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REACTION OF E-1,2-BIS[TRIPHENYL-(TRIFLUOROMETHANESULFONYLOXY)PHOSPHO]ETHYLENE, $Ph_3PCH=CHPPh_3 \cdot 2OTf$ WITH BASES: UNUSUAL PRODUCTS AND EVIDENCE FOR C_2-DIYLIDE, $Ph_3P=C=C=PPh_3$, FORMATION

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Abstract. E-1,2-di[triphenyl(trifluoromethanesulphonyloxy)phospho]ethylene **4** reacts with Et_3N or NaH in wet CH_3CN affording phosphineoxides **6** and **7** as a result of phenyl migration and related rearrangements in hydrolysed phosphonium moieties. The reaction of **4** with *t*-BuLi in CH_2Cl_2 results in nucleophilic vinylic substitution of the phosphonium group by the *t*-Bu anion. Evidence for the intermediate formation of the C_2-diylide **3** is obtained in the reaction of **4** with *n*-BuLi in CH_2Cl_2. via trapping with 3,4-dichlorobenzaldehyde.

Introduction

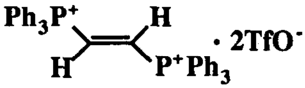
Ylides play a major role in organic chemistry. Particularly valuable and useful are phosphorus ylides because of their key role in Wittig olefinations that continue to be employed as the method of choice for the synthesis of alkenes from the simplest to the most complex[1]. In fact, the Wittig carbonyl olefination is among the most useful and widely employed modern synthetic reactions.

Especially interesting are phosphacumulene ylides **1** and diylides because of their rich chemistry and usefulness as versatile reagents in organic synthesis[2]. The parent member of the family of diylides, hexaphenylcarbodiphosphorane **2**, was first described in 1961 as a stable yellow solid with a mp of 208-210 °C[3]. Diylide **2** is widely used in synthesis[1,4] and is of substantial theoretical interest because of its unusual structure which can be formally regarded as a "complex" consisting of two donor molecules and an electron-rich, excited carbon atom[5,6]. The higher homologs, namely the C_2, **3**, C_3, and C_4 species are still unknown, however, approaches to their stabilized derivatives have been discussed in the literature[6].

$Ph_3P{=}(C{=})_nCR_2$
1
R = Ar, OAlk, etc., or 2R = O, S, NR

$Ph_3P{=}C{=}PPh_3$
2

$Ph_3P{=}C{=}C{=}PPh_3$
3

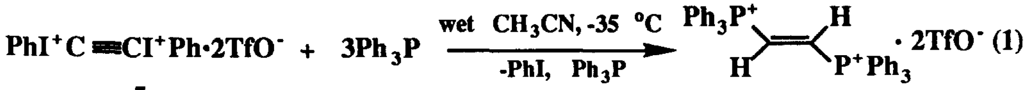


4

In this paper we describe the reaction of diphosphonium salt **4**, an obvious precursor to **3**, with various bases including evidence for the in situ formation of diylide **3**.

Results and Discussion

The starting diphosphonium salt **4**[7] was prepared in a single-step in high isolated yield by the reaction of the diiodonium acetylene **5**[7,8] with excess Ph_3P in wet CH_3CN (eq. 1). The structure of this compound (**4**) was unambiguously established by X-ray analysis[7].



5 **4**

(1)

Phosphacumulene ylides are usually prepared by the reaction of the appropriate cumulene phosphonium salts with such bases as Et_3N and pyridine in CH_3CN[9] or PhLi in ether[10]. Unstable ylides formed under these conditions can be trapped with aromatic aldehydes (the most reactive being 3,4-dichlorobenzaldehyde)[9,10]. Therefore, we examined the reactions of the bis-phosphonium salt **4** with the same kind of bases under similar conditions. However, since compound **4** is insoluble in ether, we employed CH_3CN and CH_2Cl_2 as solvents.

By monitoring of the reaction mixture with ^{31}P NMR, it was shown that there was no reaction of **4** with Et_3N in absolutely dry CH_3CN even after several days at room temperature. This observation indicates that compound **4** is significantly less reactive than monosubstituted cumulene phosphonium salts[9,10]. However, a slow reaction occurred between the reagents in the presence of traces of water. The reaction was complete after refluxing the mixture for four hours in CH_3CN, and standard work-up afforded a white crystalline product, **6**, in 72% yield (eq. 2).

$$\mathbf{4} + Et_3N \xrightarrow[\text{4 h, reflux}]{\text{wet } CH_3CN} Ph_3P^+\text{-}CH_2\text{-}CHPh\text{-}\overset{\overset{O}{\|}}{P}Ph_2\cdot TfO^- \quad (2)$$

6

The structure of compound **6** was elucidated by multinuclear NMR, mass-spectroscopy, and X-ray analysis. Specifically, the ^1H NMR shows three signals for the aliphatic protons from 3.5 to 4.6 ppm and signals for six phenyls in the aromatic region. The presence of the triflate anion is confirmed by ^{19}F NMR. In the ^{31}NMR two doublets at 24.9 and 34.5 ppm indicate the presence of the phosphonium and phosphine oxide moieties in the molecule. The ^{13}C NMR shows two highfield doublets for the aliphatic carbons and 12 multiplets for the aromatic carbons. However, the spectral data was insufficient for unambiguous assignment of the structure of compound **6**. In order to establish the exact molecular structure of this compound, a single crystal X-ray analysis was performed. The ORTEP of compound **6** is shown in Figure 1, selected bond lengths and bond angles are summarized in Tables 1,2. The X-ray data shows two different kinds of P atoms in the molecule: one of the phosphonium type without a covalent bond with the triflate anion, and the second bearing a covalently bonded oxygen atom. The bond distances and angles around C-1 and C-2 clearly indicate sp^3-geometry for these carbons.

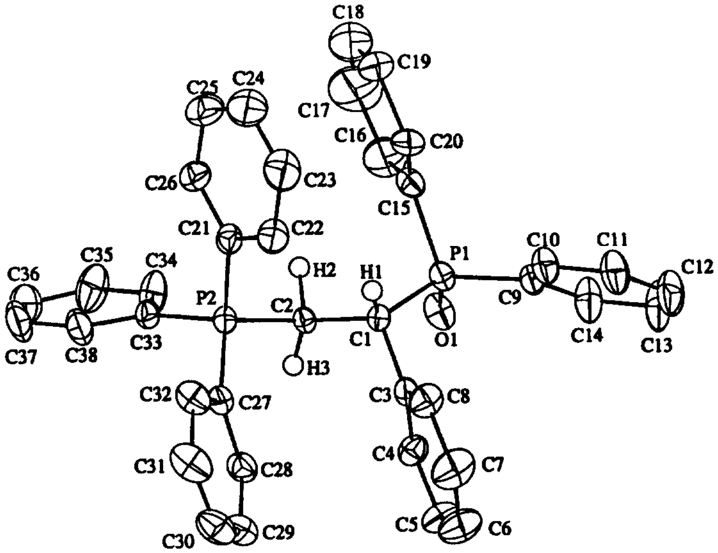


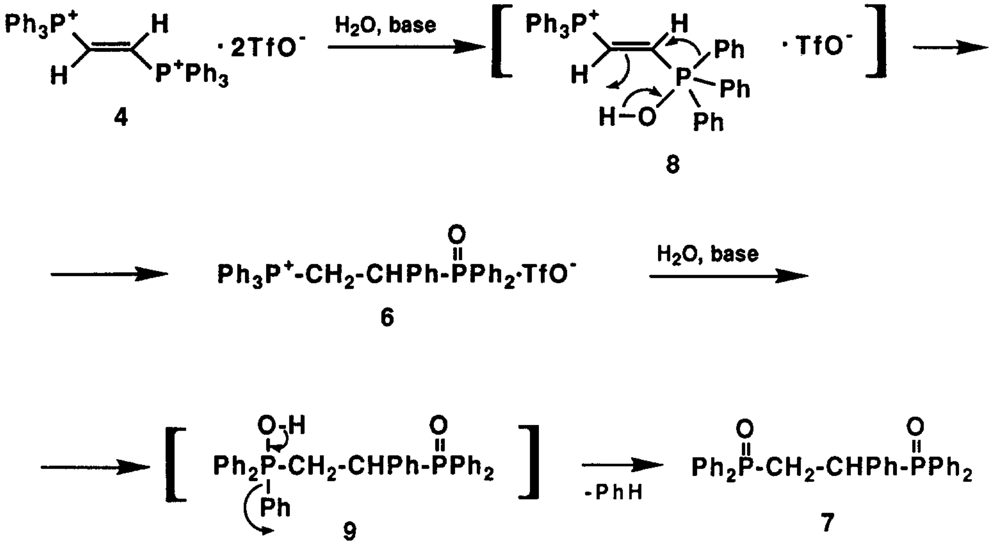
Figure 1. ORTEP of Cationic Portion of Compound 6.

Reaction of diphosphonium salt **4** with the more basic NaH in CH_3CN is complete in 1 h at room temperature with the formation of a white precipitate. The product, **7**, (eq. 3) was identified by multinuclear NMR and mass-spectroscopy. High resolution mass spectrum of this compound affords the appropriate molecular ion and fragmentation patterns. NMR spectra of compounds **7** and **6** are similar to each other with the exception of the ^{19}F NMR where the triflate resonance does not show up for **7**. Moreover, the ^{31}P NMR displays two doublets in the region typical of phosphine oxides (δ 30.4 and 35.7 ppm). The ^{1}H, ^{13}C NMR and elemental analyses are all consistent with the proposed structure **7**.

$$4 + 2NaH \xrightarrow[\text{1 h, 25 °C}]{\text{wet } CH_3CN} Ph_2\overset{O}{\overset{\|}{P}}\text{-}CH_2\text{-}CHPh\text{-}\overset{O}{\overset{\|}{P}}Ph_2 \qquad (3)$$

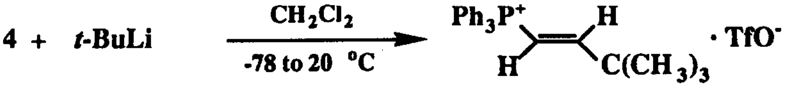
7

It is most likely that compound **6** is the precursor to the formation of **7**. According to literature precedents for mechanisms of basic hydrolysis of the phosphonium salts[11], the initial step in the reactions (2) and (3) involves a nucleophilic attack of the hydroxide ion with the formation of phosphorane **8**. Further rearrangement with a phenyl migration[12] affords the first product, **6**. Hydrolysis of **6** leads to phosphorane **9**, which eliminates benzene[13] with the formation of the phosphineoxide **7** (Scheme 1).



Scheme 1

Compound **4** reacts with *t*-BuLi (2 mol.-equiv.) in CH_2Cl_2[14] at -78 °C forming a bright yellow solution of product **10** (eq. 5) which was separated from the reaction mixture by column chromatography on silica gel in an isolated yield of 93%. According to the ^{31}P and ^{19}F NMR this compound has the phosphonium moiety and the triflate anion in its structure. Particularly characteristic are the ^{1}H and ^{13}C NMR which display signals of the *t*-Bu group and the olefinic fragment. The FAB mass spectrum contains the expected signal for the cationic part of salt **10**.



(4)

10

Use of excess *t*-BuLi does not result in the reaction of the second phosphonium moiety.

The most likely reaction path for the formation of compound **10** is a nucleophilic vinylic substitution, which can occur by a variety of mechanisms[15]. A similar reaction of nucleophilic substitution with *t*-BuLi in terminal dibromoalkenes was recently reported by Olah[16].

Reaction of compound **4** with other strong bases, such as $LiN(i\text{-}Pr)_2$, MeLi, PhLi, *n*-BuLi in different solvents usually lead to the formation of a black tar and loss of Ph_3P even at -30 - -40 °C, probably due to the decomposition of diylide **3**. However, in the reaction of **4** with *n*-BuLi in CH_2Cl_2 at -78 °C, we were able to trap the diylide **3** by adding 3,4-dichlorobenzaldehyde[17] (eq.5). A mixture of stereoisomeric cumulenes **11** were isolated from the dark yellow solution which was obtained after warming the reaction mixture to room temperature. The FAB mass spectrum of product **11** under negative ion bombardment conditions afforded the corresponding molecular ions and fragmentation pattern. The ^1H NMR displays signals for the cumulenic protons as two separate singlets for the E- and Z-isomers at δ 6.45 and 6.55 ppm with equal intensity, and an aromatic pattern consistent with the 3,4-dichlorophenyl moiety. The ^{13}C NMR further supports the structure of **11**, particularly significant are the cumulenic carbon signals at 157.6 and 157.8 ppm.

$$\mathbf{4} + 2\ n\text{-BuLi} \xrightarrow[-78\,^{\circ}\mathrm{C}]{\mathrm{CH_2Cl_2}} \underset{\mathbf{3}}{[\ \mathrm{Ph_3P{=}C{=}C{=}PPh_3}\ ]} \xrightarrow[\mathrm{CH_2Cl_2},\,-78\,^{\circ}\mathrm{C}]{2\mathrm{ArCHO}}$$

$$\longrightarrow \underset{\mathbf{11},\ \mathrm{Ar} = 3,4\text{-}\ \mathrm{Cl_2C_6H_3}}{\mathrm{ArCH{=}C{=}C{=}CHAr}} \qquad (\mathrm{E{:}Z},\ \sim 1{:}1) \qquad (5)$$

Conclusions. The experimental results for the reaction of diphosphonium salt **4** with a variety of bases demonstrate that (i) C_2-diylide **3** is unstable at room temperature but can be trapped with an aldehyde at -78 °C, (ii) reaction with bases in the presence of moisture affords novel phosphonium oxides, resulting from phenyl migration and related rearrangements, and (iii) reaction of **4** with *t*-BuLi in CH_2Cl_2 results in nucleophilic vinylic substitution of the phosphonium group by the *t*-Bu anion.

Experimental Section

General Methods. Melting points (uncorrected) were obtained with a Mel-Temp capillary melting point apparatus. Infrared spectra were recorded on a Mattson FT-IR spectrophotometer. NMR spectra were recorded on a Varian XL 300 spectrometer at 300 MHz (^1H NMR), 75 MHz (^{13}C NMR), 121 MHz (^{31}P NMR), 282 MHz (^{19}F NMR). Chemical shifts for ^1H and ^{13}C NMR are reported in parts per million (ppm) relative to internal tetramethylsilane or the proton resonance due to the residual protons in the deuteriated NMR solvent; the chemical shifts for ^{19}F and ^{31}P NMR are relative to external $CFCl_3$ and 85% H_3PO_4 respectively. Mass spectra were obtained with a VG Micromass 7050E double focusing high resolution mass spectrometer with the VG data system 2000 under positive (FAB+) or negative (FAB-) ion fast atom bombardment conditions at 8 keV. 3-Nitrobenzyl alcohol was used as a matrix in CH_2Cl_2 or $CHCl_3$ as solvent, polypropylene glycol was used as a reference for peak matching. Microanalysis were performed by Atlantic Microlab Inc, Norcross, Georgia.

Materials. All commercial reagents were ACS reagent grade and used without further purification. E-1,2-di[triphenyl(trifluoromethanesulphonyloxy)phospho]ethylene **4**[7] was prepared by a known procedure from di[phenyl(trifluoromethanesulphonyloxy)iodo]acetylene **5**[7,8] and Ph_3P in wet CH_3CN. All other solvents used were dried by distillation over CaH_2. The reaction flasks were flame-dried and flushed with nitrogen.

Reaction of 4 with Et_3N in CH_3CN. A mixture of **4** (0.48 g, 0.57 mmol), Et_3N (2 ml) and wet CH_3CN (10 ml) was refluxed for 4 h under nitrogen. The resulting yellow solution was concentrated in vacuo. Crystallization from CH_2Cl_2 - ether gave 0.295 g (72%) of 1-[Diphenyl(oxo)phospho]-2-[triphenyl-(trifluoromethanesulphonyloxy)phospho]-1-phenylethane **6**, mp 276-278 ^oC. IR (CCl_4, cm^{-1}): 3062, 2930, 2892, 1587, 1485, 1439, 1274, 1244, 1163, 1031, 888. ^1H NMR (δ, CD_3CN): 3.5 (m, 1H), 4.15 (m, 1H), 4.6 (m, 1H), 7.0-7.9 (m, 30H, 6Ph). ^{19}F NMR (δ, CD_3CN): -78.2 (s, CF_3). ^{31}P NMR (δ, CD_3CN): 24.9 (d, J = 52 Hz, P^+Ph_3), 34.5 (d, J = 52 Hz, P=O). ^{13}C NMR (δ, CD_3CN): 24.8 (d, J_{C-P} = 51 Hz, CH_2), 41.5 (d, J_{C-P} = 65 Hz, CH), 122.0 (quart. J = 320 Hz, CF_3), 118.8, 129.4, 129.6, 131.0, 131.4, 131.7, 132.1, 132.6, 133.9, 134.5, 135.1, 136.6 (all m, 6Ph). Mass spectrum (FAB+): m/z (%) 567 (18) $[M - TfO^-]^+$, 365 (100) $[M - TfO^- - Ph_2POH]^+$, 262 (50) $[Ph_3P]^+$, 202 (22) $[Ph_2POH]^+$.

X-Ray Analysis of 6. X-Ray quality single crystals were obtained by slowly evaporating a solution of **6** in CH_3CN in an open air container. The crystal was glued to a fiber glass and mounted for data collection on a CAD4 diffractometer. Cell constants were obtained from 25 reflections with $30^o < 2\Theta < 45^o$. The space group was determined from systematic absences (h0l l=2n, 0k0 k=2n) and subsequent least squares refinement. Standard reflections showed no decay during data collection.

Lorenz and Polarization corrections, and an empirical absorption correction based upon a series of of psi scans, were applied to the data. The structure was solved by the standard heavy-atom techniques with SDP/VAX package. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located and added to the structure factor calculations but were not refined, except H1, H2 and H3.

Crystallographic Data for 6. Empirical formula: $C_{39}H_{33}F_3O_4P_2S$. Formula weight: 716.703 g/mol. Crystal Data: space group $P2_1/c$; space group No 14; crystal system monoclinic, cell constants a = 10.7365 (8) Å, b = 15.8458 (9) Å, c = 21.325 (1) Å, β = 94.338 (6) deg, cell volume 3617.59 $Å^3$, Z = 4.0, calculated density 1.316 g/cm^3, crystal size 0.25x0.22x0.20 mm, absorption coeff. 20.856 cm^{-1}. Data collection description: radiation Cu 1.54056 Å, No. of reflections measured 6777, No. of unique reflections 6430, 2Θ range 4.00 to 130.00 deg., scan technique Θ/2Θ scan, scan width 0.8000 + 0.1400(tanΘ)deg, data collection position bisecting, with Θ = 0. No decay correction was applied. Absorption correction: empirical. Minimum % transmission: 91.7661. Maximum % transmission: 98.7517. Average % transmission: 95.1352. Final difference Fourier: highest peak in final diff. Fourier 0.527 $E/Å^3$. Summary of final least squares refinement: weighting scheme - non-poisson contribution; ignorance factor, P = 0.05; data rejected if $I < 3.00\ \sigma(I)$; No. of observations 4221; No. of variables 443; data to parameter ratio 9.528; shift to error ratio 0.012; error in an observ. of unit weight 1.3423; R factor 0.0645; weighted R factor 0.0649.

Table 1. Selected Bond Distances for 6[a].

	distance (Å)		distance (Å)
C1-C2	1.552 (5)	P1-O1	1.488 (3)
C1-P1	1.833 (4)	P2-C21	1.795 (4)
C2-P2	1.810 (4)	P2-C27	1.783 (4)
P1-C9	1.791 (4)	P2-C33	1.792 (4)
P1-C15	1.808 (5)	C1-C3	1.520 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2. Selected Bond Angles for 6.

	angle (deg)		angle (deg)
P1-C1-C2	105.3 (2)	C2-C1-C3	114.5 (3)
C1-C2-P2	115.6 (3)	C2-P2-C21	107.1 (2)
P1-C1-C3	111.5 (3)	C2-P2-C33	106.7 (2)
C9-P1-C15	109.6 (2)	C2-P2-C27	111.7 (2)
C9-P1-C1	107.3 (2)	O1-P1-C1	112.2 (2)
C9-P1-O1	112.2 (2)	O1-P1-C15	113.0 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Reaction of 4 with NaH in CH_3CN. A mixture of 4 (0.425 g, 0.5 mmol) and NaH (39 mg, 1.6 mmol) in wet CH_3CN (10 ml) was stirred for 1 h at room temperature under nitrogen. The white microcrystalline precipitate was filtered, washed with ether and dried in vacuo to give 0.13 g (51%) of 1,2-[Diphenyl(oxo)phospho]-1-phenylethane 7, mp 172-174 °C (from CH_2Cl_2-ether). IR (CCl_4, cm^{-1}): 3056, 2934, 2899, 1591, 1556, 1434, 1182, 1120, 1071, 695. ^1H NMR (δ, $CDCl_3$): 2.8 (m, 1H), 3.1 (m, 1H), 4.25 (m, 1H), 6.9-7.9 (m, 25H, 5Ph). ^{31}P NMR (δ, $CDCl_3$): 30.4 (d, J = 46.7 Hz, P=O), 35.7 (d, J = 46.7 Hz, P=O). ^{13}C NMR (δ, $CDCl_3$): 30.0 (d, $J_{C\text{-}P}$ = 70 Hz, CH_2), 38.7 (d, $J_{C\text{-}P}$ = 60 Hz, CH), 116.3, 127.8, 128.3, 128.5, 128.9, 129.0, 130.1, 130.7, 131.3, 131.8, 132.0, 133.8 (all m, 6Ph). Mass spectrum (FAB+): m/z (%) 507 (100) $[M + H]^+$, 305 (70) $[M - Ph_2PO + H]^+$, 185 (100) $[Ph_2P]^+$, 202 (22). HRMS for $C_{32}H_{29}P_2O_2$ $[M + H]^+$: calcd. 507.16428, found 507.16378. Anal. Calcd for $C_{32}H_{29}P_2O_2$: C, 75.8; H, 5.5. Found: C, 75.5; H, 5.4.

Reaction of 4 with *t*-BuLi in CH_2Cl_2. A solution of *t*-BuLi in pentane (0.59 ml of 1.7M solution, 1 mmol) was added to a stirred solution of 4 (0.425 g, 0.5 mmol) in CH_2Cl_2 (10 ml) at -78 °C under nitrogen. The mixture was stirred for 15 min at -78 °C, then allowed to warm to room temperature. The resulting yellow solution was filtered from LiOTf, and the solvent was evaporated. Column chromatography on silica gel (50 g) with acetone as eluent gave 0.23 g (93%) of E-1-[triphenyl(trifluoromethanesulphonyloxy)-phospho]-2-(*tert*-butyl)ethylene **10**, as a yellow oil, IR (CCl_4, cm^{-1}): 3062, 2963, 2868, 1604, 1519, 1439, 1271, 1153, 1112, 1031, 844. ^1H NMR (δ, $CDCl_3$): 1.3 (s, 9H, $3CH_3$), 6.7 (dd, $J_{H\text{-}H}$ = 21Hz, $J_{H\text{-}P}$ = 27 Hz, 1H, =CHBu-*t*), 7.5-7.9 (m, 16H, 3Ph and $=CHP^+$). ^{19}F NMR (δ, $CDCl_3$): -77.9 (s, CF_3). ^{31}P NMR (δ, $CDCl_3$): 20.2. ^{13}C NMR (δ, $CDCl_3$): 28.1 (s, $3CH_3$), 37.2 (d, J = 15 Hz, $\underline{C}Me_3$), 104.4 (d, J = 88 Hz, CHP^+), 122.0 (quart. J = 320 Hz, CF_3), 117.9 (d, J = 91 Hz), 130.6, 133.6, 135.4 (3Ph). Mass spectrum (FAB+): m/z (%) 345 (100) $[M - TfO^-]^+$. HRMS for $C_{24}H_{26}P$ $[M - TfO^-]^+$: calcd. 345.17721, found 345.17784.

Reaction of 4 with n-BuLi and 3,4-Dichlorobenzaldehyde in CH_2Cl_2. A solution of *n*-BuLi in hexane (0.6 ml of 2.5M solution, 1.5 mmols) was added to a stirred solution of **2** (0.425 g, 0.5 mmol) in CH_2Cl_2 (10 ml) at -78 °C under nitrogen. The resulting dark yellow solution was stirred for 15 min at -78 °C, then a solution of 3,4-dichlorobenzaldehyde (0.2 g, 1.14 mmol) in CH_2Cl_2 (2 ml) was added. The reaction mixture was warmed to room temperature, stirred an additional 30 min, and then filtered through silica gel (5 g) to remove polymeric byproducts and LiOTf. Additional purification by column chromatography (silica gel, pentane) gave 60 mg (35%) of a 1 : 1 mixture of E- and Z-1,4-bis(3,4-dichlorophenyl)-1,2,3-butatrienes **11**, as a yellow oil, IR (CCl_4, cm^{-1}): 3068, 2970, 2930, 1586, 1560, 1470, 1134, 1033, 883. ^1H NMR (δ, $CDCl_3$): 6.45 and 6.55 (2s, 1:1 intensity, 2H, CH of E- and Z-isomers), 6.27 and 7.35 (2dd, J = 2.0 and 8.3 Hz for both, 1H, Ar), 7.41 and 7.45 (2d, J = 8.3 Hz for both, 1H, Ar), 7.54 and 7.58 (2d, J = 2.0 Hz for both, 1H, Ar). ^{13}C NMR (δ, $CDCl_3$): 108.9 (CH), 127.0, 128.4, 128.5, 128.6, 128.7, 129.2, 130.7, 130.9, 133.1, 133.6, 133.8, 138.1 (Ar), 157.6, 157.8 (=C= for E- and Z-isomers). Mass spectrum (FAB-): m/z (%) 342 (1), 341 (2), 340 (2) $[M]^-$; 339 (3) $[M - H]^-$; 306 (30), 305 (58) $[M - Cl]^-$; 153 (100) $[C_4Cl_3]^-$.

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12. Phosphorus to carbon phenyl-migrations have been reported in the literature for the hydrolysis of phosphoranes and some related reactions[11b].
13. Elimination of benzene in the hydrolysis of phosphonium salts is a well documented process[11c].
14. It is well known[14a] that alkyllithiums, particularly, *t*-BuLi, react with CH_2Cl_2 resulting in chlorocarbene. However, in our case under low temperature conditions this process did not interfere with the observed reaction (eq. 4). (a) Closs, G.L. *J. Am..Chem.. Soc.* **1962**, *84*, 809.
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17. 3,4-Dichlorobenzaldehyde is the most reactive aldehyde toward cumulene ylides[9,10]. Use of other aldehydes and ketones (e.g. benzaldehyde and acetophenone) did not lead to trapping of **3**.