10)	CH_2Cl_2	12	70
6	Et_3N (20)	CH_2Cl_2	5	80
7	Et_3N (20)	MeCN	3	63
8	Et_3N (20)	DMSO	3	29
9	Et_3N (20)	EtOH	48	50
10	Et_3N (20)	H_2O	24	36
11	Et_3N (20)	THF	24	38
12	Et_3N (20)	DCE	3	52
13	Et_3N (20)	*n*-hexane	24	7

[a]Reaction conditions: Reactions were performed using **1a** (1 equiv) and **2a** (1.2 equiv) and the appropriate base and solvent (5 mL) at 25 °C for the time indicated. All data represent the average of two experiments. [b]Isolated yield.

Scheme 1. Synthesis of Sulfides



According to Table 1, the use of 2 equiv of potassium carbonate gave **3a** in 44% yield after a long reaction time (Table 1, entry 1). One reason for the yield observed in this case could be attributed to the low solubility of the potassium carbonate in dichloromethane, making the reaction slower or less effective. When imidazole was used as base, **3a** was not observed even after 72 h (Table 1, entry 2). The use of a stronger base such as potassium *t*-butoxide (2 equiv) led to the formation of the desired product in 43% yield after only 1 h; however, **3a** was obtained with the corresponding disulfide as a byproduct in the reaction (Table 1, entry 3). A similar yield was obtained when triethylamine was used; however, the reaction required 72 h for completion (Table 1, entry 4). Higher yields and short reaction times were observed when the amount of triethylamine was increased (Table 1, entries 5 and 6); the best result was observed when 20 equiv of triethylamine was used, where the desired product **3a** was obtained in 80% yield after 5 h (Table 1, entry 6).

The influence of other solvents in the reaction yield was also studied. Shorter reaction times for the formation of **3a** were observed when more polar solvents such as acetonitrile or dimethyl sulfoxide were used as the reaction solvent (Table 1, entries 7 and 8), possibly due to the better solubility of the phosphonium salt **2a** in these solvents; however, the yields were lower when compared to the use of dichloromethane due to the formation of higher quantities of the corresponding disulfide. The use of ethanol or water as the reaction solvent gave **3a** in lower yields and required longer reaction times (Table 1, entries 9 and 10). The use of dichloroethane gave **3a** in 52% yield after 3 h (Table 1, entry 12). Finally, the use of *n*-hexane, a less polar solvent, gave **3a** in only 7% yield after 24 h (Table 1, entry 13).

Thus, the best conditions for the preparation of the sulfide **3a** using *S*-(*p*-tolyl) *p*-toluenethiosulfonate, **1a**, and benzyltriphenylphosphonium bromide, **2a**, were observed when triethylamine (20 equiv) in dichloromethane was used as the solvent. These conditions were then applied to other phosphonium salts, and the results are described in Scheme 1.

Initially, the reactivity of different benzyltriphenylphosphonium halides was investigated. As described before, the use of benzyltriphenylphosphonium bromide gave sulfide **3a** in 80% yield after 5 h. When benzyltriphenylphosphonium chloride was used, the desired product **3a** was obtained in 74% yield after 24 h. A similar yield was observed when benzyltriphenylphosphonium iodide was used; however, the reaction proceeded faster when compared to the chloro derivative since the desired product was observed after only 5 h. This result could be attributed to the leaving group character of halogen atoms in phosphonium salts. As the use of benzyltriphenylphosphonium bromide led to a better yield, other bromide phosphonium salts were chosen to expand the scope of the reaction.

The use of a benzylic phosphonium salt containing the electron-withdrawing nitro group in the aromatic ring **2b** led to the corresponding sulfide **3b** in 65% yield after 0.5 h. A similar result was observed when a cyano or an ester group was present in the aromatic ring, where the corresponding sulfides **3c** and **3d** were obtained in 60% and 53% yield, respectively, after only 1 h reaction. The presence of halogens such as fluorine or chlorine atoms in the aromatic ring also led to the corresponding sulfides **3e** and **3f** in good yields; however, both reactions required 4 h.

The reaction is apparently sensitive to steric effects since the use of a phosphonium salt containing a nitro group at the *ortho* position led to the corresponding sulfide **3g** in only 31% yield after 1 h. This effect was further evidenced using a secondary phosphonium salt where only traces of sulfide **3h** were observed.

When the reaction was carried out using *S*-phenyl benzenethiosulfonate, **1b**, the corresponding sulfide **3i** was obtained in 55% yield after 7 h, indicating that the method is general and other thiosulfonates can be applied in the reaction.

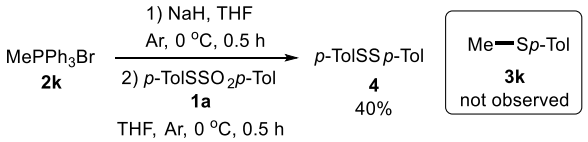
On the other hand, when a benzylic phosphonium salt containing an electron-donating group in the aromatic ring was used, the corresponding sulfide **3j** was not observed even after

https://doi.org/10.1021/acs.joc.1c00114
J. Org. Chem. 2021, 86, 5954−5964

24 h of reaction. The same behavior was observed for phosphonium salts containing methyl and allyl groups, **2j** and **2k**, where the corresponding sulfides **3k** and **3l** were not observed after a 24 h period.

Phosphonium salts containing electron-withdrawing groups in the presence of a weak base such as triethylamine led to the *in situ* formation of the corresponding stabilized phosphoranes by deprotonation.[21] In order to verify if the use of a phosphonium salt that could *in situ* generate a nonstabilized or reactive ylide could be used in the reaction, an attempt for the synthesis of sulfide **3k** was performed under anhydrous conditions using methyltriphenylphosphonium bromide, **2k**, and sodium hydride as a base in dry THF at 0 °C. After half an hour, *S*-(*p*-tolyl) *p*-toluenethiosulfonate, **1a**, was then added, and the reaction was monitored by TLC. Surprisingly, only the corresponding disulfide **4** was observed as the reaction product (Scheme 2).

Scheme 2. Reaction under Anhydrous Conditions



In this way, under the conditions studied, the reaction led to the corresponding sulfides only when benzylic phosphonium salts that could generate stabilized or semistabilized phosphoranes were used.

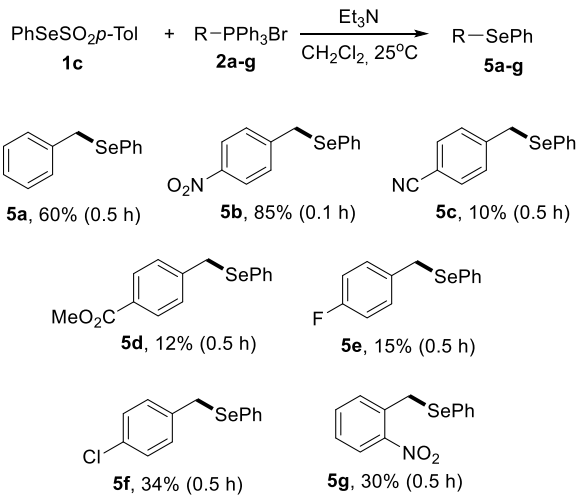
The strategy was also extended for the synthesis of selenides. In this case, *p*-tolyl phenylselenyl sulfone **1c**, prepared according to a literature procedure,[22] was submitted to the optimized conditions previously described. The corresponding selenides **5a−g** were obtained in lower yields when compared to sulfides but in a shorter reaction time in all cases.

The use of a benzyltriphenylphosphonium bromide, **2a**, gave the corresponding selenide **5a** in 60% yield after 0.5 h. Again, the reaction was faster for phosphonium salts containing electron-withdrawing groups in the aromatic ring. Selenide **5b** was obtained in 85% yield after only 0.1 h. When the cyano or the ester group was present in the aromatic ring, the corresponding selenides **5c** and **5d** were obtained in low yields after 0.5 h. The use of phosphonium salts containing halogens in the aromatic rings gave **5e** and **5f** in 15% and 34% yield, respectively. The use of a phosphonium salt containing a nitro group at the *ortho* position gave selenide **5g** in 30% yield after 0.5 h (Scheme 3). The observed lower yields can be attributed to the high reactivity of *p*-tolyl phenylselenyl sulfone, **1c**, to form the respective diselenide, obtained as a byproduct.

These experiments demonstrated that thio- or selenesulfonates can be used as convenient precursors of both sulfides and selenides but not of tellurides since an efficient method for the synthesis of tellurosulfonates has not been described so far.[23]

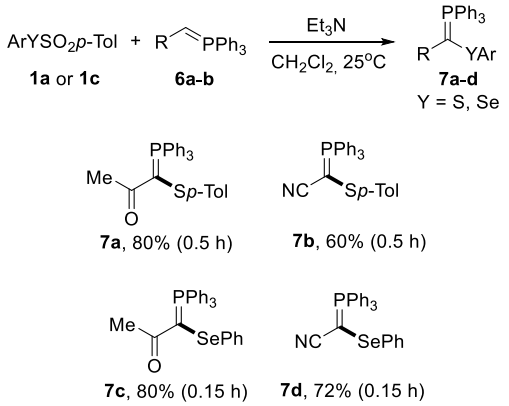
Next, our attention was focused on the use of stabilized phosphoranes, **6**, rather than benzylic phosphonium salts in the reaction. Generally, such compounds can be described as an ylene or an ylide, two resonant structures, with the ylide structure being the major contributor.[24a] This was later confirmed by NMR studies[24b] (Scheme 1). Some authors, however, describe ylides as phosphine-stabilized carbenes.[25]

Scheme 3. Synthesis of Selenides



Thus, commercially available stabilized phosphoranes and *S*-(*p*-tolyl) *p*-toluenethiosulfonate, **1a**, or *p*-tolyl phenylselenyl sulfone, **1c**, were reacted under the standardized conditions. Surprisingly, in most cases, new phosphoranes were obtained as the reaction products (Scheme 4). The new thio- or selenophosphoranes were obtained in similar yields; however, the reaction was slightly faster for the synthesis of selenophosphoranes.

Scheme 4. Synthesis of Thio- and Selenophosphoranes



Thiophosphoranes are versatile compounds and can be used, for example, as ligands in coordination chemistry[26] and in the synthesis of alkynes.[27] Selenophosphoranes were described to be inert in Wittig-type reactions with carbonyl compounds.[28] However, a latter report described the use of such compounds for the stereoselective synthesis of vinylic selenides under microwave irradiation.[29]

The only exception occurred when the reaction was performed using a stabilized phosphorane derived from Weinreb amide and **1a** or **1c**, where the corresponding phosphoranes were not observed. In this case, only the corresponding sulfide **3m** or selenide **5h** was obtained as the reaction product in a similar yield as when phosphonium salts were used (Scheme 5).

When the reactions are compared, it is clear that the nature of the group present in the phosphonium salt or phosphorane is important, since more or less stabilized carbanions can be obtained and can lead to different products in the reaction.

https://doi.org/10.1021/acs.joc.1c00114
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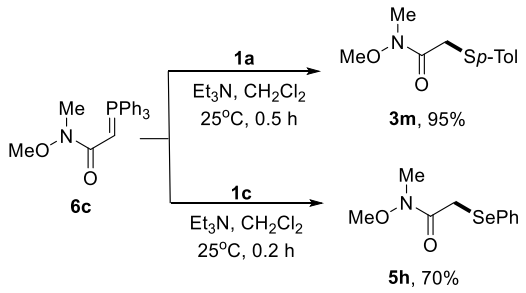
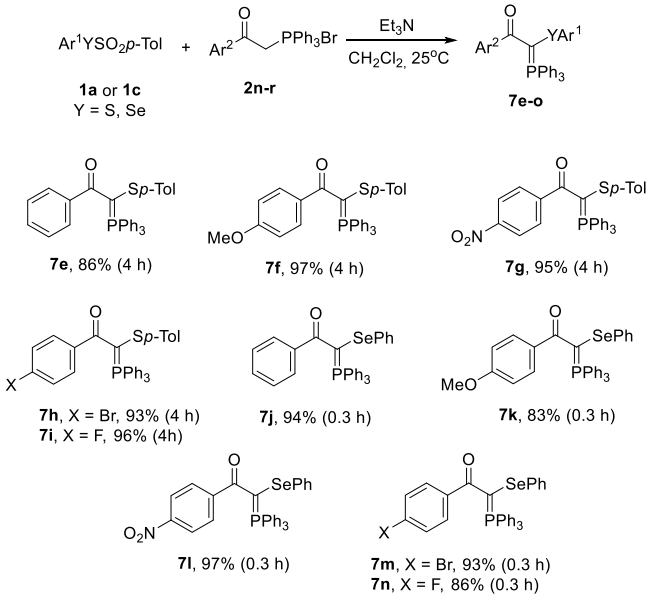
Scheme 5. Use of Weinreb Amide Phosphorane



The reactivity of a phosphorane is related to its nucleophilic character; consequently, the presence of an electron-withdrawing group in its structure would increase its stability.[30a] It is also possible to estimate the reactivity of a phosphorane from the corresponding phosphonium salt pK_a. Thus, the more acidic the α-H in the phosphonium salt, the less reactive is the phosphorane. This effect is attributed to the resonance delocalization of the negative charge into the available 3d vacant orbitals of phosphorus as well as to the Coulombic effects of the positive charge on the phosphorus atom.[30b]

In this way, the reaction of **1a** or **1c** with phosphonium salts that could generate highly stabilized phosphoranes would lead to new thio- and selenophosphoranes. This fact was evidenced by the use of phosphonium salts derived from substituted acetophenones where in all cases the corresponding new phosphoranes were obtained in good yields (Scheme 6).

Scheme 6. Synthesis of New Phosphoranes from Phosphonium Salts Derived from Substituted Acetophenones

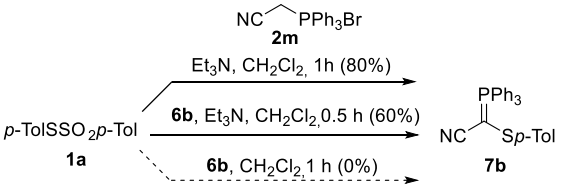


According to Scheme 6, when the reaction was performed using phenacyltriphenylphosphonium bromide and *S*-(*p*-tolyl) *p*-toluenethiosulfonate, **1a**, the new phosphorane **7e** was obtained in 86% yield after 4 h. The reaction does not appear to be affected by electronic effects, since the use of acetophenone-derived substrates containing electron-donating or electron-withdrawing groups in the aromatic ring led to the corresponding phosphoranes **7f** and **7g** in 95% and 97%, respectively. The presence of halogen atoms in the aromatic rings also gave the corresponding phosphoranes **7h** and **7i** in good yields.

When the reaction was performed using *p*-tolyl phenylselenyl sulfone, **1c**, the corresponding phosphoranes **7j**–**n** were also obtained in good yields and in a shorter reaction time when compared to the sulfur counterpart in all cases, indicating the method is general for the synthesis of thio- and selenophosphoranes.

In an attempt to explain this difference in reactivity, an experiment using the phosphonium salt (cyanomethyl)-triphenylphosphonium bromide, **2m**, and its corresponding phosphorane (triphenylphosphoranylidene)acetonitrile, **6b**, were performed. When the reaction was carried out with **1a** and phosphonium salt **2m** using triethylamine (20 equiv) as a base in dichloromethane, the resulting phosphorane **7b** was obtained as the sole product in 80% yield after 1 h. On the other hand, when **1a** and phosphorane **6b** were used under the same conditions, the desired product **7b** was obtained in 60% yield after 30 min (Scheme 7).

Scheme 7. Competitive Experiments



Mechanistically, this result suggests that the phosphonium salt **2m** would initially lead to phosphorane **6b** and its subsequent reaction with **1a** would lead to the desired product **7b**. The presence of the base is somewhat important since when the reaction was performed using **1a** and **6b** without triethylamine; only the starting materials were recovered after 1 h (Scheme 7).

For a better understanding of the operating mechanism, the progress of the reaction of **1a** and phosphonium salt **2m** was monitored by ^{31}P NMR in $CDCl_3$ at different periods. At the beginning of the reaction, ^{31}P NMR shows only a singlet at δ = 21.5 attributed to phosphonium salt **2m** (see the Supporting Information). When treated with triethylamine, the disappearance of this signal along with the appearance of two new signals at δ = 23.2, attributed to the phosphorane **6b**, and at δ = 26, attributed to the phosphorane **7b**, were immediately observed. After 1 h, the complete disappearance of the signal at δ = 23.2 attributed to **6b** and an intense signal at δ = 26 attributed to **7b** together with a small amount of triphenylphosphine oxide could be observed.

The monitoring of the reaction using the phosphorane derived from Weinreb amide, **6c**, which led exclusively to the formation of the corresponding selenide or sulfide, was also carried out through ^{31}P NMR. The phosphorane **6c** appeared as a singlet at δ 18, which completely disappeared after the addition of triethylamine and thiosulfonate, **1a**, with the appearance of a new signal at δ 27.8, attributed to the formation of a new phosphorus species, probably the Ph_3P-SO_2p-Tol complex.

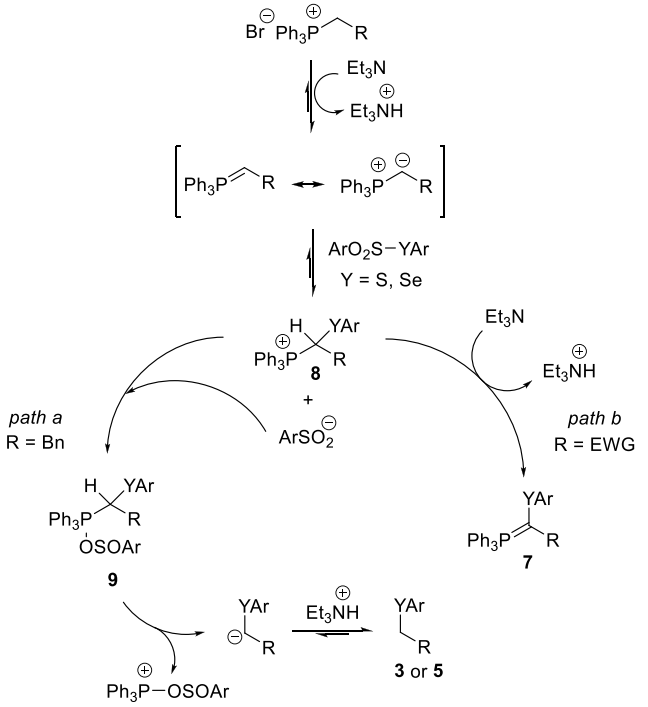
In an attempt to verify the formation of this complex, a parallel experiment was carried out where sodium *p*-toluenesulfinate was added to an NMR tube containing a solution of PPh_3 in dichloromethane and the reaction was monitored by

https://doi.org/10.1021/acs.joc.1c00114
J. Org. Chem. 2021, 86, 5954–5964

^{31}P NMR. The NMR spectrum showed a signal at δ −5.7, attributed to PPh_3, and the appearance of a signal at δ 26, attributed to the formation of Ph_3P-SO_2p-Tol complex. In order to confirm the formation of such a complex, part of the content of this tube was added to the content of the previous reaction involving **6c** where an increase in the value of the integral for the signal at δ 26 was observed.

From these observations, a mechanistic proposal is shown in Scheme 8. The reaction of phosphonium salt or phoshorane

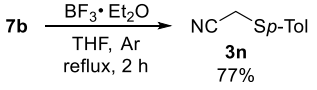
Scheme 8. Plausible Reaction Mechanism



and the thio- or selenesulfonate in the presence of triethylamine would initially lead to the formation of the intermediary **8**. When electron-withdrawing groups are present in the structure, the subsequent abstraction of the acidic α-hydrogen by the base would lead to the formation of the corresponding phosphorane **7** (Scheme 8, path b). On the other hand, when the benzyl group was present, the acidity of the α-hydrogen would be reduced; therefore, the sulfonyl anion would attack the phosphorus atom for the formation of the complex **9**, which was the driving force of the formation of a strong P−O bond in the byproduct.[31] The subsequent departure of the sulfonyl-phosphonium species followed by protonation would lead to the corresponding benzylic sulfides or selenides **3** or **5** (Scheme 8, path b).

Since the corresponding sulfides and selenides were not obtained in some cases, an attempt for the conversion of phosphorane **7b** into the corresponding sulfide **3n** was performed using boron trifluoride diethyl etherate in THF under reflux for 2 h.[32] Using this strategy, the corresponding sulfide **3n** was obtained in 77% yield (Scheme 9).

Scheme 9. Synthesis of Sulfides from Thiophosphoranes



In conclusion, a new strategy for the synthesis of selenides and sulfides based on the use of commercially available phosphonium salts and thio- and selenosulfonates under basic conditions was described. Using this strategy, the corresponding sulfides and selenides were obtained in moderate to good yields when benzylic phosphonium salts containing electron-withdrawing groups were used. When stabilized phosphoranes were used under the same reaction conditions, new thio- and selenophosphoranes were obtained in moderate to good yields. The method is simple, fast, and general, allowing further applications in the synthesis of more complex compounds.

EXPERIMENTAL SECTION

General Information. All reagents and solvents used were previously purified and dried in agreement with the literature.[33] Sodium *p*-toluenesulfinate was purchased from Aldrich Chemical Co. and was dried *in vacuo* at 60 °C before use. Reactions were monitored by thin-layer chromatography on 0.25 mm E. Merck silica gel 60 plates (F254) using UV light, vanillin, and *p*-anisaldehyde as visualizing agents. The GC/FID analysis was performed on a Varian CP-3380 gas chromatograph system coupled with a flame ionization detector. The chromatographic column was a Chrompack CP-SPL5CB capillary column (30 m × 0.25 mm, 0.25 μm) using the initial temperature of 60 °C, which was then increased to 220 °C at 10 °C min^{-1}. ^{1}H and ^{13}C{^{1}H} NMR data were recorded in $CDCl_3$. The chemical shifts are reported as delta (δ) units in parts per million (ppm) relative to the solvent residual peak as the internal reference [δ 7.26 (^{1}H NMR) and δ 77.16 (^{13}C{^{1}H} NMR)]. ^{77}Se NMR (57 MHz) and ^{31}P NMR (121 MHz) spectra were also obtained in $CDCl_3$. Spectra were calibrated using diphenyl diselenide (δ 463.0) as external reference in the case of ^{77}Se NMR, and chemical shifts were referenced to external H_3PO_4 (δ 0.0) in the case of ^{31}P NMR. Coupling constants (J) for all spectra are reported in Hertz (Hz). HRMS analyses were performed on a micrOTOF-QII mass spectrometer equipped with an Apollo II electrospray ion source (Bruker, Billerica, USA) coupled to a UFLC Prominence binary liquid chromatograph (Shimadzu, Kyoto, Japan). Samples were stored into the SIL-30AC autosampler at 15 °C prior to analysis. The direct injection (without column) of 1 μL of each sample was carried to the analyzer by a 10 mmol/L ammonium formate (Sigma-Aldrich, St Louis, USA) solution in methanol/water (1:1, v/v) at a flow rate of 200 μL/min. The HRMS data were acquired with the ESI source set as follows: nebulizer gas at 2.0 bar, dry gas at 6.0 L/min, dry temperature at 200 °C, and voltage at 4.0 kV. The mass/charge ratios were scanned (m/z 50−800 Da) in positive ion mode (ESI+). Sodium formate clusters in isopropyl alcohol within the m/z 50−800 Da range were used as the calibration standard.

General Procedures for the Preparation of Starting Materials. *Synthesis of S-(p-Tolyl) p-Toluenethiosulfonate (**1a**).* To a 50 mL flask containing sodium *p*-toluenesulfinate (1.0 equiv, 5.6 mmol, 1.0 g) [previously dried under vacuum for 1 h at 100 °C] and CuI (0.25 equiv, 1.4 mmol, 265 mg) was added CH_2Cl_2 (15 mL) followed by H_2SO_4 (7.5 equiv, 42 mmol, 4.12 g, 2.25 mL). The mixture was stirred for 13 min and then quenched with a $NaHCO_3$ saturated solution. The mixture was diluted with CH_2Cl_2 (20 mL), transferred to a separation funnel, and then washed with water (2 × 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed *in vacuo*. The crude compound was crystallized in hot hexanes to yield 600 mg (77%) of the title compound as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 9 Hz, 2H), 7.28 (d, J = 9 Hz, 2H), 7.24 (d, J = 9 Hz, 2H), 7.17 (d, J = 9 Hz, 2H), 2.45 (s, 3H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.6, 142.0, 140.4, 136.5, 130.2, 129.3, 127.6, 124.6, 21.6, 21.5. The data match with the previously described compound.[20]

*Synthesis of S-Phenyl Benzenesulfonothioate (**1b**).* To a 50 mL flask containing sodium benzenesulfinate (1.0 equiv, 5.6 mmol, 920 mg) [previously dried under vacuum for 1 h at 100 °C] and CuI (0.25

https://doi.org/10.1021/acs.joc.1c00114
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equiv, 1.4 mmol, 265 mg) was added CH_2Cl_2 (15 mL) followed by H_2SO_4 (7.5 equiv, 42 mmol, 4.12 g, 2.25 mL). The mixture was stirred for 13 min and then quenched with a $NaHCO_3$ saturated solution. The mixture was diluted with CH_2Cl_2 (20 mL), transferred to a separation funnel, and then washed with water (2 × 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed *in vacuo*. The crude compound was crystallized in hot hexanes to yield 420 mg (60%) of the title compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.52 (m, 3H), 7.49−7.38 (m, 3H), 7.37−7.29 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.8, 136.5, 133.6, 131.4, 129.4, 128.7, 127.7, 127.4. The data match with the previously described compound.[20]

*Synthesis of p-Tolyl Phenylselenyl Sulfone (**1c**).* To a 50 mL flask containing sodium *p*-toluenesulfinate (4.0 equiv, 6.4 mmol, 1.15 g), diphenyl diselenide (1.0 equiv, 1.6 mmol, 500 mg), and *N*-bromosuccinimide (2.0 equiv, 3.2 mmol, 570 mg) was added MeCN (20 mL). The reaction was monitored by TLC, and after 2 h, it was diluted with EtOAc (20 mL), transferred to a separation funnel, and then washed with water (2 × 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed *in vacuo*. The crude compound was purified by column chromatography [hexanes/EtOAc (9:1)] to yield 550 mg (55%) of the title compound as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.32 (m, 7H), 7.18 (d, J = 8 Hz, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.5, 142.7, 137.2, 130.8, 129.5, 129.2, 128.0, 127.0, 21.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 970.4. The data match with the previously described compound.[22,34]

General Procedure for the Synthesis of Sulfides (3a−m). To a 25 mL flask containing **1a** (1.0 equiv, 0.36 mmol, 100 mg) and the appropriate phosphonium salt (1.2 equiv, 0.432 mmol) was added CH_2Cl_2 (5.0 mL). The mixture was stirred until a solution was observed (approximately 5 min); then, Et_3N (20.0 equiv, 7.2 mmol, 1.0 mL) was added. The reaction was monitored by TLC and, after consumption of the starting material, diluted with CH_2Cl_2 (20 mL), transferred to a separation funnel, and then washed with a NH_4Cl saturated solution (2 × 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed *in vacuo*. The crude compound was purified by column chromatography.

*Benzyl(p-tolyl)sulfane (**3a**).* 61 mg (80%) of **3a** was obtained as a white solid after column chromatography [hexanes]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.23 (m, 5H), 7.21 (d, J = 9 Hz, 2H), 7.06 (d, J = 9 Hz, 2H), 4.06 (s, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 137.8, 136.5, 132.4, 130.7, 129.6, 128.8, 128.4, 127.0, 39.8, 21.0. The data match with the previously described compound.[35]

*(4-Nitrobenzyl)(p-tolyl)sulfane (**3b**).* 60 mg (65%) of **3b** was obtained as a yellow solid after column chromatography [hexanes/EtOAc (8:2)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 7.05 (d, J = 8 Hz, 2H), 4.07 (s, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 146.9, 145.8, 137.6, 131.7, 130.6, 129.8, 129.5, 123.5, 39.5, 21.0. The data match with the previously described compound.[36]

*4-((p-Tolylthio)methyl)benzonitrile (**3c**).* 52 mg (60%) of **3c** was obtained as white solid after column chromatography [hexanes/EtOAc (8:2)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 6.97 (d, J = 8 Hz, 2H), 3.95 (s, 2H), 2.22 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.6, 137.4, 132.1, 131.6, 130.7, 129.7, 129.4, 118.7, 110.7, 39.7, 21.0. The data match with the previously described compound.[37]

*Methyl 4-((p-Tolylthio)methyl)benzoate (**3d**).* 52 mg (53%) of **3d** was obtained as a white solid after column chromatography [hexanes]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 7.05 (d, J = 8 Hz, 2H), 4.06 (s, 2H), 3.90 (s, 3H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 143.3, 137.1, 131.5, 131.4, 129.8, 129.7, 128.9, 128.8, 52.0, 39.8, 21.0. The data match with the previously described compound.[37]

*(4-Fluorobenzyl)(p-tolyl)sulfane (**3e**).* 64 mg (76%) of **3e** was obtained as a white solid after column chromatography [hexanes]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.17 (m, 4H), 7.05 (dt, J = 8, 0.7 Hz, 2H), 6.93 (t, J = 8 Hz, 2H), 4.01 (s, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8 (d, J = 240 Hz), 136.8, 133.5 (d, J = 3 Hz), 130.9, 130.3 (d, J = 8 Hz), 129.6, 115.1 (d, J = 21 Hz), 39.0, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.53 The data match with the previously described compound.[38]

*(4-Chlorobenzyl)(p-tolyl)sulfane (**3f**).* 67 mg (75%) of **3f** was obtained was as a white solid after column chromatography [hexanes]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 7.16 (d, J = 8 Hz, 2H), 7.07 (d, J = 8 Hz, 2H), 4.01 (s, 2H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.9, 136.4, 132.8, 131.7, 131.1, 130.1, 129.7, 128.5, 39.2, 21.0. The data match with the previously described compound.[38]

*(2-Nitrobenzyl)(p-tolyl)sulfane (**3g**).* 29 mg (31%) of **3g** was obtained as a yellow oil after column chromatography [hexanes]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8 Hz, 1H), 7.40 (m, 2H), 7.21 (d, J = 8 Hz, 1H), 7.17 (d, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 7.05 (d, J = 8 Hz, 2H), 4.38 (s, 2H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ137.7, 133.8, 132.9, 132.5, 131.9, 130.8, 129.7, 128.1, 125.2, 37.8, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO_2S^+$ 260.0740; Found 260.0756.

*Benzyl(phenyl)sulfane (**3i**).* 44 mg (55%) of **3i** was obtained as a white solid after column chromatography [hexanes]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.14 (m, 10H), 4.10 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.5, 136.4, 129.8, 128.9, 128.8, 128.5, 127.2, 126.4, 137.5, 136.4, 129.8, 128.9, 128.8, 128.5, 127.2, 126.4, 39.0. The data match with the previously described compound.[39]

*N-Methoxy-N-methyl-2-(p-tolylthio)acetamide (**3m**).* 77 mg (95%) of **3m** was obtained as a white solid after column chromatography [hexanes/EtOAc (7:3)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 9 Hz, 2H), 7.03 (d, J = 9 Hz, 2H), 3.70 (s, 2H), 3.62 (s, 3H), 3.12 (s, 3H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 169.4, 136.1, 130.8, 129.9, 128.8, 60.5, 35.1, 31.5, 20.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{16}NO_2S^+$ 226.0896; Found 226.0893.

General Procedure for the Synthesis of Selenides (5a−h). To a 25 mL flask containing **1b** (1.0 equiv, 0.32 mmol, 100 mg) and the appropriate phosphonium salt (1.2 equiv, 0.384 mmol) was added CH_2Cl_2 (5.0 mL). The mixture was stirred until a solution was observed (approximately 5 min); then, Et_3N (20.0 equiv, 6.4 mmol, 0.9 mL) was added. The reaction was monitored by TLC and, after consumption of the starting material, diluted with CH_2Cl_2 (20 mL), transferred to a separation funnel, and then washed with a NH_4Cl saturated solution (2 × 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed *in vacuo*. The crude compounds were purified by column chromatography.

*Benzyl(phenyl)selane (**5a**).* 47 mg (60%) of **5a** was obtained as a dark yellow/orange oil after column chromatography [hexanes]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.44 (m, 2H), 7.27−7.18 (m, 8H), 4.12 (s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 138.6, 133.5, 130.4, 128.9, 128.8, 128.4, 127.2, 126.8, 32.2; ^{77}Se NMR (57 MHz, $CDCl_3$) δ 369.7. The data match with the previously described compound.[40]

*(4-Nitrobenzyl)(phenyl)selane (**5b**).* 79 mg (85%) of **5b** was obtained as a yellow solid after column chromatography [hexanes/EtOAc (95:5)]. ^{1}H NMR (300 MHz, $CDCl_3$) 8.05 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.30−7.19 (m, 5H), 4.08 (s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 148.9, 146.8, 134.9, 134.4, 129.4, 129.1, 128.1, 123.5, 31.3; ^{77}Se NMR (57 MHz, $CDCl_3$) δ 398.0. The data match with the previously described compound.[41]

*4-((Phenylselanyl)methyl)benzonitrile (**5c**).* 9 mg (10%) of **5c** was obtained as a yellow solid after column chromatography [hexanes/EtOAc (95:5)]. ^{1}H NMR (400 MHz, $CDCl_3$) 7.49 (d, J = 8 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 7.30−7.18 (m, 5H), 4.05 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 144.7, 135.0, 134.4, 132.1, 129.4, 129.1, 129.0, 128.0, 118.8, 110.4, 31.7; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 398.5. The data match with the previously described compound.[42]

*Methyl 4-((Phenylselanyl)methyl)benzoate (**5d**).* 12 mg (12%) of **5d** was obtained was as a yellow liquid after column chromatography [hexanes/EtOAc (95:5)]. ^{1}H NMR (400 MHz, $CDCl_3$) 7.89 (d, J = 8

https://doi.org/10.1021/acs.joc.1c00114
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Hz 2H), 7.43−7.40 (m, 2H), 7.27−7.23 (m, 3H), 7.20 (d, J = 8 Hz, 2H), 4.09 (s, 2H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 166.9, 144.3, 137.0, 134.1, 131.5, 129.7, 129.0, 128.8, 127.7, 52.0, 31.9; ^{77}Se NMR (77 MHz, $CDCl_3$) δ 388.9. The data match with the previously described compound.[43]

*(4-Fluorobenzyl)(phenyl)selane (**5e**).* 13 mg (15%) of **5e** was obtained as a yellow liquid after column chromatography [hexanes/EtOAc (95:5)]. ^1H NMR (400 MHz, $CDCl_3$) 7.46−7.39 (m, 2H), 7.31−7.20 (m, 3H), 7.13 (dd, J = 8.7, 5.3 Hz, 2H), 6.91 (t, J = 8.7 Hz, 2H), 4.06 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 161.7 (d, J = 245.3 Hz), 134.4 (d, J = 3.1 Hz), 133.8, 130.3 (d, J = 8.0 Hz), 129.9, 129.0, 127.5, 115.2 (d, J = 21.5 Hz), 31.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 380.3. The data match with the previously described compound.[44]

*(4-Chlorobenzyl)(phenyl)selane (**5f**).* 31 mg (34%) of **5f** was obtained as a light yellow solid after column chromatography [hexanes/EtOAc (95:5)]. ^1H NMR (400 MHz, $CDCl_3$) 7.44−7.41 (m, 2H), 7.26−7.23 (m, 3H), 7.19 (d, J = 8 Hz, 2H), 7.09 (d, J = 8 Hz, 2H), 4.03 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 137.3, 133.9, 132.6, 130.1, 129.0, 128.5, 127.6, 31.4; ^{77}Se NMR (77 MHz, $CDCl_3$) δ 383.2. The data match with the previously described compound.[42]

*(2-Nitrobenzyl)(phenyl)selane (**5g**).* 28 mg (30%) of **5g** was obtained as a yellow liquid after column chromatography [hexanes/EtOAc (95:5)]. ^1H NMR (400 MHz, $CDCl_3$) 8.01 (dd, J_1 = 8 Hz, J_2 = 1.8 Hz, 1H), 7.44−7.21 (m, 7H), 7.00 (dd, J_1 = 8 Hz, J_2 = 1.8 Hz, 1H), 4.36 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 135.4, 135.2, 133.0, 131.9, 129.0, 128.1, 127.8, 125.5, 29.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 404.0. The data match with the previously described compound.[45]

*N-Methoxy-N-methyl-2-(phenylselanyl)acetamide (**5h**).* 57 mg (70%) of **5h** was obtained as a yellow oil after column chromatography [hexanes/EtOAc (8:2)]. ^1H NMR (300 MHz, $CDCl_3$) δ 7.56−7.51 (m 2H), 7.23−7.18 (m, 3H), 3.65 (s, 2H), 3.59 (s, 3H), 3.11 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 170.4, 132.3, 130.5, 128.9, 128.1, 126.6, 60.3, 31.6, 25.7; ^{77}Se NMR (57 MHz, $CDCl_3$) δ 316.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{14}NO_2Se^+$ 260.0184; Found 260.0186.

General Procedure for the Synthesis of Phosphoranes. *Synthesis of Thiophosphoranes (**7a−b, 7e−i**).* To a 25 mL flask containing **1a** (1.0 equiv, 0.36 mmol, 100 mg) and the appropriate phosphorus ylene (1.2 equiv, 0.432 mmol) was added CH_2Cl_2 (5.0 mL). The mixture was stirred until a solution was observed (approximately 5 min); then, Et_3N (20.0 equiv, 7.2 mmol, 1.0 mL) was added. The reaction was monitored by TLC and, after consumption of the starting material, diluted with CH_2Cl_2 (20 mL), transferred to a separation funnel, and then washed with a NH_4Cl saturated solution (2 × 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed *in vacuo*. The crude compounds were purified by column chromatography.

*1-(p-Tolylthio)-1-(triphenylphosphoraneylidene)propan-2-one (**7a**).* 126 mg (80%) of **7a** was obtained as a pale yellow solid after column chromatography [hexanes/EtOAc (7:3)]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47−7.39 (m, 9H), 7.33−7.27 (m, 6H), 6.97 (d, J = 8 Hz, 2H), 6.87 (d, J = 8 Hz, 2H), 2.27 (s, 3H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.8 (d, J = 14.1 Hz), 140.1, 133.7, 133.6 (d, J = 9.5 Hz), 131.7 (d, J = 2.5 Hz), 129.0, 128.2 (d, J = 12.1 Hz), 126.7 (d, J = 90.0 Hz), 124.5, 55.9 (d, J = 103.6 Hz), 25.5 (d, J = 7.6 Hz), 20.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}OPS^+$ 441.1436; Found 441.1441.

When the reaction was carried out on a larger scale by employing **1a** (2.9 mmol, 800 mg) and the phosphorus ylene **6a** (3.5 mmol, 1.12 g) in CH_2Cl_2 (40 mL) using Et_3N (58 mmol, 8 mL), the indicated product (**7a**) was obtained in 70% yield (900 mg).

*2-(p-Tolylthio)-2-(triphenylphosphaneylidene)acetonitrile (**7b**).* 91 mg (60%) of **7b** was obtained as a white solid after column chromatography [hexanes/EtOAc (7:3)]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65−7.55 (m, 9H), 7.49−7.43 (m, 6H), 7.12 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.2 Hz, 2H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.4, 134.6, 133.6 (d, J = 9.7 Hz), 132.9 (d, J = 2.4 Hz), 128.9 (d, J = 12.2 Hz), 126.1, 124.8 (d, J = 91.5 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}NPS^+$ 424.1283; Found 424.1285.

*1-Phenyl-2-(p-tolylthio)-2-(triphenylphosphaneylidene)ethan-1-one (**7e**).* 156 mg (86%) of **7e** was obtained as a white solid after column chromatography [hexanes/EtOAc (7:3)]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 7.9, 1.7 Hz, 2H), 7.60 (ddd, J = 12.2, 8.3, 1.3 Hz, 6H), 7.51 (dd, J = 7.5, 1.8 Hz, 3H), 7.40 (ddd, J = 8.7, 5.4, 2.4 Hz, 6H), 7.33−7.24 (m, 3H), 7.08 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.2 (d, J = 14.0 Hz), 140.7 (d, J = 10.9 Hz), 140.5 (d, J = 2.2 Hz), 133.8, 133.7 (d, J = 9.4 Hz), 131.7 (d, J = 3.0 Hz), 129.1, 129.0, 128.3 (d, J = 12.1 Hz), 128.1, 127.3, 126.6 (d, J = 90.0 Hz), 124.8, 57.4 (d, J = 101.4 Hz), 20.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}OPS^+$ 503.1593; Found 503.1604.

*1-(4-Methoxyphenyl)-2-(p-tolylthio)-2-(triphenylphosphaneylidene)ethan-1-one (**7f**).* 186 mg (97%) of **7f** was obtained as a white solid after column chromatography [hexanes/EtOAc (7:3)]. ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (d, J = 8.8 Hz, 2H), 7.57 (ddd, J = 12.1, 8.4, 1.3 Hz, 6H), 7.48 (td, J = 7.4, 1.8 Hz, 3H), 7.37 (td, J = 7.7, 3.0 Hz, 6H), 7.08 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 3.76 (s, 3H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.9 (d, J = 13.6 Hz), 160.5, 140.6 (d, J = 2.0 Hz), 133.8, 133.6 (d, J = 9.3 Hz), 132.9 (d, J = 10.9 Hz), 131.6 (d, J = 2.7 Hz), 130.1, 129.0, 128.3 (d, J = 12.0 Hz), 126.9 (d, J = 90.1 Hz), 124.8, 112.6, 56.6 (d, J = 103.0 Hz), 55.2, 20.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{30}O_2PS^+$ 533.1699; Found 533.1707.

*1-(4-Nitrophenyl)-2-(p-tolylthio)-2-(triphenylphosphaneylidene)-ethan-1-one (**7g**).* 187 mg (95%) of **7g** was obtained as an orange solid after column chromatography [hexanes/EtOAc (7:3)]. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.9 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.64−7.52 (m, 9H), 7.47−7.38 (m, 6H), 7.00 (d, J = 8.3 Hz, 2H), 6.94 (d, J = 8.1 Hz, 2H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.3 (d, J = 15.1 Hz), 147.8, 147.7 (d, J = 11.2 Hz), 139.5 (d, J = 2.0 Hz), 134.3, 133.7 (d, J = 9.5 Hz), 132.2 (d, J = 2.8 Hz), 129.3, 128.8, 128.6 (d, J = 12.2 Hz), 125.6 (d, J = 90.3 Hz), 124.6, 122.7, 59.0 (d, J = 99.9 Hz), 20.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{27}NO_3PS^+$ 548.1444; Found 548.1453.

*1-(4-Bromophenyl)-2-(p-tolylthio)-2-(triphenylphosphaneylidene)ethan-1-one (**7h**).* 195 mg (93%) of **7h** was obtained as a pale yellow solid after column chromatography [hexanes/EtOAc (7:3)]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.5 Hz, 2H), 7.62−7.53 (m, 6H), 7.50 (td, J = 7.3, 1.6 Hz, 3H), 7.38 (td, J = 8.0, 2.4 Hz, 8H), 7.03 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.1 Hz, 2H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.9 (d, J = 14.2 Hz), 140.0 (d, J = 2.2 Hz), 139.6 (d, J = 11.1 Hz), 134.0, 133.6 (d, J = 9.4 Hz), 131.8 (d, J = 3.0 Hz), 130.4, 129.8, 129.1, 128.4 (d, J = 12.1 Hz), 126.2 (d, J = 90.2 Hz), 124.6, 123.3, 57.6 (d, J = 101.4 Hz), 20.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{27}BrOPS^+$ 581.0698; Found 581.0694.

*1-(4-Fluorphenyl)-2-(p-tolylthio)-2-(triphenylphosphaneylidene)-ethan-1-one (**7i**).* 180 mg (96%) of **7i** was obtained as a pale yellow solid after column chromatography [hexanes/EtOAc (7:3)]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 8.7, 5.7 Hz, 2H), 7.52 (ddd, J = 12.1, 8.3, 1.3 Hz, 6H), 7.45 (dd, J = 7.6, 1.8 Hz, 3H), 7.34 (td, J = 7.6, 3.1 Hz, 6H), 7.00 (d, J = 8.2 Hz, 2H), 6.92−6.84 (m, 4H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.7 (d, J = 14.1 Hz), 163.2 (d, J = 247.9 Hz), 140.1 (d, J = 2.2 Hz), 136.7 (dd, J = 11.1, 3.0 Hz), 133.9, 133.6 (d, J = 9.5 Hz), 131.7 (d, J = 2.9 Hz), 130.3 (d, J = 8.3 Hz), 129.0, 128.3 (d, J = 12.1 Hz), 126.4 (d, J = 90.1 Hz), 124.6, 114.0 (d, J = 21.2 Hz), 57.2 (d, J = 101.9 Hz), 20.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.07 (t, J = 8.0 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{27}FOPS^+$ 521.1499; Found 521.1510.

https://doi.org/10.1021/acs.joc.1c00114
J. Org. Chem. 2021, 86, 5954−5964

*Synthesis of Selenophosphoranes (**7c,d, 7j−n**).* To a 25 mL flask containing **1c** (1.0 equiv, 0.32 mmol, 100 mg) and the appropriate phosphorus ylene (1.2 equiv, 0.384 mmol) was added CH_2Cl_2 (5.0 mL). The mixture was stirred until a solution was observed (approximately 5 min); then, Et_3N (20.0 equiv, 6.4 mmol, 0.9 mL) was added. The reaction was monitored by TLC and, after consumption of the starting material, diluted with CH_2Cl_2 (20 mL), transferred to a separation funnel, and then washed with a NH_4Cl saturated solution (2 × 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed *in vacuo*. The crude compounds were purified by column chromatography.

*1-(Phenylselanyl)-1-(triphenylphosphoranylidene)propan-2-one (**7c**).* 121 mg (80%) of **7c** was obtained as a yellow solid after column chromatography [hexanes/EtOAc (8:2)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.44 (m, 9H), 7.37 (dd, J = 7.5, 3.1 Hz, 6H), 7.29 (d, J = 7.1 Hz, 2H), 7.12 (t, J = 7.1 Hz, 2H), 7.07 (t, J = 7.1 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.06 (d, J = 10.3 Hz), 138.13 (d, J = 2.1 Hz), 133.59 (d, J = 9.4 Hz), 131.60 (d, J = 2.9 Hz), 128.44, 128.22 (d, J = 12.2 Hz), 127.41, 127.24 (d, J = 90.6 Hz), 125.07, 52.29 (d, J = 96.2 Hz), 26.73 (d, J = 8.0 Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 338.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}OPSe^+$ 475.0725; Found 475.0725.

*2-(Phenylselanyl)-2-(triphenylphosphoranylidene)acetonitrile (**7d**).* 105 mg (72%) of **7d** was obtained as a yellow oil after column chromatography [hexanes/EtOAc (6:4)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 77.63−7.33 (m, 15H), 7.28−7.23 (m, 2H), 7.05−6.97 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 135.4, 132.7 (d, J = 9.6 Hz), 131.8 (d, J = 3.0 Hz), 128.1, 127.9 (d, J = 12.3 Hz), 127.4, 124.9, 124.6 (d, J = 91.9 Hz); ^{77}Se NMR (57 MHz, $CDCl_3$) δ 339.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ 28.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}NPSe^+$ 458.0571; Found 458.0574.

*1-Phenyl-2-(phenylselanyl)-2-(triphenylphosphaneylidene)-ethan-1-one (**7j**).* 161 mg (94%) of **7j** was obtained as a pale yellow solid after column chromatography [hexanes/EtOAc (7:3)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.0, 1.7 Hz, 2H), 7.59 (ddd, J = 12.2, 7.1, 1.7 Hz, 6H), 7.48 (td, J = 7.3, 1.6 Hz, 3H), 7.37 (td, J = 7.7, 3.0 Hz, 6H), 7.30−7.22 (m, 5H), 7.12−7.01 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.6 (d, J = 10.5 Hz), 141.7 (d, J = 11.1 Hz), 138.6 (d, J = 2.0 Hz), 133.7 (d, J = 9.4 Hz), 131.7 (d, J = 3.0 Hz), 128.9, 128.4, 128.3 (d, J = 12.2 Hz), 127.6 (d, J = 89.5 Hz), 127.5, 127.5, 126.6, 125.1, 52.8 (d, J = 93.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 343.6. The data match with the previously described compound.[46]

*1-(4-Methoxyphenyl)-2-(phenylselanyl)-2-(triphenylphos-phaneylidene)ethan-1-one (**7k**).* 150 mg (83%) of **7k** was obtained as a pale yellow solid after column chromatography [hexanes/EtOAc (7:3)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.7 Hz, 2H), 7.59 (ddd, J = 12.1, 8.4, 1.3 Hz, 6H), 7.51−7.44 (m, 3H), 7.41−7.33 (m, 6H), 7.29 (d, J = 6.9 Hz, 2H), 7.14−7.02 (m, 3H), 6.77 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.5 (d, J = 10.3 Hz), 160.5, 138.8 (d, J = 1.9 Hz), 133.9 (d, J = 11.2 Hz), 133.7 (d, J = 9.4 Hz), 131.7 (d, J = 2.9 Hz), 130.2, 128.5, 128.4 (d, J = 12.2 Hz), 127.4, 127.4 (d, J = 90.7 Hz), 125.2, 112.5, 55.2, 51.9 (d, J = 94.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.8; ^{77}Se NMR (77 MHz, $CDCl_3$) δ 344.6. The data match with the previously described compound.[46]

*1-(4-Nitrophenyl)-2-(phenylselanyl)-2-(triphenylphosphaneyl-idene)ethan-1-one (**7l**).* 180 mg (97%) of **7l** was obtained as a pale yellow solid after column chromatography [hexanes/EtOAc (7:3)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 7.60 (ddd, J = 12.3, 8.4, 1.3 Hz, 6H), 7.54−7.48 (m, 3H), 7.40 (td, J = 7.8, 3.2 Hz, 6H), 7.20 (dd, J = 8.0, 1.6 Hz, 2H), 7.13−7.04 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.4 (d, J = 11.5 Hz), 148.8 (d, J = 11.8 Hz), 147.5, 137.6 (d, J = 1.9 Hz), 133.6 (d, J = 9.5 Hz), 132.1 (d, J = 3.0 Hz), 128.6, 128.6, 128.4 (d, J = 12.2 Hz), 127.2, 126.0 (d, J = 90.7 Hz), 125.4, 122.5, 54.2 (d, J = 91.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 340.0. The data match with the previously described compound.[46]

*1-(4-Bromophenyl)-2-(phenylselanyl)-2-(triphenylphosphaneyl-idene)ethan-1-one (**7m**).* 183 mg (93%) of **7m** was obtained as a pale yellow solid after column chromatography [hexanes/EtOAc (7:3)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.53 (m, 8H), 7.48 (td, J = 7.4, 1.7 Hz, 3H), 7.36 (ddd, J = 8.7, 6.7, 3.4 Hz, 8H), 7.26−7.21 (m, 2H), 7.11−7.01 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.2 (d, J = 10.8 Hz), 140.6 (d, J = 11.4 Hz), 138.2 (d, J = 1.9 Hz), 133.6 (d, J = 9.5 Hz), 131.8 (d, J = 2.8 Hz), 130.2, 129.8, 128.5, 128.3 (d, J = 12.2 Hz), 127.3, 126.6 (d, J = 90.6 Hz), 125.2, 123.0, 52.9 (d, J = 93.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.5; ^{77}Se NMR (77 MHz, $CDCl_3$) δ 342.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{25}BrOPSe^+$ 614.9986; Found 614.9991.

*1-(4-Fluorphenyl)-2-(phenylselanyl)-2-(triphenylphosphaneyl-idene)ethan-1-one (**7n**).* 152 mg (86%) of **7n** was obtained as a pale yellow solid after column chromatography [hexanes/EtOAc (7:3)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.5, 5.7 Hz, 2H), 7.62 (dt, J = 12.2, 8.0 Hz, 6H), 7.55−7.47 (m, 3H), 7.40 (td, J = 7.7, 3.0 Hz, 6H), 7.30 (d, J = 7.4 Hz, 2H), 7.11 (dt, J = 12.8, 6.8 Hz, 3H), 6.95 (t, J = 8.7 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.1 (d, J = 10.7 Hz), 163.1 (d, J = 247.9 Hz), 138.3 (d, J = 1.9 Hz), 137.7 (dd, J = 11.5, 3.5 Hz), 133.6 (d, J = 9.5 Hz), 131.7 (d, J = 2.9 Hz), 130.2 (d, J = 8.3 Hz), 128.5, 128.3 (d, J = 12.0 Hz), 127.3, 126.8 (d, J = 90.7 Hz), 125.2, 113.9 (d, J = 21.3 Hz), 52.5 (d, J = 93.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.5; ^{77}Se NMR (77 MHz, $CDCl_3$) δ 343.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{25}FOPSe^+$ 555.0787; Found 555.0795.

*Synthesis of 2-(p-Tolylthio)acetonitrile (**3n**) from **7b** Using a Boron Trifluoride Diethyl Etherate Complex.* To a 25 mL dried flask under argon containing **7b** (1.0 equiv, 0.227 mmol, 100 mg) was added THF (5.0 mL). The mixture was stirred at room temperature for 5 min, and $BF_3{\cdot}Et_2O$ (2.0 equiv, 0.45 mmol, 56 μL) was added. The mixture was heated to reflux in an oil bath, and the reaction was monitored by TLC. After consumption of the starting material, it was diluted with CH_2Cl_2 (20 mL), transferred to a separation funnel, and then washed with a $NaHCO_3$ saturated solution (2 × 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed *in vacuo*. The crude compound was purified by column chromatography [hexanes/EtOAc (9:1)] to yield 29 mg (77%) of **3n** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 6 Hz, 2H), 7.12 (d, J = 6 Hz, 2H), 3.43 (s, 2H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 169.4, 136.1, 130.8, 129.9, 128.8, 60.5; 35.1, 31.5, 20.0. The data match with the previously described compound.[47]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00114.

FAIR data, including the primary NMR FID files, for compounds **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3i**, **3m**, **3n**, **5a**, **5b**, **5c**, **5d**, **5e**, **5f**, **5g**, **5h**, **7a**, **7b**, **7c**, **7d**, **7e**, **7f**, **7g**, **7h**, **7i**, **7j**, **7k**, **7l**, **7m**, and **7n** (ZIP)

Copies of ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra (PDF)

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https://doi.org/10.1021/acs.joc.1c00114
J. Org. Chem. 2021, 86, 5954−5964

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support for this work was provided by CNPq, CAPES, and FACEPE. I.M.R.M. and B.G.S. are thankful for their FACEPE-CNPq fellowships. P.H.M is also thankful for his CNPq fellowship.

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