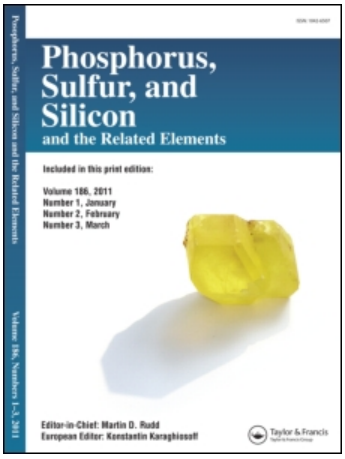

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DIETHYL ETHYNYLPHOSPHONATE: A VERSATILE SYNTHON FOR THE PREPARATION OF 1-ALKYNYL- AND 1,3-BUTADIY NE-1,4-DIYLPHOSPHONATES

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DIETHYL ETHYNYLPHOSPHONATE: A VERSATILE SYNTHON FOR THE PREPARATION OF 1-ALKYNYL- AND 1,3-BUTADIYNE-1,4-DIYLPHOSPHONATES

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The cross-coupling reaction between diethyl ethynylphosphonate (**1**) and several aromatic iodides under the Sonogashira conditions ($Cl_2Pd(PPh_3)_2$ / CuI / Et_3N) gives only minute amounts of the expected 1-alkynylphosphonates. Yields of about 20% are achieved upon using $Pd(OAc)_2$ / 2 PPh_3 / Et_3N in place of the previous catalytic system. Side-reactions involving **1** and the amine are shown to be responsible for these low yields. Metalation of **1** with EtMgBr and *t*-BuLi has been carried out and the M-C≡C-P(O)$(OEt)_2$ (M = MgBr, Li) derivatives have been characterized *via* reaction with Me_3SiCl or Ph_3SiCl. The easy access to the organolithium compound has made possible the synthesis of the zinc analog (M = ZnCl) which reacts with aromatic iodides (C_6H_5I, *p*-$MeOC_6H_4I$, *p*-$O_2NC_6H_4I$, *p*-IC_6H_4I, 2-iodothiophene), in the presence of $Pd(PPh_3)_4$, to give diethyl 1-alkynylphosphonates in reasonable yields. Oxidative dimerization of **1** under the Hay conditions (CuCl / TMEDA-acetone / air) gives the symmetrical diacetylenic diphosphonate $(EtO)_2(O)P$-C≡C-C≡C-P(O)$(OEt)_2$ in high yield.

Keywords: Diethyl ethynylphosphonate; diethyl 1-alkynylphosphonates; diacetylenic diphosphonates; C_{sp}-H activation; cross-coupling reactions; magnesium, lithium and zinc reagents

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INTRODUCTION

1-Alkynylphosphonates R-C≡C-P(O)$(OR')_2$ are convenient starting materials for the preparation of vinylphosphonates[1–3] and have been used as substrates in halogenopalladation,[4] cyclization,[5,6] and Michael-type addition reactions.[1,7–9] Also, the triple bond present in these molecules is amenable to coordination to a transition metal fragment,[10] and transformation of the phosphonate group into the corresponding phosphonic acid functionality, followed by reaction of this group with a suitable metal salt, brings about the possibility of preparing layered materials with interesting properties.[11]

Various methods have been published in the literature concerning the synthesis of 1-alkynylphosphonates. The first method (Scheme 1) consists of heating at a fairly high temperature an alkynyl halide R-C≡C-X and a trialkylphosphite (Michaelis-Arbuzov reaction).[12] When the alkynyl halide is not reactive enough, a catalyst ($NiCl_2$) must be used to promote the reaction.[13]

$$R{-}C{\equiv}C{-}X + P(OR')_3 \xrightarrow{\Delta} R{-}C{\equiv}C{-}P(O)(OR')_2 + R'X$$

SCHEME 1

Another way of preparing 1-alkynylphosphonates is by nucleophilic attack of $(R'O)_2(O)PNa$ onto R-C≡C-X (Scheme 2).[14]

$$R{-}C{\equiv}C{-}X + (R'O)_2(O)PNa \longrightarrow R{-}C{\equiv}C{-}P(O)(OR')_2 + NaX$$

SCHEME 2

One major limitation of these two reactions, however, is that some alkynyl bromides are known to be explosive.[15]

A third route consists of allowing a metal acetylide to react with an halogenophosphate (Scheme 3).[1,6,9,15,16]

$$R{-}C{\equiv}C{-}M + XP(O)(OR')_2 \longrightarrow R{-}C{\equiv}C{-}P(O)(OR')_2 + MX$$

M = Li, MgBr
X = Cl, F

SCHEME 3

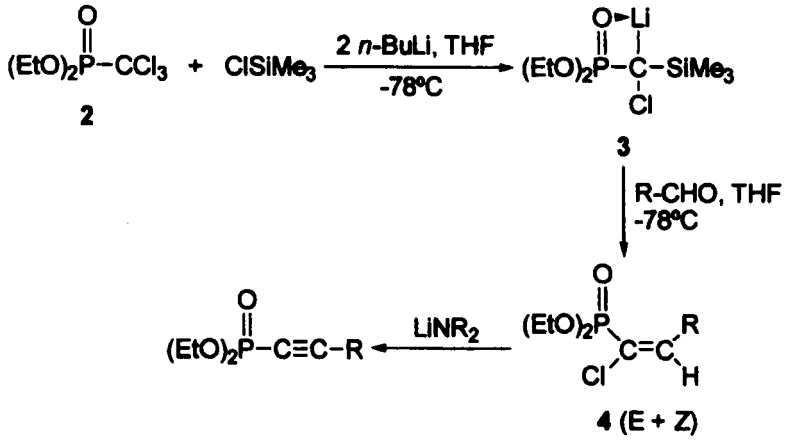
This method of preparation gives poor to good yields depending on the reagents and is restricted to phosphonates for which the starting alkyne is available.

The acetylene-allene-acetylene rearrangement of dialkylpropargylphosphites can also be employed to synthesize 1-alkynylphosphonates, but the scope of this reaction is rather limited.[17]

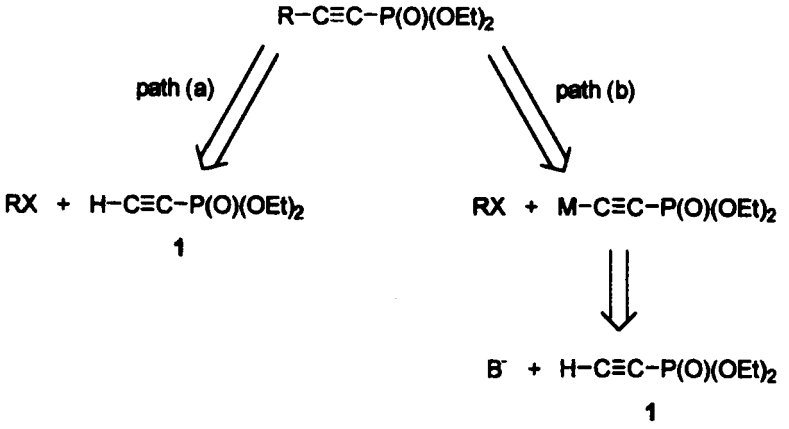
A common feature of these methods is that they all involve the formation of the C_{sp}- phosphorus bond from reagents containing a carbon-carbon triple bond. A different strategy consists of elaborating the carbon-carbon triple bond within a molecule that already possesses a carbon-phosphorus bond. This approach has been followed by several groups.[18,19] In particular, Savignac and co-workers have described a most elegant and powerful method that gives high yields (87–96%) of 1-alkynylphosphonates (Scheme 4):[19a] first, a mixture of trichloromethylphosphonate **2** and chlorotrimethylsilane is allowed to react with 2.1 equivalents of *n*-butyllithium yielding the corresponding α-phosphorylated α-silylated α-chlorinated carbanion **3**. The second step consists in the reaction between carbanion **3** and an aldehyde, resulting in the formation of a α-silylated α-chlorinated β-lithiated hydroxyphosphonate which, *via* a Peterson olefination process, spontaneously and quantitatively eliminates to give an isomeric mixture of the two expected α-chlorovinylphosphonates **4**. Deprotonation of vinylphosphonate **4** with one equivalent of a lithium dialkylamide and elimination of LiCl from the intermediate anion furnish the corresponding 1-alkynylphosphonate.

Our synthetic approach is different from those described above in that it consists of making the C_{sp}-R bond. Two different paths have been considered to carry out such reaction (Scheme 5).

Path (a) is the most straightforward route to 1-alkynylphosphonates and involves selective metal-catalyzed cross-coupling of a terminal alkyne with an aromatic halide. Alternatively, C_{sp}-R bond formation may be accomplished by metal-catalyzed cross-coupling of an anionic species with an aromatic halide (path (b)). Path (a) and path (b) both require the use of diethyl ethynylphosphonate H-C≡C-P(O)$(OEt)_2$ (**1**) as a key starting compound. Path (b) presents the additional difficulty that it necessitates the preparation of the Grignard or organoalkali metal reagents derived from **1**, and attempts to do so have proven to be problematic in the past.[9] Alkyne **1** also offers the advantage that symmetrical diacetylenic



SCHEME 4

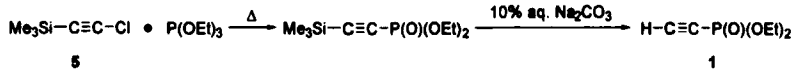


SCHEME 5

phosphonates can be prepared from it through metal-promoted C_{sp}-C_{sp} bond formation.

RESULTS AND DISCUSSION

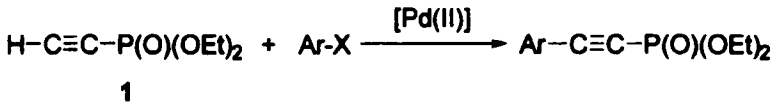
The key precursor H-C≡C-P(O)$(OEt)_2$ (**1**) is synthesized from 1-trimethylsilyl-2-chloroacetylene (**5**) by following the method described by Burt and Simpson (Scheme 6).[12d]



SCHEME 6

Chloroalkyne **5** is prepared in good yield (90%) from *trans*-dichloroethylene using the procedure reported by West and Quass.[20] The overall yield for the transformation **5** → **1** is 81%.

We originally thought of preparing 1-alkynylphosphonates *via* path (a) by using a palladium(II) complex to generate the catalytic species (Scheme 7).



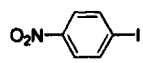
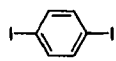
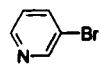
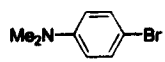
SCHEME 7

Preliminary studies were carried out with the catalytic system developed by Sonogashira and co-workers, *i.e.* $Cl_2Pd(PPh_3)_2$ (5% molar) / CuI (10% molar) / Et_3N (solvent).[21] The typically used secondary amines diethylamine and diisopropylamine were replaced by triethylamine as these amines add across the triple bond of R-C≡C-P(O)$(OEt)_2$.[1,6,7,9] Three parameters were modified in these experiments, *i.e.*, the nature of the aromatic ring, the nature of the halogen attached to the aromatic ring, and the reaction temperature. Five substrate molecules were tested, namely bromobenzene, iodobenzene, 2-bromothiophene, 2-iodothiophene, and *p*-diiodobenzene. Stirring these halides in the presence of Sonogashira's catalyst, at room temperature, for periods ranging from sixteen hours to six days, did not furnish the expected products and various amounts of unchanged **1** were recovered. Heating the above iodides at temperatures between 45 and 85°C, for periods ranging from two hours to overnight, did produce small amounts of the desired cross-coupling products and led to complete disappearance of **1** in the case of the experiments run overnight.

The Sonogashira reaction being quite sensitive to the nature of the ligands borne by the palladium center and to the presence of coordinating species in solution, we thought of using the catalytic system developed by

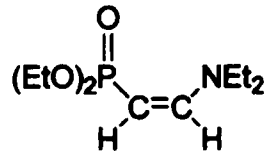
Dieck and Heck, *i.e.* $Pd(OAc)_2$ / 2 PPh_3 / Et_3N.[22] When iodobenzene and 2-iodothiophene are used as substrates, the desired products are obtained in about 20% yield after purification by column chromatography (Table I). 3-Bromopyridine gives similar results but the coupling product cannot be isolated by column chromatography. In the case of *p*-diiodobenzene, the monosubstituted product *p*-IC_6H_4-C≡CP(O)$(OEt)_2$ is obtained in 18% yield. An analysis of the crude reaction mixture by ^{31}P NMR spectroscopy indicates that the disubstituted product *p*-$(EtO)_2P(O)C{\equiv}C$-C_6H_4-C≡CP(O)$(OEt)_2$ has also formed and its amount is estimated to be 7–8%. The best results are observed with *p*-iodonitrobenzene (35%); the presence of an electron-withdrawing group on the aromatic ring favors the coupling reaction as previously noted by Dieck and Heck.[22a] On the other hand, the coupling reaction does not occur when *p*-bromo-*N,N*-dimethylaniline is used as a substrate.

TABLE I Reaction of H-C≡C-P(O)$(OEt)_2$ with Aromatic Halides[a]

Entry	*Ar-X*	*Temperature / Reaction time*	*Yield (%)*[b]
1		65°C / 4 h	21
2		65°C / 12 h	20
3		85°C / 2 h	35
4		85°C / 24 h	18[c]
5		85°C / 24 h	20[d]
6		85°C / 24 h	0

[a]Catalyst: $Pd(OAc)_2$ (5% molar), PPh_3 (10% molar), Et_3N (solvent).
[b]Yields are given for isolated products.
[c]The yield is that of *p*-$IC_6H_4C{\equiv}CP(O)(OEt)_2$. A ^{31}P NMR analysis showed that 7–8% of disubstituted product was present in the crude reaction mixture.
[d]Determined by ^{31}P NMR spectroscopy. The cross-coupling product could not be purified by column chromatography.

Some additional comments concerning this reaction must be made: we have observed that the ^{31}P NMR spectra of the crude reaction mixtures were all very similar, *i.e.*, three signals with roughly the same intensities were present. The signal corresponding to the desired coupling product ($\delta = -5$ to -10 ppm) was accompanied by two additional resonances at +18 and +29 ppm. These additional signals were not observed in the coupling reactions carried out under the Sonogashira conditions. The exact nature of the compounds giving rise to these resonances has not been clearly established, but the following can be said about these species: these side-products are formed when alkyne **1** is heated in neat triethylamine at 85°C for 24 h, in the absence of an aromatic halide, with and without added catalyst. The presence of the catalyst speeds up the formation of these products. The signal at $\delta = +18$ ppm is in the range typically found for R-P(O)$(OEt)_2$ phosphonates where R is a substituted vinyl group.[3] A possible structure for this compound is **6**. Structure **6** would result from a Michael-type addition reaction of triethylamine onto **1**.



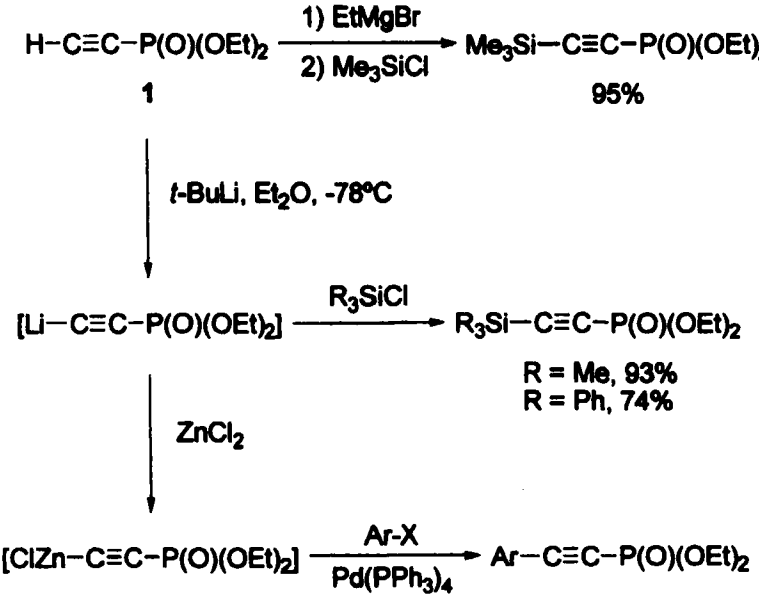
6 (E + Z)

A chemical shift of +29 ppm seems to suggest that we are in the presence of a R-P(O)$(OEt)_2$ phosphonate where R is a saturated organic substituent. We have shown that this signal did not correspond to triphenylphosphine oxide. The presence of these side-products is most likely responsible for the low yields observed in the coupling reactions.

An alternative way of forming carbon-carbon bonds is by coupling an organozinc derivative with an aromatic halide in the presence of a palladium(0) complex (path (b)).[23] The organozinc compound derived from **1** is readily prepared by metal exchange with the lithium or Grignard derivatives M-C≡C-P(O)$(OEt)_2$ (M = Li, MgX). However, it was briefly mentioned in the literature that, in the case of **1**, deprotonation with 1-methylpyrrolidine, *t*-BuOLi in Et_2O or DMF, and lithium diisopropylamide, followed by treatment with benzaldehyde, gave tars.[9] It is not clear

whether these problems are due to the instability of the acetylide anion or to the nature of the base. In order to elucidate this point, **1** was reacted with EtMgBr and *t*-BuLi and the anion was quenched with Me_3SiCl and Ph_3SiCl (Scheme 8).

In each case, complete disappearance of **1** was observed and high yields of Me_3Si-C≡C-P(O)$(OEt)_2$ and Ph_3Si-C≡C-P(O)$(OEt)_2$ were obtained, meaning that complete deprotonation of **1** had been achieved. On the other hand, the desired reaction product D-C≡C-P(O)$(OEt)_2$ was not obtained upon quenching the anion with CD_3OD. Also, the reaction between *n*-Bu_3SnCl and the organolithium derivative led to an intractable mixture.



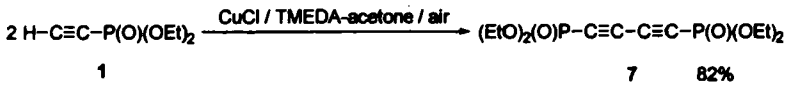
SCHEME 8

The expected cross-coupling products were obtained by allowing the organozinc derivative of **1**, prepared by the reaction between the organolithium reagent and $ZnCl_2$, to react with various aromatic halides in the presence of $Pd(PPh_3)_4$ (Table II).

Reasonable yields (calculated with respect to **1**) were obtained with aromatic iodides (Entries 1–5). Replacement of the hydrogen on the benzene

ring para to the iodine by an electron-donating (MeO) or electron-withdrawing (NO_2) substituent does not seem to have much impact on the course of the coupling reaction and the yields. When *p*-diiodobenzene and two equivalents of the organozinc reagent are used (Entry 5), a mixture of the mono- and disubstituted products is obtained as revealed by ^{31}P NMR spectroscopy. The *p*-$(EtO)_2(O)P$-C≡C-C_6H_4-C≡C-$P(O)(OEt)_2$ / *p*-IC_6H_4-C≡C-$P(O)(OEt)_2$ ratio is 1:2. A third signal was also observed at +22 ppm that could not be assigned. On the other hand, no cross-coupling product is detected when aromatic bromides are used instead of iodides, *i.e.* with bromobenzene, 3-bromopyridine and *p*-bromodimethylaniline; unchanged **1** is recovered after work-up. These results show some similarity with those obtained by Negishi and co-workers in the case of the $Pd(PPh_3)_4$-catalyzed cross-coupling reaction between 3-bromopyridine and phenylzinc chloride.[23d] With 3-bromopyridine, an additional experiment was carried out in the presence of *N, N, N', N'*-tetramethylethylenediamine (TMEDA) to activate the organozinc derivative. The latter reagent was consumed almost completely but an intractable mixture of products was obtained as revealed by ^{31}P NMR spectroscopy.

Symmetrically-substituted diacetylenes can be prepared from terminal alkynes using the Hay coupling reaction.[24] We have performed this reaction with H-C≡C-$P(O)(OEt)_2$ (**1**) and obtained diacetylenic diphosphonate **7** in 82% yield after purification by column chromatography (Scheme 9).

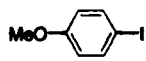
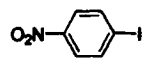
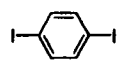
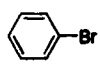
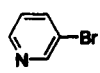
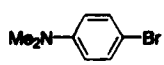


SCHEME 9

In conclusion, the work presented here shows that diethyl ethynylphosphonate (**1**) is a useful synthon for the preparation of diethyl 1-alkynylphosphonates. The cross-coupling reaction between **1** and aromatic iodides takes place with very low to low yields depending on the palladium(II) complex employed. Organometallic reagents M-C≡C-$P(O)(OEt)_2$ (M = Li, MgBr) are obtained in good yields by metalation of **1** with *t*-BuLi and EtMgBr, and these intermediates have been trapped with chlorosilanes. The reaction between Li-C≡C-$P(O)(OEt)_2$ and $ZnCl_2$ gives the organozinc compound ClZn-C≡C-$P(O)(OEt)_2$ that reacts with iodobenzene and its derivatives in the presence of catalytic amounts of tet-

rakis(triphenylphosphine)palladium(0). The yields that are observed make this reaction an alternative route to that described by Diziere and Savignac.[19] Oxidative dimerization of **1** allows the synthesis of the new symmetrically-substituted diacetylene compound $(EtO)_2(O)P\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}P(O)(OEt)_2$ in high yield.

TABLE II Palladium-Catalyzed Coupling of $ClZn\text{-}C{\equiv}C\text{-}P(O)(OEt)_2$ with Ar-X[a]

Entry	*Ar-X*	*Reaction Conditions*	*Yield (%)*[b]
1		r.t. / 12 h	64
2		r.t. / 12 h	62
3		r.t. / 12 h	56
4		r.t. / 12 h	48
5		r.t. / 12 h	[c]
6		40°C / 24 h	0[d]
7		40°C / 24 h	0[d]
8		40°C / 24 h	0[d]

[a]Catalyst: $Pd(PPh_3)_4$ (2.6% molar).
[b]Yields are given for isolated products.
[c]Two equivalents of organozinc derivative per mole of *p*-diiodobenzene were used. A 2:1 mixture of the mono- and disubstituted products was obtained.
[d]No reaction was observed. Phosphonate **1** was recovered quantitatively.

Work is currently in progress to synthesize the phosphonic acids derived from the above phosphonates and prepare metal complexes with these acids.

EXPERIMENTAL

General

All manipulations were carried out under an inert atmosphere of dinitrogen or argon using standard Schlenk-line techniques. Solvents were refluxed on and distilled from the appropriate drying agents prior to use: THF, Et_2O (Na/benzophenone); Et_3N, TMEDA, CH_2Cl_2 (CaH_2). ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded on Bruker instruments of the following types: AC 250, WP 200 SY, and AVANCE DPX 200. Chemical shifts were referenced as follows: ^1H (protio impurities of the NMR solvents), ^{13}C (NMR solvents), ^{29}Si (tetramethylsilane), ^{31}P (85% H_3PO_4). Infrared spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer operating at a 4 cm^{-1} resolution. Mass spectra were obtained on a Jeol JMS-DX300 instrument. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out at the Laboratoire de Microanalyse of the Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM) or at the Service Central de Microanalyse of the Centre National de la Recherche Scientifique (CNRS), Vernaison, France.

Materials

Chemicals were purchased from Acros Organics, Janssen or Fluka and were used without further purification. *tert*-Butyllithium was purchased as a solution in pentane and the methyllithium-lithium bromide complex as a solution in diethyl ether. Me_3SiCl was distilled from magnesium powder. Ph_3SiCl was prepared *via* chlorination of triphenylsilane with chlorine gas in CCl_4 at 0°C.[25] $Me_3Si\text{-}C{\equiv}C\text{-}Cl$ was prepared in 90% yield by a slight modification of the procedure reported by West and Quass[20], using diethyl ether as the only solvent. The synthesis of $H\text{-}C{\equiv}C\text{-}P(O)(OEt)_2$ (**1**) was carried out using a published method.[9] We have found that purification by column chromatography (SiO_2, Et_2O) was easy and more effective than distillation.

Coupling reaction between 1 and ArX in the presence of palladium(II) acetate

Reaction between 1 and C_6H_5I (typical procedure)

A solution of H-C≡C-P(O)$(OEt)_2$ (**1**) (5.00 g, 30.84 mmol) and C_6H_5I (6.92 g, 33.93 mmol) in Et_3N (20 mL) was added to a mixture of $Pd(OAc)_2$ (0.35 g, 1.54 mmol) and PPh_3 (0.81 g, 3.08 mmol). The suspension was heated (see Table I) until complete disappearance of **1** was observed, as determined by infrared spectroscopy. After cooling, the reaction mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and the volatiles were removed *in vacuo*.

Note: The ^{31}P NMR spectra of all of the crude reaction mixtures showed one signal corresponding to the expected compound ($\delta = -5$ to -10 ppm) accompanied by two signals at +18 and +29 ppm in a roughly 1:1:1 ratio. These side-products were not identified (see text).

The residue was dissolved in ethyl acetate and chromatographed on silica gel using diethyl ether as the eluent. The desired phosphonate ($R_F(SiO_2, Et_2O) = 0.22$ or $R_F(SiO_2, CH_3COOEt) = 0.45$) was obtained in 21% yield (1.54 g, 6.48 mmol) as a brown oil. IR (CCl_4, cm^{-1}): ν(C≡C) 2189, ν(P=O) 1263, ν(P-OEt) 1029. ^1H NMR ($CDCl_3$, δ, ppm): 7.61–7.40 (m, 5H, Ph), 4.25 (dq, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 8.7$ Hz, 4H, CH_2), 1.43 (dt, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.7$ Hz, 6H, CH_3). The ^{13}C NMR data for the acetylenic carbons (δ and $^nJ_{CP}$) and the ^{31}P chemical shift are in agreement with literature values.[19a] MS (FAB+, NBA): m/z (assignment, relative intensity) 477 ($[2M+H]^+$, 12), 239 ($[M+H]^+$, 100), 211 ($[M-C_2H_4+H]^+$, 7), 183 ($[M-2C_2H_4+H]^+$, 38). Anal. Calcd for $C_{12}H_{15}O_3P$: C, 60.50; H, 6.35; O, 20.15; P, 13.00. Found: C, 60.36; H, 6.55; O, 18.91; P, 12.14.

Reaction between 1 and 2-iodothiophene

Reaction temperature: 65°C. Reaction time: 12 h. The residue was chromatographed on silica gel using ethyl acetate as the eluent. The expected phosphonate ($R_F(SiO_2, Et_2O) = 0.22$ or $R_F(SiO_2, CH_3COOEt) = 0.45$) was obtained in 20% yield (1.48 g, 6.06 mmol) as an orange oil. IR (CCl_4, cm^{-1}): ν(C≡C) 2174, ν(P=O) 1270, ν(P-OEt) 1022. ^1H NMR ($CDCl_3$, δ, ppm): 7.50–7.05 (m, 3H, thiophenyl), 4.26 (dq, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 8.6$ Hz, 4H, CH_2), 1.44 (dt, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.7$ Hz, 6H, CH_3). The ^{13}C NMR data for the acetylenic carbons (δ and $^nJ_{CP}$) and the

^{31}P chemical shift are in agreement with literature values.[19a] MS (FAB+, NBA): m/z (assignment, relative intensity) 489 ($[2M+H]^+$, 18), 245 ($[M+H]^+$, 100), 217 ($[M-C_2H_4+H]^+$, 8), 189 ($[M-2C_2H_4+H]^+$, 37). Anal. Calcd for $C_{10}H_{13}O_3PS$: C, 49.18; H, 5.36; O, 19.65; P, 12.68; S, 13.13. Found: C, 49.22; H, 5.46; O, 19.05; P, 12.12; S, 11.60.

Reaction between 1 and p-$O_2NC_6H_4I$

Reaction temperature: 85°C. Reaction time: 2 h. The residue was chromatographed on silica gel using ethyl acetate as the eluent. The expected product ($R_F(SiO_2, Et_2O) = 0.20$ or $R_F(SiO_2, CH_3COOEt) = 0.43$) was obtained as an orange powder in 35% yield (1.23 g, 4.34 mmol). Mp 78.1–79.0°C. IR (CCl_4, cm^{-1}): ν(C≡C) 2195, ν(P=O) 1265, ν(P-OEt) 1025. ^1H NMR ($CDCl_3$, δ, ppm): 8.29 (d, $^3J_{HH} = 8.9$ Hz, 2H, Ar), 7.77 (d, $^3J_{HH} = 8.6$ Hz, 2H, Ar), 4.29 (dq, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 8.6$ Hz, 4H, CH_2), 1.46 (dt, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.6$ Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 149.0 (s, C^4), 134.0 (d, $^4J_{CP} = 2.5$ Hz, $C^{2,6}$), 126.6 (d, $^3J_{CP} = 5.6$ Hz, C^{ipso}), 124.2 (d, $^5J_{CP} = 0.4$ Hz, $C^{3,5}$), 95.9 (d, $^2J_{CP} = 51.7$ Hz, *C*≡C-P), 83.6 (d, $^1J_{CP} = 294.6$ Hz, ≡C-P), 64.0 (d, $^2J_{CP} = 5.6$ Hz, CH_2), 16.6 (d, $^3J_{CP} = 6.9$ Hz, CH_3). ^{31}P NMR ($CDCl_3$, δ, ppm): -6.9. MS (FAB+, NBA): m/z (assignment, relative intensity) 567 ($[2M+H]^+$, 7), 284 ($[M+H]^+$, 100), 256 ($[M-C_2H_4+H]^+$, 6), 228 ($[M-2C_2H_4+H]^+$, 29). Anal. Calcd for $C_{12}H_{14}NO_5P$: C, 50.89; H, 4.98; N, 4.95; P, 10.94. Found: C, 51.18; H, 5.31; N, 4.60; P, 10.68.

Reaction between 1 and p-IC_6H_4I

Reaction temperature: 85°C. Reaction time: 24 h. The residue was chromatographed on silica gel using ethyl acetate as the eluent. An orange powder corresponding to *p*-IC_6H_4-C≡C-P(O)$(OEt)_2$ was obtained in 18% yield (0.36 g, 0.99 mmol). IR (CCl_4, cm^{-1}): ν(C≡C) 2191, ν(P=O) 1262, ν(P-OEt) 1027. ^1H NMR ($CDCl_3$, δ, ppm): 7.77 (d, $^3J_{HH} = 8.5$ Hz, 2H, Ar), 7.31 (d, $^3J_{HH} = 8.2$ Hz, 2H, Ar), 4.26 (dq, $^3J_{HH} = 7.0$ Hz, $^3J_{HP} = 8.5$ Hz, 4H, CH_2), 1.44 (dt, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.7$ Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 138.3 (d, $^5J_{CP} = 0.4$ Hz, $C^{3,5}$), 134.2 (d, $^4J_{CP} = 2.5$ Hz, $C^{2,6}$), 119.4 (d, $^3J_{CP} = 5.7$ Hz, C^{ipso}), 98.2 (d, $^2J_{CP} = 52.7$ Hz, *C*≡C-P), 98.0 (d, $^6J_{CP} = 0.8$ Hz, C^4), 80.3 (d, $^1J_{CP} = 298.4$ Hz, ≡C-P), 63.7 (d, $^2J_{CP} = 5.6$ Hz, CH_2), 16.6 (d, $^3J_{CP} = 7.0$ Hz, CH_3). ^{31}P NMR ($CDCl_3$, δ, ppm): −5.8. MS (FAB+, NBA): m/z (assignment, relative intensity) 728 ($[2M]^+$, 6), 365 ($[M+H]^+$, 100),

337 ([M-C_2H_4+H]$^+$, 9), 309 ([M-2C_2H_4+H]$^+$, 45). Anal. Calcd for $C_{12}H_{14}IO_3P$: C, 39.58; H, 3.88; P, 8.51. Found: C, 42.80; H, 4.88; P, 7.73.

Reaction between 1 and 3-bromopyridine

Reaction temperature: 85°C. Reaction time: 24 h. A ^{31}P NMR analysis of the crude reaction mixture indicated the presence of the expected product with a molar ratio of about 20%. Purification by column chromatography was attempted using silica gel and alumina as stationary phases but no improvement was observed as far as purity is concerned. IR (CCl_4, cm^{-1}): ν(C≡C) 2194, ν(P=O) 1255, ν(P-OEt) 1032. The ^{31}P chemical shift agrees with that reported in the literature.[19a]

Reaction between 1 and p-$Me_2NC_6H_4Br$

Reaction temperature: 85°C. Reaction time: 24 h. A ^{31}P NMR analysis of the crude reaction mixture showed a signal at −7.8 ppm corresponding to unreacted **1** in addition to the aforementioned signals at +18 and +29 ppm.

Deprotonation of H-C≡C-P(O)$(OEt)_2$ and subsequent metal-exchange reactions

Me_3Si-C≡C-P(O)$(OEt)_2$ from BrMg-C≡C-P(O)$(OEt)_2$

A 2.16 M solution of EtMgBr (4.28 mL, 9.25 mmol) was added dropwise to a solution of H-C≡C-P(O)$(OEt)_2$ (1.50 g, 9.25 mmol) in diethyl ether (60 mL) cooled at 0°C. The mixture was allowed to come to room temperature and stirred overnight.

Me_3SiCl (1.01 g, 9.25 mmol) was added dropwise to the above solution kept at −30°C. The mixture was allowed to come to room temperature overnight while stirring. Filtration of the suspension through a glass frit and concentration of the filtrate *in vacuo* gave an oil. A ^{31}P NMR analysis of the oil showed that it contained 95% molar of Me_3Si-C≡C-P(O)$(OEt)_2$. Purification by column chromatography using silica gel as a stationary phase and diethyl ether as the eluent resulted in partial desilylation: a 40:60 mixture of H-C≡C-P(O)$(OEt)_2$ and Me_3Si-C≡C-P(O)$(OEt)_2$ was obtained. ^{31}P NMR ($CDCl_3$, δ, ppm): −7.8 (Me_3Si-C≡C-P(O)$(OEt)_2$, −7.9 (H-C≡C-P(O)$(OEt)_2$).

Me_3Si-C≡C-P(O)(OEt)$_2$, Ph_3Si-C≡C-P(O)(OEt)$_2$ and ClZn-C≡C-P(O)(OEt)$_2$ from Li-C≡C-P(O)(OEt)$_2$

A solution of *t*-BuLi in hexane is added dropwise to a cold (-78°C) solution of H-C≡C-P(O)(OEt)$_2$ in diethyl ether. The mixture is stirred at that temperature for 15 min, giving a white suspension of Li-C≡C-P(O)(OEt)$_2$.

Me_3SiCl (1.38 g, 12.70 mmol) was added dropwise to a suspension of Li-C≡C-P(O)(OEt)$_2$ kept at −78°C and prepared from H-C≡C-P(O)(OEt)$_2$ (1.03 g, 6.35 mmol) in diethyl ether (40 mL) and *t*-BuLi (5.48 mL of a 1.16 M solution, 6.35 mmol). The mixture was allowed to come to room temperature and stirred overnight. Filtration of the suspension through a bed of alumina and concentration of the filtrate *in vacuo* gave an oil. A ^{31}P NMR analysis of the oil showed that it contained 93% molar of Me_3Si-C≡C-P(O)(OEt)$_2$. Spectroscopic data for Me_3Si-C≡C-P(O)(OEt)$_2$: ^{13}C NMR ($CDCl_3$, δ, ppm): 108.2 (d, $^2J_{CP}$ = 37.9 Hz, *C*≡C-P), 94.5 (d, $^1J_{CP}$ = 270.5 Hz, ≡C-P), 62.8 (d, $^2J_{CP}$ = 5.5 Hz, CH_2), 15.8 (d, $^3J_{CP}$ = 6.3 Hz, CH_3), −1.2 (s, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$, δ, ppm): −7.9. ^{29}Si NMR ($CDCl_3$, δ, ppm): −14.7 (d, $^3J_{SiP}$ = 4.3 Hz). The infrared and ^1H NMR data have been published previously.[9]

Ph_3SiCl (2.49 g, 8.45 mmol) in diethyl ether (40 mL) was added dropwise to a suspension of Li-C≡C-P(O)(OEt)$_2$ cooled at −78°C and prepared from H-C≡C-P(O)(OEt)$_2$ (1.25 g, 7.68 mmol) in diethyl ether (60 mL) and *t*-BuLi (6.62 mL of a 1.16 M solution, 7.68 mmol). The mixture was allowed to come to room temperature and stirred overnight. The reaction mixture was hydrolyzed with a saturared solution of NH_4Cl, extracted with diethyl ether, and the organic layer was dried over $MgSO_4$. Removal of the volatiles *in vacuo* gave a white powder that contained 74% molar of Ph_3Si-C≡C-P(O)(OEt)$_2$ as determined by ^{31}P NMR spectroscopy. Spectroscopic data for Ph_3Si-C≡C-P(O)(OEt)$_2$: IR (CCl_4, cm^{-1}): ν(C≡C) 2199, 2155, ν(P=O) 1241, ν(P-OEt) 1027. ^1H NMR ($CDCl_3$, δ, ppm): 7.69–7.41 (m, 15H, Ph), 4.24 (dq, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 8.8 Hz, 4H, CH_2), 1.41 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 0.6 Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 136.0 ($C^{3,5}$), 131.6 (C^{ipso}), 131.0 (C^4), 128.7 ($C^{2,6}$), 104.5 (d, $^2J_{CP}$ = 38.0 Hz, *C*≡C-P), 99.0 (d, $^1J_{CP}$ = 268.4 Hz, ≡C-P), 63.9 (d, $^2J_{CP}$ = 5.7 Hz, CH_2), 16.5 (d, $^3J_{CP}$ = 6.8 Hz, CH_3). ^{31}P NMR ($CDCl_3$, δ, ppm): −8.3. ^{29}Si NMR ($CDCl_3$, δ, ppm): −27.9 (d, $^3J_{SiP}$ = 4.6 Hz).

A suspension of $ZnCl_2$ in diethyl ether is added to a suspension of Li-C≡C-P(O)(OEt)$_2$ cooled at −78°C. The mixture is allowed to warm to

room temperature and stirred for 4 h. A pink suspension of diethyl chlorozincethynylphosphonate ClZn-C≡C-P(O)$(OEt)_2$ is obtained.

Coupling reaction between ClZn-C≡C-P(O)$(OEt)_2$ and ArX in the presence of $Pd(PPh_3)_4$

Diethyl phenylethynylphosphonate (typical procedure)

A suspension of ClZn-C≡C-P(O)$(OEt)_2$ was prepared as described previously from H-C≡C-P(O)$(OEt)_2$ (1.53 g, 9.47 mmol) in solution in diethyl ether (40 mL), *t*-BuLi (4.83 mL of a 1.96 M solution, 9.47 mmol), and $ZnCl_2$ (1.29 g, 9.47 mmol) suspended in diethyl ether (60 mL). The suspension was added to a solution of C_6H_5I (1.93 g, 9.47 mmol) and $Pd(PPh_3)_4$ (0.28 g, 0.24 mmol, 2.6% molar). After overnight stirring, the reaction mixture was hydrolyzed with a saturated solution of NH_4Cl, extracted with ethyl acetate, and the organic layer was dried over $MgSO_4$. The volatiles were removed *in vacuo*. The residue was chromatographed (SiO_2, Et_2O). The title compound was obtained as a brown oil in 64% yield (1.45 g, 6.09 mmol). Same spectroscopic data as those presented above.

Diethyl 2-thiophenylethynylphosphonate

The residue was chromatographed (SiO_2, Et_2O). The title compound was obtained as an orange oil in 62% yield (1.87 g, 7.66 mmol). Same spectroscopic data as those presented above.

Diethyl p-methoxyphenylethynylphosphonate

The residual oil was purified by column chromatography (SiO_2, CH_3COOEt). The title compound ($R_F(SiO_2, Et_2O) = 0.12$ or $R_F(SiO_2, CH_3COOEt) = 0.32$) was obtained as a brown oil in 56% yield (1.87 g, 6.97 mmol). IR (CCl_4, cm^{-1}): ν(C≡C) 2183, ν(P=O) 1262, ν(P-OEt) 1032. ^1H NMR ($CDCl_3$, δ, ppm): 7.5 (d, $^3J_{HH} = 9.0$ Hz, 2H, Ar), 6.8 (d, $^3J_{HH} = 8.9$ Hz, 2H, Ar), 4.2 (dq, $^3J_{HH} = 7.1$ Hz, $^3J_{HP} = 8.6$ Hz, 4H, CH_2), 3.8 (s, 3H, OCH_3), 1.4 (dt, $^3J_{HH} = 7.1$ Hz, $^4J_{HP} = 0.7$ Hz, 6H, CH_3). The ^{13}C NMR data for the acetylenic carbons (δ and $^nJ_{CP}$) and the ^{31}P chemical shift are in agreement with values reported elsewhere.[19a] MS (FAB+, NBA): m/z (assignment, relative intensity) 537 ($[2M+H]^+$, 8), 269

([M+H]$^+$, 100), 213 ([M-2C_2H_4+H]$^+$, 29). Anal. Calcd for $C_{13}H_{17}O_4P$: C, 58.21; H, 6.39; O, 23.86. Found: C, 57.74; H, 6.40; O, 23.56.

Diethyl p-nitrophenylethynylphosphonate

The residual oil was chromatographed (SiO_2, CH_3COOEt). The title compound was obtained as an orange powder in 48% yield (1.26 g, 4.44 mmol). Same spectroscopic data as those presented above.

Reaction between ClZn-C≡C-P(O)(OEt)$_2$ and p-IC$_6$H$_4$I

A ^{31}P NMR analysis of the crude oil indicated the presence of a 2:1 mixture of p-IC_6H_4-C≡C-P(O)$(OEt)_2$ and p-$(EtO)_2$(O)P-C≡C-C_6H_4-C≡C-P(O)$(OEt)_2$ and also showed a small signal at +22.3 ppm. The two major compounds could not be separated by column chromatography on silica gel using ethyl acetate as the eluent.

p-IC_6H_4-C≡C-P(O)$(OEt)_2$: same spectroscopic data as those presented above.

p-$(EtO)_2$(O)P-C≡C-C_6H_4-C≡C-P(O)$(OEt)_2$: IR (CCl_4, cm^{-1}): ν(C≡C) 2191. ^{31}P NMR ($CDCl_3$, δ, ppm): – 6.5.

Reactions of C$_6$H$_5$Br, 3-bromopyridine and p-Me$_2$NC$_6$H$_4$Br with ClZn-C≡C-P(O)(OEt)$_2$

The mixture was refluxed for 24 h. No reaction was observed. A ^{31}P NMR analysis in $CDCl_3$ solution of the residue after work-up showed a single line at –7.8 ppm corresponding to **1**.

Synthesis of (EtO)$_2$P(O)-C≡C-C≡C-P(O)(OEt)$_2$

The preparation of the Hay catalyst and the coupling reaction were carried out by following a reported protocol.[24c] 5.76 g (35.5 mmol) of H-C≡C-P(O)$(OEt)_2$ and 200 mL of acetone were placed in a 250-mL three-necked round-bottomed flask equipped with a magnetic stir-bar. 25 mL of the Hay catalyst were added to the flask *via* syringe. Air was bubbled into the solution for about four hours, during which time it turned into a dark green suspension. The mixture was kept overnight and the solvents were removed *in vacuo*, leaving a dark oil in the flask. The residue was hydrolyzed with 150-mL of a saturated solution of NH_4Cl and ethyl acetate was added. After filtration and extraction with three 150-mL por-

tions of ethyl acetate, the organic fractions were washed with two 130 mL portions of distilled water and dried over $MgSO_4$. The solvents were removed *in vacuo* giving 5.28 g (92% yield) of crude oil which was purified by column chromatography on Florisil. Elution was first carried out with CH_2Cl_2 to remove polar side-products and then with THF. The yellow band that migrates was collected, giving 4.67 g (82% yield) of $(EtO)_2P(O)$-C≡C-C≡C-$P(O)(OEt)_2$. The diacetylenic phosphonate first becomes orange, then brown, upon prolonged exposure to light at room temperature. IR (CCl_4, cm^{-1}): ν(C≡C) 2111, ν(P=O) 1272, ν(P-OEt) 1025. ^1H NMR ($CDCl_3$, δ, ppm): 4.15 (dq, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 8.7 Hz, CH_2), 1.34 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.8 Hz, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 79.3 (dd, $^2J_{CP}$ = 52.3 Hz, $^3J_{CP}$= 9.0 Hz, *C*≡C-P), 73.1 (dd, $^1J_{CP}$ = 286 Hz, $^4J_{CP}$ = 2.5 Hz, ≡C-P), 64.2 (5 lines, CH_2), 16.1 (5 lines, CH_3). ^{31}P NMR ($CDCl_3$, δ, ppm): -9.4. MS (FAB+, NBA): m/z (assignment, relative intensity) 645 ($[2M+H]^+$, 7), 323 ($[M+H]^+$, 100), 295 ($[M-C_2H_4+H]^+$, 9), 267 ($[M-2C_2H_4+H]^+$, 5), 239 ($M-3C_2H_4+H]^+$, 7), 211 ($[M-4C_2H_4+H]^+$, 40), 137 ($[P(O)(OEt)_2]^+$, 12). Anal. Calcd for $C_{12}H_{20}O_6P_2$: C, 44.73; H, 6.26; O, 29.79. Found: C, 45.93; H, 6.83; O, 27.50.

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