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Rhodium-catalyzed thiophosphinoylation reaction of 1,2-dienes with diphosphine disulfides

Mieko Arisawa, Masahiko Yamaguchi [*,†]

Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University, Aoba, Sendai 980-8578, Japan

A R T I C L E I N F O

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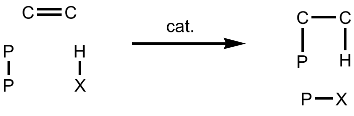
A B S T R A C T

In the presence of $RhH(PPh_3)_4$, the reaction of 1,2-alkadienes, tetramethyldiphosphine disulfide, and camphorsulfonic acid gave (*E*)-2-dimethylthiophosphinoyl-2-alkenes. The reaction involved the P–P cleavage and the transfer of the thiophosphinoyl group to 1,2-alkadienes with concomitant formation of thiophosphinic anhydride.

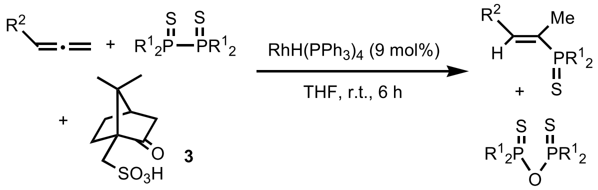
We have been developing transition-metal-catalyzed methods for the synthesis of organophosphorus compounds, in particular, the addition reaction and the C–H substitution reaction for the formation of C–P bond.[1] For the former reaction, we previously reported the rhodium- and palladium-catalyzed synthesis of phosphonium salts by the addition of triarylphosphines to alkynes,[2] 1,2-dienes,[3] 1,3-dienes,[4] and alkenes.[5] As for the latter, the rhodium-catalyzed reaction of 1-alkynes and tetraphenyldiphosphine in the presence of a nitrobenzene gave 1-phosphinoyl-1-alkynes.[6] This reaction proceeded via the metal-catalyzed addition of the P–P bond with the nitrobenzene followed by the C–H substitution of the 1-alkyne. We considered the P–P bond cleavage method by transition metal catalysis to be attractive, because such reaction can be extended to the development of organophosphorus synthesis using inexpensive elemental phosphorus. Thus, understanding the metal-catalyzed P–P bond cleavage and the reactivity of the resulted metal intermediates was required.[7] Described in this study is the rhodium-catalyzed reaction of 1,2-alkadienes and tetraalkyldiphosphine disulfides in the presence of camphorsulfonic acid giving (*E*)-2-dialkylthiophosphinoyl-2-alkenes. The three-component reaction involved the cleavage of the P–P bond and the addition of the thiophosphinoyl group to an unsaturated compound with the concomitant formation of thiophosphinic anhydride (Scheme 1). A few C–P bond-forming reactions by P–P bond cleavage and transfer to alkynes have been reported under radical or metal-catalyzed conditions,[8] and such catalyzed reaction with 1,2-dienes was not known.[9]



Scheme 1.

When an equimolar mixture of 1,2-undecadiene **1**, tetramethyldiphosphine disulfide **2**, and camphorsulfonic acid **3** in THF was treated with $RhH(PPh_3)_4$ (9 mol %) at room temperature for 6 h, (*E*)-2-dimethylthiophosphinoyl-2-undecene **4** was obtained in 83% yield (Table 1, entry 2). Catalyst decomposition appeared to compete with the C–P bond formation, and less catalyst loading resulted in lower yields. The stereochemistry was determined by the presence of NOE between the 1-methyl protons and 4 methylene protons. The P–H coupling constant with the olefinic proton coupling constant $^3J = 24$ Hz was also consistent with this stereochemistry. Since the (*E*)-isomer was selectively obtained at low

Table 1
Rhodium-catalyzed dialkylthiophosphinoylation reaction of 1,2-dienes



Entry	R^1	R^2	Yield (%)
1	Me	n-C_6H_{13}	82
2		n-C_8H_{17}	83
3		$Ph(CH_2)_2$	79
4		$Ph(CH_2)_4$	74
5		$PhCO_2(CH_2)_2$	74
6		$PhCO_2(CH_2)_3$	89
7		n-$C_4H_9(C_2H_5)CH$	91
8	Et	n-C_8H_{17}	87
9	n-Pr	n-C_8H_{17}	90

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* Corresponding author.
E-mail address: yama@mail.pharm.tohoku.ac.jp (M. Yamaguchi).

[†] WPI Advanced Institute for Materials Research, Tohoku University, Aoba, Sendai, Japan.

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conversion, it was suggested to be a kinetic product. Camphorsulfonic acid was recovered in more than 90% yield, which was confirmed by the ^{1}H NMR analysis of the crude product with the addition of an authentic sample. Notably, dimethylthiophosphinic anhydride **5** was isolated in 80% yield, the structure of which was confirmed by ^{31}P NMR at δ 87.5, being consistent with the reported values.[10] EI-MS analysis results showed the parent peak, which gave a correct elemental analysis ($C_4H_{12}OP_2S_2$).

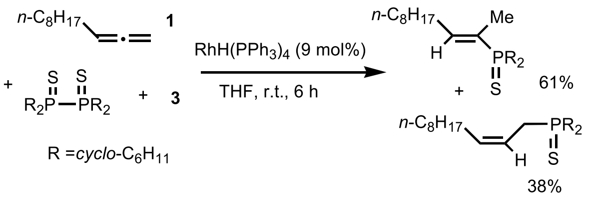
When less than 1 equiv of **3** was used, the yield decreased with poor reproducibility. Comparable results were obtained with other acids, methanesulfonic acid (85%), *p*-chlorobenzenesulfonic acid (63%), and *p*-toluenesulfonic acid monohydrate (74%). A trace amount of **4**, however, was obtained in the presence of trifluoromethanesulfonic acid. The reaction was applied to several 1,2-dienes with primary and secondary alkyl groups as shown in Table 1. Tetraethyl- and tetrapropyldiphosphine disulfides[11] gave the corresponding (*E*)-2-dialkylthiophosphinoyl-2-alkenes at 87% and 90% yields, respectively, which were accompanied by the dialkylthiophosphinic anhydrides.

The reaction of a bulky diphosphine, tetracyclohexyldiphosphine disulfide, resulted in a lower yield of the product along with an isomer (*Z*)-1-thiophosphinoyl-2-alkene in 38% yield (Scheme 2). The structure of the byproduct suggested its formation by the P–H addition of HPS(*cyclo*-C_6H_{11})$_2$. The involvement of a different mechanism in this reaction from the above reaction was also supported by the lack of thiophosphinic anhydride. Tetraphenyldiphosphine and its dioxide did not give the organophosphorus compounds.

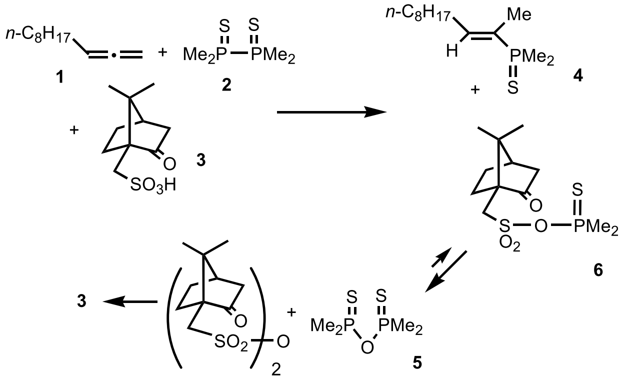
When **2** and **3** were treated in THF at room temperature for 6 h in the absence and presence of RhH(PPh_3)$_4$ (9 mol %), **2** and **3** were recovered quantitatively as indicated by ^{1}H NMR. It was not likely that $HPSMe_2$ was the reactive intermediate in this reaction. The regioselectivity in the C–P bond formation did not coincide with the hydrophosphinoylation mechanism, since the nickel- and palladium-catalyzed P–H addition reactions to 1,2-dienes were reported to give allylphosphorus compounds.[12] An exception was reported only in an ytterbium-catalyzed reaction.[13] The results suggested that P–P bond cleavages, transfer of the thiophosphinoyl group to 1,2-diene, and acid anhydride formation took place on the rhodium metal.

The present reaction involved the transfer of a thiophosphinoyl group to 1,2-dienes, and the fate of the other thiophosphinoyl group was a subject of interest. It is likely that what was initially formed was a mixed anhydride **6** of **3** and dimethylthiophosphinic acid, which then underwent disproportionation giving **5** and camphorsulfonic anhydride (Scheme 3). The latter anhydride was hydrolyzed to **3**, although the origin of water was unclear. Use of 20 mol % camphorsulfonic acid in the presence of varying amounts of water decreased the yield, and the acid could not be catalytic. Various attempts failed to detect camphorsulfonic anhydride and mixed anhydride **6**.

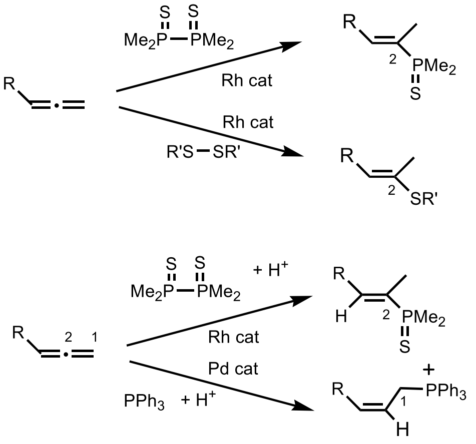
We previously reported that a rhodium-catalyzed reaction of organic disulfides with 1,2-alkadienes gave (*E*)-2-alkylthio-2-alkenes (Scheme 4).[14] The same regio- and stereoselectivities were observed in the rhodium-catalyzed C–P and C–S bond-forming reactions via P–P and S–S bond cleavage, although the reactive heteroatom species could be different, diphosphine and thiol. Another notable feature of this reaction was the difference from the palladium-catalyzed phosphine addition reaction to 1,2-dienes previously reported.[3] The C–P bond was formed at the 1-carbon of 1,2-dienes in the phosphine addition, whereas the C–P bond was formed at the 2-carbon in the present reaction. The origin of the different orientation may be ascribed to the difference in the metal, or alternatively, the difference in the phosphorous group.



Scheme 2.



Scheme 3.



Scheme 4.

In summary, a rhodium complex catalyzed the three-component reaction of tetraalkyldiphosphine disulfide, 1,2-dienes, and camphorsulfonic acid giving (*E*)-2-thiophosphinoyl-2-alkenes. The rhodium catalyst is involved in the P–P bond cleavage, transfer of the phosphorous group, and anhydride formation. It may be interesting that a thermodynamically high-energy compound of acid anhydride was formed as the product of the metal-catalyzed reaction.

Synthesis of (E)-2-dimethylthiophosphinoyl-2-undecene **4**: In a two-necked flask were placed 1,2-undecadiene (0.125 mmol, 19.0 mg), tetramethylbiphosphine disulfide **2** (0.125 mmol, 23.3 mg), anhydrous (*R*)-(−)-camphor-10-sulfonic acid **3** (0.125 mmol, 29.0 mg), and RhH(PPh_3)$_4$ (9 mol %, 13 mg) in distilled THF (1 mL) under an argon atmosphere, and the solution was stirred at room temperature for 6 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give **4** (25.6 mg, 83%) and dimethylthiophosphinic anhydride **5** (10.1 mg, 0.05 mmol, 80% based on **2**) as pale yellow oil.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.10.075.

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