Mechanistic Aspects of the Phosphine-Catalyzed Isomerization of Allenic Sulfones to 2-Arylsulfonyl 1,3-Dienes

Carissa S. Hampton and Michael Harmata*

Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, United States

Supporting Information

ABSTRACT: When an allenic sulfone is treated with a phosphine nucleophile and a proton shuttle, an isomerization to a 2-arylsulfonyl 1,3-diene occurs. Mechanistic aspects of the process were investigated leading to the formulation of a mechanism for the reaction. Some further optimization studies of this process are reported.



■ INTRODUCTION

In 1988, both the Trost and Lu groups simultaneously reported the isomerization of α,β -alkynones to conjugated (E,E)- α,β : γ,δ dienones by palladium and ruthenium catalysis, respectively.¹ This reaction was performed stereoselectively, resulting in the formation *E,E*-dienones. The mechanism proposed for the process suggested a hydridometal species and the formation of an allene as an intermediate in the isomerization (Scheme 1). The isomerization was initially thought to require transitionmetal catalysis to induce the rearrangement.

Scheme 1. Proposed Mechanism for the Isomerization of Alkynones Catalyzed by a Metal-Hydride Complex



In 1992, Trost and Kazmaier reported that the same isomerization could be performed by phosphine catalysis alone.² The reaction was highly chemoselective, requiring an alkyne conjugated to the carbonyl group. Observations supported a mechanistic path involving a series of prototopic shifts induced by nucleophilic addition of the phosphine to the triple bond as presented in Scheme 2.³

A similar type of isomerization was demonstrated in the mid-1990s in which acetylenic phosphorus compounds were isomerized by palladium catalysis⁴ and then separately by phosphine catalysis⁵ (Scheme 3). Mechanistic proposals were similar to that shown above for the carbonyl compounds.

Guo and Lu's reinvestigation of the isomerization of acetylenic carbonyl compounds found that the catalytic





Scheme 3. Isomerization of Acetylenic Phosphorus Compounds



isomerization could be differentiated into two types: a reaction that is catalyzed by phosphines alone or a reaction in which a transition metal is required. Thus, phosphines and transition metals play a different role in the isomerization of acetylenic compounds.⁶

During a study of the functionalization of allenic sulfones, we discovered two new reactions.⁷ When an allenic sulfone was treated under palladium catalysis, a 1-arylsulfonyl 1,3-diene was formed, but when treated under nucleophilic catalysis, using a phosphine in the presence of a proton transfer agent, a 2-arylsulfonyl 1,3-diene was isolated (Scheme 4).

The isomerization of an allenic sulfone to a 1-arylsulfonyl 1,3-diene is similar to the isomerization of allenic and acetylenic carbonyl compounds^{1a,8} and acetylenic phosphorus compounds^{4,9} previously reported. The ability of these carbonyl and phosphorus derivatives to isomerize solely by phosphine catalysis is possible because these functional groups do not behave as leaving groups. This is the key to the regiodivergent

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Scheme 4. Regiodivergent Synthesis of 1- and 2-Arylsulfonyl 1,3-Dienes



nature of our reactions. The sulfone functional group can act as a leaving group,¹⁰ thereby generating a new product when an allenic sulfone is treated with a nucleophile such as a phosphine in the presence of a proton shuttle. However, prior to our work, the isomerization to the 2-arylsulfonyl 1,3-diene had no precedent in the literature to the best of our knowledge. We recently reported the discovery of this reaction⁷ and herein report our studies of the mechanism of this process and further examination of its reaction parameters.

RESULTS AND DISCUSSION

Examination of Reaction Parameters. As we previously described,⁷ the best catalyst system for the conversion of aryl allenic sulfones to 2-arylsulfonyl 1,3-dienes was a mixture of triphenylphosphine (20 mol %) as the nucleophile and phenol (20 mol %) as a proton shuttle agent. The scope of this reaction was examined with several substrates; the products formed along with their yields are shown in Figure 1.⁷



Figure 1. 2-Arylsulfonyl-1,3-dienes prepared via isomerization.

The results shown in Figure 1 were obtained with a catalyst loading of 20 mol %. We wondered if the process might be improved and thus pursued limited optimization of the reaction, using the triphenylphosphine and phenol reactants that were initially successful using allene 17 as our substrate. The control conditions employed 20 mol % of triphenylphosphine and phenol in THF at a 0.1 M concentration of allene starting material and were varied from there.

We first examined the effect of concentration and catalyst loading. Diluting the reaction concentration to 0.05 M (based on 17) led to a significant increase in yield although the reaction required a slightly longer time of 1.5 h to complete (Table 1, entry 2). Lower and higher concentrations proved detrimental to the yield of the process (Table 1).

Table 1. Concentration Effects on the Phosphine-Catalyzed Conversion of 17 to 19^a

	Ts Me Me 17	PPh ₃ , Phenol THF, reflux Me 19	
entry	conc (M)	time (h)	yield (%)
1	0.025	3	59
2	0.05	1.5	82
3	0.075	1.2	70
4	0.10	1	68
5	0.15	0.67	57
6	0.25	0.67	54

 $^a{\rm The}$ reactions were conducted with 20 mol % of catalyst and cocatalyst.

While the isomerization proceeded with as little as 5 mol % of triphenylphosphine (Table 2, entry 2), the reaction did not

Table 2. Effects of Catalyst Loading on the Phosphine-Catalyzed Reaction a

	Ts Me PPh ₃ , Ph Me THF, rei	enol flux Me 19	
entry	catalyst loading (mol %)	time (h)	yield (%)
1	2.5	24	ь
2	5.0	25	62
3	10.0	1.5	83
4	20	1	68
		1	

^aThe reactions were conducted at 0.1 M. b 17 was recovered in 73% yield.

proceed at all at half that amount of catalyst (Table 2, entry 1). However, the yield peaked at 10 mol % of phosphine and phenol (Table 2, entry 3) with more catalyst resulting in a lower yield of the target diene (Table 2, entry 4).

Next, the effect of solvent on the reaction was examined. THF was the solvent we used initially and we found that it was the best solvent for the nucleophilic isomerization among the solvents we examined, giving 19 in 68% yield in 1 h (Table 3, entry 1). The only other comparable solvent was tert-butyl methyl ether, which afforded a 63% yield of 19 after reflux for 2 h at 55 °C. All other solvents either required longer reaction times or afforded decreased yields of the product. It is also noteworthy that this reaction is able to proceed in water with no addition of a proton-transfer agent, as the water serves this purpose. This is similar to the reports by Xue¹¹ and Li¹² of triphenylphosphine-catalyzed reactions in aqueous solutions. Under these conditions the reaction is complete within 3 h (Table 3, entry 8) but the yield is low (42%). Using a mixed solvent system of THF/H₂O (1:8) to increase solubility, with water as the proton-transfer agent in the absence of phenol, gave a yield of 63% of the diene 19 in only 2 h at reflux temperature (Table 3, entry 9).

During the course of these studies, the role of the phosphorus catalyst was surveyed by using different trivalent phosphorus compounds. In the phosphine-catalyzed isomer-

Table 3. Solvent Effects on the Phosphine-Catalyzed Reaction^a

	Ts Me Me 17	le PPh ₃ , Phenol	Ts Me 19	
entry	solvent	temp (°C)	time (h)	yield (%)
1	THF	65	1	68
2	toluene	80	7.5	53
3	DMF^{b}	80	1	35
4	DMC ^c	90	2.5	52
5	TBME ^d	55	2	63
6	MeCN	82	4.75	57
7	CH_2Cl_2	40	9	39
8	H_2O^e	100	3	42
9	THF:H ₂ O ^{e,f}	100	2	63

^{*a*}The reactions were conducted with 20 mol % of triphenylphosphine and phenol at 0.1 M. ^{*b*}DMF = N_iN -dimethylformamide. ^{*c*}DMC = dimethyl carbonate. ^{*d*}TBME = *tert*-butyl methyl ether. ^{*e*}No phenol was used in this reaction; water is the proton-transfer agent. ^{*f*}THF/H₂O = 1:8.

izations of acetylenic carbonyls, the proposed mechanisms show the addition of the phosphine to the acetylene followed by proton transfer with an acidic compound such as phenol.³ The phosphorus catalyst must be chosen in consideration of both steric and electronic effects.¹³ The nature of steric and electronic effects of trivalent phosphine ligands was detailed in a review by Tolman in 1977.¹³ The steric environment of a trivalent phosphorus ligand could be evaluated by determining the approximate amount of "space" the ligand consumes about a metal center, referred to as the cone angle.^{13,14} The electronic properties of phosphorus ligands could be ranked on the basis of the change in the CO stretching frequency of monosubstituted transition metal carbonyls, which can be quantified.^{13,15}

The results of using different trivalent phosphorus catalysts are shown in Table 4. When the more nucleophilic tri-*n*-

 Table 4. Effect of the Phosphine/Phosphite on the

 Nucleophilic Reaction

	Ts Me Me 17	Phosphine(ite Phenol (20 THF, reflu	e) (20 mol%) 0 mol%), Ix, 0.1 M	Ts Me 19
entry	phosphi	ne(ite)	time	yield (%)
1	PPh ₃		1 h	68
2	PBu ₃		12 min	40
3	Р(<i>p</i> -(ОМ	$e)C_{6}H_{4})_{3}$	15 min	77
4	$P(p-tol)_3$		20 min	84
5	$P(o-tol)_3$		29 h	а
3	PCy ₃		26 h	Ь
4	P(Oi-Pr) ₃		29 h	с
a	1 : 500	· · · · · b· -	,	: 0.404 : 11 61

^{*a*}17 was recovered in 50% yield. ^{*b*}17 was recovered in 84% yield. ^{*c*}17 was recovered in 71% yield.

butylphosphine was used, the reaction was complete within 12 min but with a large sacrifice in yield (Table 4, entry 2). It is possible that oligomeric products were formed as in the report by Trost and Kazmaier,² but these were not pursued. The reactions employing tris(*p*-methoxyphenyl)phosphine and tri*p*-tolylphosphine were completed quickly and in yields comparable to that of simple triphenylphosphine. Although tricyclohexylphosphine is formally more nucleophilic than triphenylphosphine from an electronic perspective, steric effects appear to dominate in this case. The cone angle of PCy₃ is 170° , while that of triphenylphosphine is 145° . Steric effects thus slow the reaction significantly such that after 26 h 84% of 17 was recovered (Table 4, entry 3). The sterically hindered tri*o*-tolylphosphine with a cone angle of 194° also failed to produce any diene product. In addition, less nucleophilic trivalent phosphites such as triisopropyl phosphite failed to catalyze the reaction, with 71% of 17 being recovered after 29 h at reflux (Table 4, entry 4). These results correlate well with Trost and Kazmaier's work.²

At the suggestion of a reviewer, we have also examined a selection of proton shuttle agents. We observed that the more acidic the proton shuttle source the longer the time required for complete consumption of starting material and the lower the yields (Table 5, entries 1 and 2). Phenols with an acidity similar

Table 5. Examination of Proton Shuttle Agents

	Ts Me PPh ₃ (Me proton shu 17 THF, re	(20 mol%) ttlle (20 mol%) flux, 0.1 M	9
entry	proton shuttle	time (h)	yield (%)
1	AcOH	5	31
2	$4-(NO_2)C_6H_4OH$	15	43
3	PhOH	1	68
4	2,6-di-MeC ₆ H ₃ OH	1.3	75
5	3,5-di-MeC ₆ H ₃ OH	1.3	66
6	4-(OMe)C ₆ H ₄ OH	4.5	56
7	BHT ^a	4	54
^a BHT = 2,6-di- <i>tert</i> -butyl-4-methylphenol.			

to that of phenol, such as 3,5-dimethylphenol and the slightly more hindered 2,6-dimethylphenol, produced the diene in similar yields in relatively the same amount of time (Table 5, entries 4-5). In addition, the use of a sterically hindered phenol significantly slowed the reaction and lowered the yield (Table 5, entry 7).

After these studies with 17, the best conditions included a 10 mol % loading of triphenylphosphine and phenol at 0.1 M in THF at reflux. This improved the yield of **19** to 83% as compared to 68% in our original work (Scheme 5).⁷

Scheme 5. Optimum Reaction Conditions for the Phosphine-Catalyzed Formation of 19					
	PPh ₃ (10 mol %)	-			
	PhOH (10 mol %)	Is			



While these reaction conditions appeared ideal for 17, it is likely that the other dienes would also experience an increase in yield when treated under these reaction conditions. Therefore, a few allenic sulfones were reacted, and the results are shown in Table 6. It was seen that the results were varied. For dienes 19 and 29 the yield was increased by $\sim 20\%$, whereas for 28 the yield was almost the same as in our earlier study, and for the heteroaromatic 24, the yield actually decreased slightly relative to our original results. This outcome is not unexpected because

Table 6. Comparison of Reaction Conditions



entry	product	conditions	time	yield (%)
1	19	Α	1h	68
2	19	В	1.5h	83
3	24	А	35 min	71
4	24	В	1.5h	61
5	28	А	15 min	68
6	28	В	50 min	64
7	29	Α	45 min	63
8	29	В	1.5h	83

these conditions were optimized for a single allene example and there may be other factors that influence the reaction for other allenes.

It should also be noted that this reaction can proceed in the presence of sulfinate anions and a proton shuttle without phosphine to initiate the reaction. The competition between phenol and p-toluenesulfinate as nucleophiles and the insolubility of the sodium sulfinate salt in the THF solvent led to a drastic reduction in the rate of reaction. This problem was presumably exacerbated due to the depletion of the proton shuttle, the phenol, which was consumed via nucleophilic attack on the allene, resulting in the formation of 30. As a result, while some of the diene 19 was formed, the vinyl ether 30 and other unidentifiable products were produced as well. All of these side products had the same R_f value on TLC and could not be separated by column chromatography and were thus not rigorously characterized. This process improved when BHT was used in place of phenol. Steric factors reduced the tendency for nucleophilic attack on the allene, thus allowing the BHT to act as a simple proton shuttle. The reaction could be completed within 36 h in this case, but at only a 60% yield (Scheme 6).

Scheme 6. Sulfinate-Promoted Generation of a 2-Arylsulfonyl 1,3-Diene



Mechanistic Studies. A sulfone group can act as both a leaving group and a nucleophile, whereas a carbonyl group cannot. The phosphine-catalyzed reaction that we discovered is thus a beautiful example of the "chameleon" nature of the sulfone group.^{8,10,16} In contrast to the 1-substituted-1,3-diene obtained from alkynes or allenes bearing functional groups such as carbonyls^{2,3,6,17} or pentavalent phosphorus functionalities,^{5,18} when an allenic sulfone is treated under phosphine catalysis in the presence of a proton-transfer agent, a 2-arylsulfonyl 1,3-diene is generated. The phosphine-catalyzed isomerization of acetylenic and allenic carbonyls and acetylenic and allenic phosphorus compounds is initiated by addition of the

phosphine to the electrophilic unsaturation and, through a series of proton shifts and elimination, results in an isomerization. Addition of phosphines to unsaturated bonds has also been used to catalyze other reactions as well.¹⁹ A similar type of addition has been reported in the sulfonylation of an unsaturated bond.²⁰

In due consideration of what was known in the literature, we proposed the mechanism shown in Scheme 7 for the

Scheme 7. Proposed Mechanism of the Phosphine-Catalyzed Reaction



phosphine-catalyzed generation of 2-arylsulfonyl 1,3-dienes from allenic sulfones. For the formation of **19**, nucleophilic addition of triphenylphosphine to **17** produces the sulfonylstabilized carbanion **31**, which then deprotonates phenol to produce **32** (Scheme 7). Elimination of a *p*-tolylsulfinate anion to afford the phosphonium salt **33** is achieved by deprotonation of **32** by phenoxide. This is the critical step in generating the small amounts of *p*-tolylsulfinate ion required to produce **19**.^{20d,e,21} Thus, nucleophilic addition of the *p*-tolylsulfinate anion to **17** produces **34**. This is followed by a protonation/ deprotonation sequence (the proton shuttle) that leads to **19** (Scheme 7).

Crossover Experiments. In order to support our proposed mechanism of the phosphine-catalyzed reaction, a mixture of two allenes with different aryl groups and different alkyl substituents, chosen so that we could easily differentiate the products, was treated under standard reaction conditions with triphenylphosphine and phenol. An intramolecular sulfone transposition should lead to only two products, but a mixture of four products should be obtained if free sulfinate anions are generated during the course of the transformation as we had proposed, assuming they were productively involved in generating the products. In the event, the reaction of a 1:1 mixture of 36 and 37 afforded a mixture of all four possible 2arylsufonyl 1,3-dienes (Scheme 8A). The percentages represent percent composition based on ¹H NMR analysis of the crude reaction mixture (compared with spectra of the pure compounds prepared individually), not absolute yields, as the dienes were inseparable. This result implies that after conjugate addition of triphenylphosphine to the allene a sulfinate anion is liberated. This may attack other allene molecules liberating more sulfinate anions and generating the 2-arylsulfonyl 1,3-

Scheme 8. Nucleophilic Crossover Reactions^a



^aPercentages represent composition, not isolated yields.

dienes. This process was also examined with another mixture of allenes, 17 and 38 (Scheme 8B). Again, all four possible diene products were generated in this crossover reaction.

Since we have shown that the reaction could proceed in the presence of *p*-toluenesulfinate hydrate and BHT,⁷ this would imply that the sulfinate ions necessary to advance the reaction must come as a result of expulsion after the addition of the sulfinate anion to the allene.^{20d,e,21,22} Therefore, if a sulfinate that differed from the sulfone group on the allene was employed, two different diene products should be produced, one containing a sulfone group from the added sulfinate anion and the other containing the sulfone group initially on the allene. To examine this hypothesis, the reaction of **37** with sodium *p*-toluenesulfinate hydrate was performed and did indeed lead to both dienyl products **19** and **24** (Scheme 9).

Scheme 9. Sulfinate Crossover Reaction



After 3 days the reaction was still not complete, so it was stopped and the components were analyzed. On the basis of the amount of p-toluenesulfinate used, **19** was formed in 94% yield, and based on the amount of **37** recovered, **24** was formed in 68% yield.

Reaction Intermediates. In an attempt to identify intermediates in the proposed mechanism, we wanted to pursue the isolation and/or identification of phosphonium salts (i.e., **32**) from the left-hand side of the proposed mechanism (Scheme 7). In order for this to work, once the phosphine adds to the allene further reaction must be avoided. To this end, 1 equiv of phosphine was added to a solution of **17** in the presence of 10 mol % of phenol. The reaction was stopped after

30 min in an attempt to isolate a phosphonium phenoxide salt of **32** or a phosphonium sulfinate salt of **33** (Scheme 10).

Scheme 10. Attempted Isolation of a Reaction Intermediate



A crude ³¹P NMR of the phosphine/phenol-catalyzed reaction showed three different phosphorus peaks (Figure 2).



Figure 2. Crude ³¹P NMR of the phosphine-catalyzed reaction.

The peak at -4.75 ppm corresponds to the literature value of triphenylphosphine,²³ and the peak at 29.7 ppm corresponds to the literature value of triphenylphosphine oxide.²⁴ At 22.43 ppm, there is a very small phosphorus peak that we have assigned to either **32** or the vinyl phosphonium ion **33**. This chemical shift compares very closely to the vinyl phosphonium salts prepared by Arisawa and Yamaguchi in their report of the metal-catalyzed addition of triphenylphosphine and methane-sulfonic acid to alkynes.²⁵ For example, they reported that treatment of **39** with triphenylphosphine, methanesulfonic acid, and tetrakis(triphenylphosphine)palladium (0), followed by anion exchange with lithium hexafluorophosphate, generated the vinyl phosphonium salt **40** (Scheme 11). This compound

Scheme 11. Preparation of Vinyl Phosphonium Salts from Alkynes



displays a peak at 24.3 ppm in the ³¹P NMR. Other examples of similar reactions generate vinyl phosphonium salts with phosphorus peaks in the range of 13.7–25.2 ppm. Therefore, our proposal here is reasonable. Even in the shortened reaction time in Scheme 10, the small amount of phenol in the solution allows the reaction to continue and diene formation to occur. All attempts to isolate the phosphonium salts **32** and/or **33** were unfruitful.

During the reaction shown in Scheme 10, a compound much more polar than 17 or 19 was visualized by TLC analysis. This compound was isolated in 12% yield and was determined to be the disulfone 41, a proposed intermediate in the right-hand side of the proposed mechanism (Scheme 7). The isolation of 41 was interesting, but we needed to be sure that this intermediate could lead to dienyl products. To examine this possibility, 41 could be prepared directly by the reaction of 17 with sodium *p*toluenesulfinate and *p*-toluenesulfonic acid in a yield of 88%. This disulfone could then be converted to diene 19 by treatment with in situ-generated sodium phenoxide (from phenol and sodium hexamethyldisilylamide) in THF in 20 min in 91% yield (Scheme 12).



In an effort to prepare a vinyl phosphonium salt that was isolable, we developed a process similar to that performed by Arisawa and Yamaguchi but that did not require a precious metal.²⁵ Nucleophilic addition of triphenylphosphine to an electrophilic allene could lead to a salt if the initial adduct could be guenched. We reasoned that the use of p-toluenesulfonic acid would interrupt the reaction because the tosylate conjugate base would not be basic enough to deprotonate a compound like 32 (see Scheme 7) at the methyl group. This would prevent any further reaction so that formation of a phosphonium sulfonate salt would be possible. We thus treated 17 with 1 equiv of triphenylphosphine in the presence of 1 equiv of p-toluenesulfonic acid. The crude product from this reaction was then treated with potassium hexafluorophosphate in ethanol to effect anion exchange upon which a white solid precipitated (Scheme 13). This was the phosphonium salt 42,

Scheme 13. Formation of the Phosphonium Salt 42



which was identified by NMR and an X-ray crystal structure. At room temperature, the methylene group of **42** has a hindered rotation and the peaks are broadened so significantly in the ¹H NMR that they almost blend in with the baseline. If the probe is cooled to 253 K, the peaks can be resolved, each to a broad doublet of doublets with different chemical shifts. The ³¹P NMR chemical shift of **42** is 23.6 ppm for the phosphonium ion, which also correlates well with Arisawa and Yamaguchi's vinyl phosphonium salts as well as the peak proposed to be either **32** or **33** in the spectrum presented in Figure 2.

If **42** is an intermediate in the overall process, it should lead to a dienyl product under the appropriate conditions. Thus, the phosphonium salt **42** was treated with potassium phenoxide, generated in situ from phenol and potassium carbonate; then **37** was added to the reaction and the mixture was stirred for 6 days at reflux (Scheme 14). Both **19** and **24** were formed in the reaction, indicating that it is possible for the *p*-toluenesulfinate





anion to be expelled from the phosphonium salt and to add to other allenes present in solution to produce dienes. The sparse solubility of potassium carbonate in THF may be the cause of the long reaction time, and it is possible that the reaction is taking place on the surface of the potassium carbonate. We therefore used sodium hexamethyldisilazide, a soluble base, to deprotonate the phenol to promote the reaction of the phosphonium salt to dienyl products (Scheme 14). This proved much more effective in rapidly producing dienyl products. We therefore conclude that the phosphonium salt 42 is a viable intermediate in the reaction pathway leading to the diene products that are observed and that it is likely to be an intermediate in the formation of diene 19 as detailed in Scheme 7.

CONCLUSION

The evidence we have obtained supports the proposed nucleophile-catalyzed mechanism for the formation of 2-arylsulfonyl 1,3-dienes from the corresponding allenic sulfones. Crossover experiments support the generation of free sulfinate anions in the process. The fact that both **41** and **42** lead to diene products supports the idea that they are intermediates in the process. ³¹P NMR evidence supports the generation of **32** and/or **33** as intermediates in the catalytic cycle. Although we have not pursued it, we note that the synthesis of **42** represents a potentially general way of producing vinylphosphonium salts in a straightforward fashion without the need for transition-metal catalysis.

EXPERIMENTAL SECTION

All reactions were carried out in oven-dried glassware and cooled in a desiccator prior to use. Tetrahydrofuran (THF) was purchased and distilled from sodium benzophenone prior to use. The starting allenes were prepared by methods akin to those introduced by Toru, Sharpless, Braverman, and Harmata.²⁶ All reactions were monitored by thin-layer chromatography (TLC) on glass-backed silica gel plates with fluorescent UV indicator. Flash chromatography was carried out using 230-400 mesh silica gel with HPLC-grade solvents. Unless stated otherwise, all commercially available reagents were used as received. All compounds were characterized by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy using either a 300, 500, or 600 MHz spectrometer. Proton spectra were reported in δ units, parts per million (ppm), relative to trimethylsilane internal standard (0.00 ppm). Carbon spectra were reported in ppm relative to deuterated chloroform (77.0 ppm). ³¹P NMR spectra were obtained on a 250 MHz spectrometer at 101.25 MHz in CDCl₃ with H_3PO_4 (δ 80.0 ppm) as an external reference. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a FT-IR spectrometer. High-resolution mass spectra were acquired on a FTICR-MS with ESI.

Procedure for Isomerization. To an oven-dried round-bottom flask with an argon balloon was added the catalyst (phosphorus reagent or sulfinate salt, 20 mol % unless otherwise stated), co-catalyst (phenol, 20 mol % unless otherwise stated), and dry solvent (0.1 M, unless otherwise stated). Then the allenic sulfone was added to the reaction flask and heated to reflux. The reaction was monitored by TLC (15% EtOAc/hexanes). Either upon reaction completion or prolonged reaction time with no change in TLC, the reaction was cooled to room temperature. Water was added to the reaction flask, and the mixture was extracted three times with CH_2Cl_2 . The organic layers were combined and washed with water and brine. The solution was dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation. The crude residue was purified by column chromatography (5% EtOAc/hexanes) to isolate **19**.

Procedure for Nucleophilic Crossover Experiments. In an oven-dried round-bottom flask with an argon balloon were dissolved phenol (0.011 g, 0.120 mmol, 20 mol %) and triphenylphosphine (0.032 g, 0.120 mmol, 20 mol %) in dry THF (6.0 mL). Then 1-methyl-4-((3-methylbuta-1,2-dien-1-yl)sulfonyl)benzene 17 (0.067 g, 0.300 mmol) and 2-((2-cyclohexylidenevinyl)sulfonyl)thiophene 38 (0.076 g, 0.300 mmol) were added to the reaction flask and heated to reflux. After 45 min at reflux, the reaction was cooled to room temperature. Water was added to the reaction flask, and the mixture was extracted with CH₂Cl₂ three times. The organic layers were combined and washed with dilute NaOH, water, and brine. The solution was dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation. The crude mixture was analyzed by ¹H NMR.

Procedure for Sulfinate Crossover Experiment. In an ovendried round-bottom flask with an argon balloon were dissolved BHT (2,6-di-tert-butyl-4-methylphenol, 0.021 g, 0.093 mmol, 20 mol %) and sodium *p*-toluenesulfinate (0.027 g, 0.140 mmol, 30 mol %) in dry THF (9.3 mL). Then 2-((3-methylbuta-1,2-dien-1-yl)sulfonyl)thiophene 37 (0.100 g, 0.467 mmol) was added to the reaction flask and the mixture heated to reflux. After 3 days at reflux, the reaction was cooled to room temperature. Water was added to the reaction flask, and the mixture was extracted with CH_2Cl_2 three times. The organic layers were combined and washed with dilute NaOH, water, and brine. The solution was dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation. The crude product was purified by flash column chromatography (5% EtOAc/hexanes) to yield a mixture of 1.0:0.9 mixture of 24 (68% brsm)/19 (94% based on TsNa) and recovered starting material (0.024 g, 24%).

4,4'-(3-Methylbut-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (41). In an oven-dried round-bottom flask were dissolved 1-methyl-4-((3-methylbuta-1,2-dien-1-yl)sulfonyl)benzene 17 (0.100 g, 0.4498 mmol), p-toluenesulfonic acid monohydrate (0.0801 g, 0.4498 mmol), and sodium p-toluene sulfinate hydrate (0.0736 g, 0.4498 mmol) in THF (4.5 mL) and the mixture heated to reflux for 5 h until complete consumption of starting material by TLC (25% EtOAc/hexanes). Water was added to the reaction flask, and the mixture was extracted with CH2Cl2 three times. The organic layers were combined and washed with brine. The solution was dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation. The crude product was purified by flash column chromatography (15% EtOAc/ hexanes) to yield 41 in 88%: ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 4.54 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 2.11 (s3H), 2.04 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 158.7, 145.1, 144.0, 139.2, 136.6, 129.9, 129.6, 128.5, 127.7, 127.6, 56.1, 25.9, 23.4, 21.7, 21.6; IR (cm⁻¹) 3023, 2919, 1616, 1592, 1493, 1441, 1398, 1318, 1298, 1219, 1183, 1135, 1084, 817, 754, 714, 659; HRMS m/z calcd for $(C_{19}H_{22}O_4S_2)Na^+$ 401.0852, found 401.0849.

Conversion of 41 to 19. In a oven-dried round-bottom flask was dissolved phenol (0.0373 g, 0.396 mmol) in dry THF (3.5 mL), sodium hexamethyldisilylamide (0.037 mL, 0.0376 mmol, 1.0 M in THF) was added, and the mixture was stirred for 20 min. Then a solution of **41** (0.150 g, 0.396 mmol) in dry THF (0.5 mL) was added to the reaction flask and the mixturew heated to reflux for 20 min and monitored by TLC (25% EtOAc/hexanes). The reaction was cooled

to room temperature, diluted with CH_2Cl_2 , and washed with brine. The organic layer was dried over anhydrous sodium sulfate, concentrated by rotary evaporation, and purified by column chromatography (10% EtOAc/hexanes) to yield **19** in 91%.

Formation of Phosphonium salt 42. (3-Methyl-1-tosylbut-2en-2-yl)triphenylphosphonium Hexafluorophosphonate (42). In an oven-dried round-bottom flask were dissolved 1-methyl-4-((3methylbuta-1,2-dien-1-yl)sulfonyl)benzene 17 (0.500 g, 2.249 mmol), triphenylphosphine (0.590 g, 2.249 mmol), and ptoluenesulfonic acid hydrate (0.387 g, 2.249 mmol) in dry THF (22.5 mL), and the mixture was heated to reflux for 9 h until the triphenylphosphine was no longer visible by TLC analysis. The reaction was then cooled to room temperature and concentrated by rotary evaporation. Crude NMR was acquired. The crude reside was then dissolved in absolute ethanol (22.5 mL), and potassium hexafluorophosphate (0.621 g, 3.374 mmol) was added. The reaction was stirred at room temperature for 4 h (a precipitate began forming at 2 h). The reaction was filtered over filter paper and washed with absolute ethanol. The solid material was dissolved in chloroform and filtered over filter paper, rinsing with chloroform. The filtrate was concentrated by rotary evaporation to yield the phosphonium salt 42 (1.07 g, 75%) as a white solid (mp = 212-213 °C): ¹H NMR (300 MHz, CDCl₃, at 253 K) δ 7.96-7.65 (m, 15H), 7.32-7.20 (m, 4H), 4.71 (t, J = 18.6 Hz, 1H, diastereotopic CH₂), 3.52 (t, J = 13.5 Hz, 1H, diastereotopic CH₂), 2.55 (d, J = 1.5 Hz, 3H), 2.40 (s, 3H), 1.79 (d, J = 1.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 174.6 (m), 145.5, 135.6, 134.8, 134.6 (d, J = 10.0 Hz), 130.3 (d, J = 12.5 Hz), 130.1, 127.4, 119.0 (d, J = 87.5 Hz), 101.9 (d, J = 87.5 Hz), 56.4 (d, J = 13.8 Hz), 29.3 (d, J = 8.8 Hz), 26.6 (d, J = 12.5 Hz), 21.6; ³¹P NMR $(101.25 \text{ MHz}, \text{CDCl}_3) \delta - 143.8 (\text{PF}_6, \text{ septet}, J = 712.8 \text{ Hz}), 23.6; \text{ IR}$ (cm⁻¹) 3060, 3019, 2966, 2921, 1593, 1487, 1434, 1401, 1311, 1213, 1144, 1103, 1037, 997, 829, 751; HRMS m/z calcd for $(C_{30}H_{30}O_2PS)^+$ 485.1698, found 485.1695.

Procedure for Crossover of 42 with 37. In a oven-dried roundbottom flask was dissolved phenol (0.003 g, 0.033 mmol) in dry THF (2 mL), sodium hexamethyldisilylamide (0.032 mL, 0.032 mmol, 1.0 M in THF) was added, and the mixture was stirred for 20 min. Then a solution of **42** (0.064 g, 0.102 mmol) in dry THF (0.5 mL) was added to the reaction flask and the mixture heated to reflux for 20 min. The solution was cooled slightly, and a solution of **37** (0.034 g, 0.159 mmol) in dry THF (0.5 mL) was added. The reaction was then heated to reflux again and monitored by TLC (20% EtOAc/hexanes). The reaction was cooled to room temperature, diluted with CH₂Cl₂, and washed with brine. The organic layer was dried over anhydrous sodium sulfate, concentrated by rotary evaporation, and purified by column chromatography (7–10% EtOAc/hexanes) to yield an inseparable mixture of **24:19** that was analyzed by ¹H NMR.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02097.

NMR data for compounds **41** and **42** and NMR of reaction mixtures of crossover experiments (PDF) X-ray crystal structure data of **42** (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: harmatam@missouri.edu.

Notes

The authors declare no competing financial interest.

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