Diphosphanylethenes

Synthesis of (*E*)-1,2-Diphosphanylethene Derivatives from Alkynes by Radical Addition of Tetraorganodiphosphane Generated In Situ**

*Akinori Sato, Hideki Yorimitsu, and Koichiro Oshima**

Organophosphorus compounds serve as reagents, ligands for transition metals, biologically active substances, and building blocks of nanoarchitectures, and thus play vital roles in organic chemistry. Among them, (*E*)-1,2-bis(diphenylphosphanyl)ethene has recently attracted increasing attention in the field of self-assembly.[1] Construction of hierarchical structures for use as new functional materials[2] calls for derivatives of (*E*)-1,2-bis(diphenylphosphanyl)ethene that have functional groups to induce further assembly. However, there are a limited number of methods for the synthesis of such peculiar diphosphanylethene skeletons; these syntheses are always carried out under harsh and/or strongly basic conditions.[3] Highly efficient and mild reactions affording (*E*)-1,2-bis(diphenylphosphanyl)ethene derivatives are therefore required.

Here we report a general, facile, and reliable synthesis of (*E*)-diphosphanylethene derivatives starting from an alkyne and a tetraorganodiphosphane. Radical addition of a tetraorganodiphosphane across a C–C triple bond seems to be a straightforward strategy for the synthesis of 1,2-diphosphanylethenes.[4,5] However, tetraorganodiphosphanes are so sensitive to oxygen that their preparation, purification, and handling are quite difficult and must be carried out under a strictly inert atmosphere.[6] The inherent instability of diphosphanes in the presence of oxygen poses a serious problem in their synthetic use. The present diphosphanylation reaction employs a tetraorganodiphosphane that is cleanly generated in situ prior to the reaction. The high efficiency of this method will allow the 1,2-diphosphanylethenes synthesized to be applicable in organic materials science.

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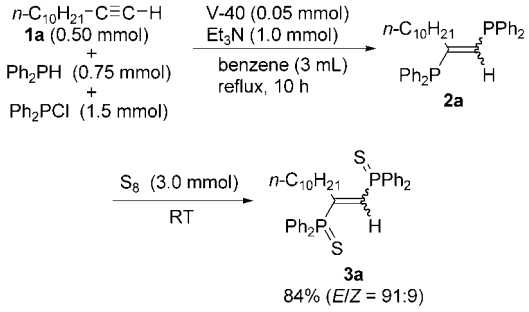
A mixture of 1-dodecyne (**1a**), diphenylphosphane,[7] chlorodiphenylphosphane, triethylamine, and 1,1′-azobis(cyclohexanecarbonitrile) (V-40)[8] was heated in boiling benzene for 10 h (Scheme 1). The product was isolated as a 91:9 mixture of *E* and *Z* isomers of phosphane sulfide **3a** in 84% yield. These two stereoisomers were separable from each other by thorough chromatographic purification on silica gel.



Scheme 1.

The presence of an excess of chlorodiphenylphosphane is essential for the success of the reaction: the use of a smaller amount (1.0 mmol) of chlorodiphenylphosphane gave (1-dodecenyl)diphenylphosphane sulfide (**4**, 9%, $E/Z = 18:82$) along with **3a** (78%, $E/Z = 90:10$). Complete conversion of diphenylphosphane to tetraphenyldiphosphane is important to avoid contamination by monoadduct **4**.

Tetraphenyldiphosphane is commercially available. However, the reaction of **1a** (0.75 mmol) with the purchased tetraphenyldiphosphane[9] (1.5 mmol) yielded both **3a** (60%, $E/Z = 88:12$) and **4** (27%, $E/Z = 37:63$). It is worth noting that addition of chlorodiphenylphosphane to the reaction mixture suppressed the generation of **4**, and generated **3a** (87%, $E/Z = 89:11$) selectively.

A variety of terminal alkynes undergo this radical diphosphanylation reaction (Table 1). Aryl-substituted acetylenes react with tetraphenyldiphosphane prepared in situ to yield 1-aryl-1,2-bis(diphenylthiophosphanyl)ethenes in excellent yield with high stereoselectivity (entries 1–5). The *E* configuration of the major isomer of **3c** was determined by X-ray crystallographic analysis (see the Supporting information). Purification of **2b** under argon allowed us to isolate this compound in 78% yield ($E/Z = 92:8$). Ester (entries 3 and 7), iodo (entry 4), keto (entry 5), and thioester (entry 8) moieties remained unchanged under the reaction conditions; these groups are not tolerated in the conventional incorporation of a diphenylphosphanyl group which requires the use of a highly nucleophilic and basic metal diphenylphosphide.[3] Gratifyingly, an carbon(sp^3)–halogen bond was also stable during the reaction, although **1j** is prone to form the corresponding Wittig salt (entry 9). Tetracyclohexyldiphosphane, prepared in situ from dicyclohexylphosphane[7] and chlorodicyclohexylphosphane, added to **1b** in a similar fashion to afford (*E*)-**3b′** in excellent yield after careful separation from contaminants such as (*Z*)-**3b′** (Scheme 2).

The reactions with *tert*-butylacetylene failed to yield the desired product, and internal alkynes such as diphenylacety-

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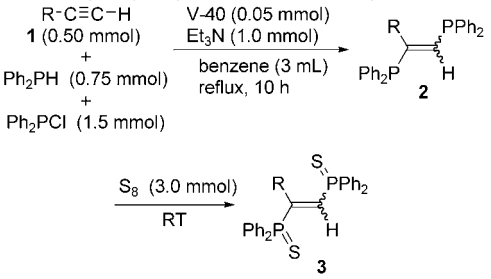
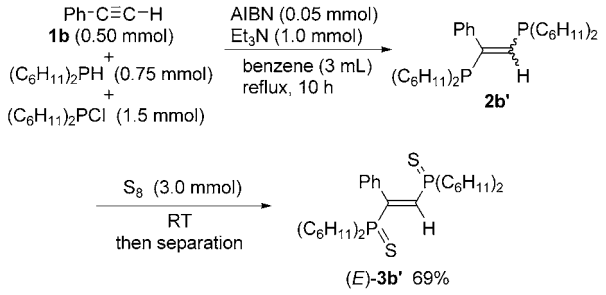
Table 1: Radical diphosphanylation of terminal alkynes.



Entry	**3**	R	Yield [%][a]	*E*/*Z*[a]
1	**3b**	Ph	87 (96)[b]	93:7
2	**3c**	*p*-$MeOC_6H_4$	89	94:6
3	**3d**	*p*-$MeOC(O)C_6H_4$	95	94:6
4	**3e**	*p*-IC_6H_4	83	94:6
5	**3f**	*p*-AcC_6H_4	96	95:5
6	**3g**	$PhCH_2OCH_2CH_2CH_2$	78	90:10
7	**3h**	$EtOC(O)(CH_2)_6$	86	90:10
8	**3i**	$AcS(CH_2)_9$	80	90:10
9	**3j**	$Cl(CH_2)_9$	86	91:9

[a] Determined by ^{31}P NMR spectroscopy with $(MeO)_3P{=}O$ as internal standard. [b] Performed on a 5.0-mmol scale.

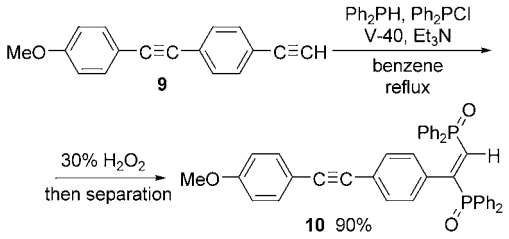


Scheme 2.

lene and 6-dodecyne also remained intact. Under the same reaction conditions 4-pentyn-1-ol or 3-butyn-2-one gave complex mixtures containing small amounts of the desired products.

The reaction clearly proceeds via a radical pathway, as demonstrated in Scheme 3. The formation of **5** necessitates addition of a phosphorus-centered radical[10] followed by 5-*exo-dig* radical cyclization. Isomerization of **6** to **7** reduces the steric hindrance in the cyclization, and subsequent radical S_H2 substitution[11] affords the doubly phosphinated diene.[12]

The high efficiency of this reaction might offer a reliable method for the synthesis of organic compounds for use in single-molecule devices, self-assembled monolayers (Table 1, entry 8), or optically intriguing organic materials. Scheme 4 illustrates the synthesis of a new fluorescent compound **10** which exhibits a couple of intense absorption bands in the UV region ($\lambda_{max} = 302$, 320 nm; $\varepsilon = 2.0 \times 10^4\,M^{-1}cm^{-1}$ for both) and blue fluorescence ($\lambda_{max} = 469$ nm) upon irradiation at 302 or 320 nm.



Scheme 4.

In summary, we have developed a highly efficient and concise diphosphanylation reaction for terminal alkynes. The radical addition of a tetraorganodiphosphane to an alkyne affords 1,2-diphosphanylethenes in good yield with high *E* selectivity. The required tetraorganodiphosphane was readily prepared by mixing a diorganophosphane and a chlorodiorganophosphane in situ in the presence of triethylamine, which allowed us to avoid the troublesome isolation of tetraorganodiphosphane. The mild reaction conditions offer excellent functional-group compatibility and hence provide a powerful tool for the synthesis of important compounds by introducing two phosphorus atoms in one shot.

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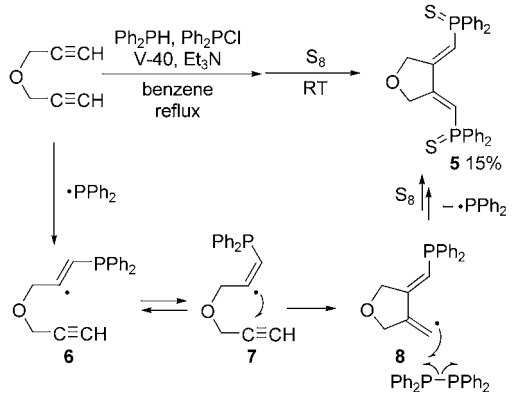

Scheme 3.

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[7] *Caution: Liquid diorganophosphanes undergo very rapid oxidation in air. They are highly pyrophoric, especially when wiped with a tissue in air.*
[8] Use of AIBN decreased the yield slightly by 10%.
[9] Obtained from Aldrich. Diphosphane from Acros Co. led to a similar result. Note that ^{1}H NMR analysis of the purchased $Ph_2P{-}PPh_2$ revealed no detectable amount of $HPPh_2$ in the commercial material.
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[12] Along with **5**, the crude mixture contained several byproducts, which could not be exactly identified. 2,3-Bis(diphenylthiophosphanyl)-2-propenyl propargyl ether seemed to be the main byproduct.

