Preparation of vinylphosphines by means of free radical addition of diphenylphosphine to alkynes and allenes

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(Received November 20th, 1990)

Abstract

Diphenylphosphine adds readily to alkynes and allenes under free radical conditions. Alkynes normally give E-vinylphosphines as the primary (kinetic) product, but Z-vinylphosphines are the main products isolated. Allenes generally give complex product mixtures in which the predominant components are vinyl phosphines formed via addition of the $Ph_2P^{\cdot}$ radical to the central carbon atom of the allene fragment.

Introduction

The free radical addition of phosphine to alkenes was described as early as 1952 [1]. Though that report was followed by others involving substituted phosphines [2a], little work has apparently been carried out on corresponding additions to alkynes and allenes [2b]. Rauhut et al. [3] studied the reactions of bis(2-cyanoethyl)phosphine with 1-heptyne and 1-octyne, which gave complex product mixtures. Märkl [4] carried out addition of phenylphosphine to 1,5-hexadiyne to form the dihydrophosphepine $PhP\overline{CH=CH(CH_2)_2CH=}CH$. There has been only one report of a reaction between a phosphine and an allene [5], the reaction again giving a mixture of products. It thus appeared of interest to study the reactions between diphenylphosphine and various alkynes and allenes in order to obtain detailed information on the regio- and stereo-chemistry of such reactions, and thus on the suitability of the reactions for the preparation of vinylphosphines.

Results and discussion

(a) 1-Alkynes

Two groups have reported preliminary observations on the addition of $Ph_2P^{\cdot}$ to 1-alkynes: phenylacetylene reacts after 7 days at 100°C to give the Z-alkenylphosphine [6], while 1-octyne does not react after 4 days at 100°C [7]. We find that the reaction between phenylacetylene and diphenylphosphine occurs in the presence of AIBN or upon UV-irradiation with the same regiochemistry as that previously described [6]:

$$PhC\equiv CH + Ph_2PH \xrightarrow[\text{or } h\nu]{AIBN} E/Z - PhCH=CHPPh_2$$
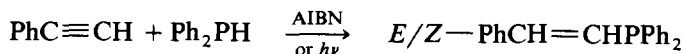
Analogous products are obtained from 1-pentyne, 3,3-dimethyl-1-propyne, N,N-dimethylpropargylamine and 1-trimethylsiloxy-1-cyclohexylacetylene. In each case an E/Z isomer mixture is formed, and with one exception the Z isomer predominates in the final product mixture (details are given in Table 1). However, as is clear from a study of the time-dependence of the E/Z ratio (see footnotes to Table 1), the E isomer can predominate in the initial stages of the reaction, possibly because its precursor radical is more stable:
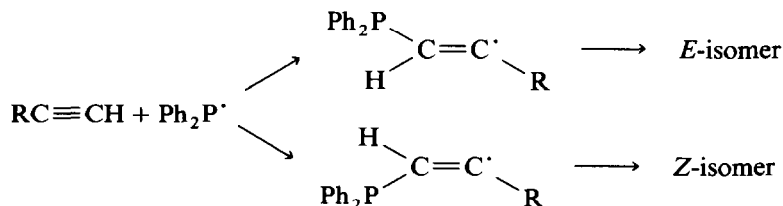
The final product composition thus apparently represents a "steady-state" situation, the initially formed E-vinylphosphine isomerising to a considerable extent during the reaction to the Z-isomer.

By-products of the type $Ph_2PCH=C(R)PPh_2$ are observed when R = Pr and Me_2NCH_2; the amounts of by-product are 5 and 20%, respectively, and in the latter case this amount increases to 35% when two equivalents of diphenylphosphine are used. The value of $^3J(P,P)$ is in each case 163 Hz; in the light of the values of $^3J(P,P)$ for the E/Z pair $Ph_2PCH=CHPPh_2$ reported by McFarlane [8] (E 13.4 Hz, Z 105.5 Hz) these by-products must have a Z geometry.
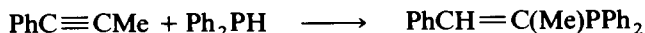
Table 1

Reaction conditions and product ratios for the addition of diphenylphosphine to alkynes $RC\equiv CR'$

R	R'	Reaction conditions	Consumption (%) [a]	E/Z ratio	Yield (%) GLC (isolated)
Ph	H	46 h AIBN	100	18/82 [b]	95 (73)
		3.5 d $h\nu$	91	[c]	91 (76)
Pr	H	4 d $h\nu$	92	48/52	91 (38)
^{t}Bu	H	10 h AIBN	98	39/61	83 (25)
Me_2NCH_2	H	6.5 d AIBN	75	88/12	53
		4 d $h\nu$	100	33/67 [d]	43
cyclohexyl-OSiMe$_3$	H	3.5 d AIBN	95	39/61	87
Ph	Me	10 h AIBN	100	3/97	100 (87)
		3 d $h\nu$	96	13/87	96 (82)
Me_2NCH_2	CONMe$_2$	2 h AIBN	100	12/88	85
$MeOCH_2$	CONMe$_2$	16 h $h\nu$	100	42/58	90
		22 h AIBN	100	35/65	98

[a] W.r.t. Ph_2PH. [b] Time-dependence of E/Z ratio at % phosphine consumption as follows: 2 h (95%) 70/30, 10 h (98%) 48/52, 18 h (100%) 27/73. [c] Time-dependence of E/Z ratio at % consumption as follows: 2 h (5%) 100/0, 10 h (25%) 78/22, 19 h (63%) 51/49, 42 h (78%) 32/68. [d] Time-dependence of E/Z ratio at % consumption as follows: 3.5 h (5%) 30/70, 21 h (40%) 25/75, 3 d (90%) 16/84.

(b) Non-terminal alkynes

The regiochemistry of the reaction with 1-phenyl-1-propyne is, as expected, governed by the mesomeric stabilising effect of the phenyl residue:

$$PhC \equiv CMe + Ph_2PH \longrightarrow PhCH = C(Me)PPh_2$$

The presence of two functionally substituted residues does not lower the regiospecificity:

$$RC \equiv CCONMe_2 + Ph_2PH \longrightarrow RCH = C(CONMe_2)PPh_2$$

$$(R = Me_2NCH_2, MeOCH_2)$$
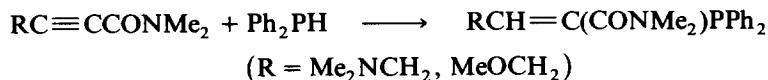
In all three cases E/Z isomer mixtures are formed in which the Z isomer again predominates (see Table 1). The reason for the regiochemistry observed in the last two cases is not clear, though it appears possible to postulate an interaction between the nitrogen lone pair in the $CONMe_2$ fragment and either occupied or empty orbitals on phosphorus: such an interaction has previously been discussed in the literature [9].

(c) Allenes

It is known that carbon-centred radicals preferably attack allenes at one of the terminal carbon atoms of the allene moiety [10,11], whereas other radicals (e.g. $R_3Sn^{\cdot}$ [12], Br [13,14]) preferably attack the central carbon.

The reaction between allene and phosphine is reported to give a small amount of isopropenylphosphine, together with a large amount of polymeric product [5]. We find that the reaction of allene with diphenylphosphine is also complex: apart from allyl- and isopropenyl-diphenylphosphine, products derived formally from an addition of Ph_4P_2 are observed.

The reaction of a monosubstituted allene with diphenylphosphine can give up to six products:
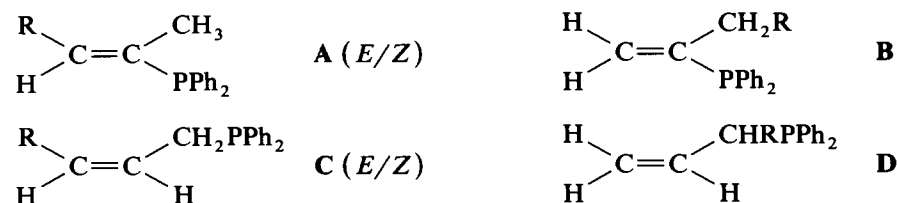
It is found (see Table 2) that no products of type **D** are formed. In the case of methoxyallene **A** is the sole product, while with phenylallene a small amount of **B** is also formed. Mixtures containing products of type **A**, **B** and **C** are obtained when $R = {}^{n}Bu$, ${}^{c}Hex$, ${}^{t}Bu$ and Me_3Sn, though **C** is normally the minor product.

Pasto [10] has discussed the regioselectivity of the attack of free radicals on monosubstituted allenes; his interpretation involves the irreversible formation [13] of two radicals (I and II) of different thermodynamic stabilities when the central carbon is attacked.

Table 2

Reaction conditions and product composition in addition of diphenylphosphine to allenes $RR'CH=C=CR''_2$ [a]

$$R'^{\backsim}_{R^{\backsim}}C=C{\scriptstyle<}^{CHR''_2}_{PPh_2} \qquad R''^{\backsim}_{R''^{\prime\prime}}C=C{\scriptstyle<}^{CHRR'}_{PPh_2} \qquad R'^{\backsim}_{R^{\backsim}}C=C{\scriptstyle<}^{CR''_2PPh_2}_{H}$$

$$\qquad\quad A \qquad\qquad\qquad\quad B \qquad\qquad\qquad\quad C$$

R	R'	R''	Reaction conditions	Yield (%) GLC	Yield (%) (isolated)	B.p. (°C/10⁻³ mmHg)	A E	A Z	B	C E	C Z
MeO	H	H	46 h $h\nu$	78	26	117–119	93	7			
			5 h AIBN	96			61	39			
Ph	H	H	21 h AIBN	95	80	m.p. 89–96	72	14	13		
Bu	H	H	40 h $h\nu$	96			55	25	5	15	
			5 h AIBN	91	35	133–140	53	27	11	9	
cHex	H	H	42 h $h\nu$	77			48	20	14	18	
			42 h AIBN	88	20	160–163	57	13	12	18	
tBu	H	H	40 h $h\nu$	98	25	120–126	48	11	7	22	12
			20 h AIBN	98			45	19	9	20	7
Me₃Sn	H	H	42 h $h\nu$	40			40	15	20	25	
			18 h AIBN	50			18	10	17	25	30
(cyclohexylidene)		H	18 h AIBN	94	36	156–164	76				24
Cyclononadienyl [b]											
Me	Me	Me	20 h AIBN	100			100		100		
			40 h $h\nu$	55 [c]	35	154–156 [d]					

[a] Phosphine consumption ≥ 98% unless otherwise stated. [b] Adduct with 1,2-cyclononadiene. [c] Phosphine consumption 67%. [d] Decomposed on attempted distillation.

This reasoning can also be applied to the present case. Attack at the terminal carbon atoms is probably reversible [15], so that the main product of attack at the central carbon atom is the thermodynamically favoured allylphosphine.

A complication arises when $R = Me_3Sn$. In this case radicals I and II can undergo loss of a β-trimethylstannyl radical, leading to the formation of $Ph_2PCH=C=CH_2$, which undergoes hydrophosphorylation to give the observed by-product $Ph_2PCH_2C(PPh_2)=CH_2$.

Cyclohexylideneallene, formally a 1,1-disubstituted allene, is attacked predominantly at the central atom; this contrasts with the finding by Pasto [10], that attack on such allenes is *solely* at the central carbon.

1,2-Cyclononadiene, a 1,2-disubstituted allene, is attacked solely at the central carbon atom, the addition product being formed in quantitative yield.
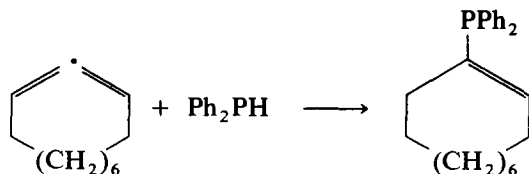
Tetramethylallene is also attacked exclusively at the central carbon, in keeping with its behaviour in hydrostannylation [12].
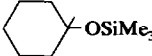
These results make it clear that no general rules governing free radical attack on allenes can be formulated.

(d) Isomer identification

Isomer identification was carried out on the basis of a multinuclear NMR analysis. Since the NMR data for the vinylphosphines arising from the addition of diphenylphosphine to alkynes show features of more general importance they will

Table 3

^{31}P chemical shifts and selected proton NMR data ^{a} for compounds of the type E/Z–$RCH=CR'PPh_2$

R	R'	E/Z	$\delta(^{31}P)$	$\delta(=CH)/^3J(PH)$	$\delta(R')/^2J(PH)$	$^3J(HH)$
Ph	H	E	−13.3	$^{b/c}$	6.95/1.0	10.8
		Z	−26.4	$^{b/c}$	6.47/2.6	12.8
Pr	H	E	−15.1	6.45/24.0	6.19/2.2	11.5
		Z	−32.9	6.27/31.8	6.21/5.7	16.6
^{t}Bu	H	E	−15.1	6.33/17.4	6.13/3.8	17.4
		Z	−31.0	6.47/28.1	6.03/4.4	12.6
Me_2NCH_2	H	E	−15.4	6.16/13.8	6.42/8.9	16.7
		Z	−32.4	6.53/22.6	6.40/13.1	11.6
⬡-OSiMe₃	H	E	−15.1	6.25/14.1	6.33/8.8	16.8
		Z	−30.3	6.66/25.9	6.19/4.3	12.8
Ph	Me	E	6.8	6.69/13.8	2.01/7.5 ^{d,e}	
		Z	−14.8	6.87/17.4	1.80/2.9 ^{d,e}	
Me_2NCH_2	$CONMe_2$	E	−6.9	$^{b/c}$	2.08	
		Z	−10.3	7.05/21.6	2.08	
$MeOCH_2$	$CONMe_2$	E	−7.4	$^{b/c}$	2.90	
		Z	−15.4	7.05/21.6	2.78	

^{a} $\delta(^{31}P)$ vs. external 85% H_3PO_4, $\delta(^1H)$ vs. TMS. ^{b} Hidden. ^{c} Not detected. ^{d} $^3J(PH)$. ^{e} $^4J(HH)$ 1.6 Hz.

be described separately elsewhere [16]. The present paper gives only ^{31}P chemical shifts and selected structure-relevant proton data for the adducts, which suffice to characterise the various isomers clearly. The data are listed in Table 3. It is found that the Z isomer always absorbs to higher field than the E isomer: such behaviour was originally reported by Grim et al. [17] and Duncan and Gallagher [18], who prepared the vinylphosphines from vinyl bromides of known geometry.

The complex product mixtures obtained from most of the allenes require multi-nuclear information for their structural assignment. Table 4 contains structure-relevant phosphorus and proton NMR data for vinylphosphines formed from diphenyl-phosphine and allenes. In the case of the E/Z isomer pairs A, both the phosphorus chemical shift and $^3J(P,H)$ make assignment unambiguous. B contains two vinylic protons with an inter-proton coupling (where measurable) of ca. 1.7 Hz.

Only a few allylphosphines C were observed, and in this case it is difficult to distinguish between E and Z isomers. The ^{31}P chemical shifts lie between -16.1 and -18.4 ppm; the literature values for allyldiphenylphosphine are -17.9 [19] and -17.3 ppm [20]. Because of the complexity of the spectra and the small amounts of

Table 4

Selected NMR data ^{a} for vinylphosphines derived from allenes $RR'C=C=CR''_2$

$$\underset{R}{\overset{R'}{}}C=C\underset{PPh_2}{\overset{CHR''_2}{}} \qquad \underset{R''}{\overset{R'}{}}C=C\underset{PPh_2}{\overset{CHRR'}{}}$$

| | | | | E/Z-A | | B | |
R	R'	R''	Cpd.	$\delta(^{31}P)$	$\delta(=CH)$	$^3J(P,H)$
MeO	H	H	E-A	-2.8	6.57	10.4
			Z-A	-21.7	6.53	15.0
Ph	H	H	E-A	6.7	6.69	13.8
			Z-A	-14.9	6.87	17.4
			B	-4.1	5.10, 5.42	13.8, 22.0
Bu	H	H	E-A	5.1	5.98	16.4
			Z-A	-19.2	6.27	24.6
			B	-4.8	5.02, 5.65	5.7, 20.5
^{c}Hex	H	H	E-A	4.9	5.79	17.4
			Z-A	-18.5	6.02	25.6
^{t}Bu	H	H	E-A	11.8	6.06	19.7
			Z-A	-15.2	6.42	28.4
			B	-0.8	^{f}	^{f}
Me$_3$Sn ^{b}	H	H	E-A	5.9 ^{b}	5.96	11.2
			Z-A	-21.8^c	6.05	31.4
			B	-2.8^d	4.64, 5.48	9.8, 18.4
⬡=		H	A	-13.0		
Cyclononadienyl ^{e}			E-A	0.5	5.79	12.8
Me	Me	Me	A/B	-13.1		

^{a} In ppm vs. external 85% H_3PO_4. ^{b} $\delta(^{119}Sn)$ -31.6 ppm, $^3J(^{119}Sn,^{31}P)$ 24.4 Hz. ^{c} $\delta(^{119}Sn)$ -39.3 ppm, $^3J(^{119}Sn,^{31}P)$ 20.3 Hz. ^{d} $\delta(^{119}Sn)$ 0.0 ppm, $^3J(^{119}Sn,^{31}P)$ 10.2 Hz. ^{e} Adduct with 1,2-cyclononadiene. ^{f} Not determined.

C present, complete analysis of the spectra was not possible, and so no table of NMR data is provided.

Experimental

All manipulations involving organophosphorus compounds were carried out under argon because the vinylphosphines are readily oxidised.

^{31}P, ^{13}C and non-routine ^1H NMR spectra were recorded with a Bruker AM 300 spectrometer; samples were dissolved in $CDCl_3$, and 85% H_3PO_4 and TMS were used as external and internal standards, respectively.

Reactions between diphenylphosphine and alkynes or allenes were generally carried out by one of two standard procedures. In each case 7.5 mmol (1.4 g) diphenylphosphine and an equimolar amount of the alkyne/allene were used. This mixture was either (a) heated at 80°C in the presence of a catalytic amount of AIBN or (b) irradiated with light from a high pressure mercury lamp (Heraeus TQ-150), in both cases with magnetic stirring. The progress of the reaction was monitored by proton NMR spectroscopy at 60 MHz (Varian EM-360 spectrometer). After the time shown in Table 1 had elapsed the reaction mixture was analysed by GLC and NMR spectroscopy. Solid products were recrystallised from chloroform and liquid products were isolated as colourless oils after fractional distillation. In some cases decomposition was observed on attempted distillation.

A different procedure was used for the reaction between diphenylphosphine and allene. Diphenylphosphine (7.5 mmol) was introduced into a quartz Schlenk tube. Allene was passed slowly through the phosphine during UV-irradiation of the tube. After 8 h the phosphine consumption was 65% and the reaction was interrupted. GLC analysis showed the presence of 10 volatile components, including 35% allyldiphenylphosphine [21], 17% diphenylphosphine oxide [22], 15% 1,3-bis(diphenylphosphino)propane [8,23] and 21% 1,2-bis(diphenylphosphino)propane [$\delta(^{31}P)$ −0.4, −22.6 ppm, $^3J(P,P)$ 21.2 Hz].

Tables 1 and 2 contain details of reaction conditions and isomer ratios; in the case of the reactions with allenes physical properties of the products are given (Table 2).

● The physical properties and elemental analysis data for those adducts between diphenylphosphine and alkynes $RC\equiv CR'$, which were purified either by distillation or recrystallisation are as follows:

PhCH=CHPPh$_2$, pure Z-isomer, m.p. 87–89°C (lit. [6] 89–90°C).

C$_3$H$_7$CH=CHPPh$_2$, b.p. 116–120°C/0.001 mmHg. Anal. Found: C, 80.0; H, 7.1. C$_{17}$H$_{19}$P calc.: C, 80.3; H, 7.5%.

^{t}BuCH=CHPPh$_2$, b.p. 124–134°C/0.001 mmHg. Anal. Found: C, 80.3; H, 7.9 C$_{18}$H$_{21}$P calc.: C, 80.6; H, 7.8%.

PhCH=C(Me)PPh$_2$, pure Z-isomer, m.p. 97°C. Anal. Found: C, 83.9; H, 6.5. C$_{21}$H$_{19}$P. calc.: C, 83.5; H, 6.3%.

● Elemental analysis values were also obtained for several adducts between diphenylphosphine and allenes RCH=C=CH$_2$:

Adduct with MeOCH=C=CH$_2$. Anal. Found: C, 74.9; H, 6.5. C$_{16}$H$_{17}$OP calc.: C, 75.0; H, 6.6%.

Adduct with BuCH=C=CH$_2$. Anal. Found: C, 81.1; H, 8.1 C$_{19}$H$_{22}$P calc. C, 81.1; H, 7.9%.

Adduct with $^{t}BuCH=C=CH_2$. Anal. Found: C, 81.1; H, 8.1. $C_{19}H_{22}P$ calc. C, 81.1; H, 7.9%.

Adduct with $^{c}C_6H_{11}CH=C=CH_2$. Anal. Found: C, 82.2; H, 7.6. $C_{21}H_{24}P$ calc.: C, 82.1; H, 7.8%.

Adduct with ◯$C=C=CH_2$. Anal. Found: C, 81.7; H, 8.3. $C_{20}H_{24}P$ calc.: C, 81.3; H, 8.1%.

Adduct with 1,2-cyclononadiene. Anal. Found: C, 82.2; H, 8.6. $C_{21}H_{25}P$ calc.: C, 81.8; H, 8.2%.

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