LAOSOOKSATHIT, SURIN

A DIRECT SYNTHESIS OF VINYLIC PHOSPHONATES FROM VINYLIC HALIDES AND HALIDE EXCHANGE AT VINYLIC POSITION CATALYZED BY COPPER(I) HALIDE COMPLEXES OF TRIVALENT PHOSPHORUS

City University of New York PH.D. 1981

A DIRECT SYNTHESIS OF VINYLIC PHOSPHONATES FROM VINYLIC HALIDES AND HALIDE EXCHANGE AT VINYLIC POSITION CATALYZED BY COPPER(I) HALIDE COMPLEXES OF TRIVALENT PHOSPHORUS

by

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ABSTRACT

A series of vinylic halides has been investigated in their reactions with copper(I) halide complexes of phosphite triesters. With trialkyl phosphite complexes and vinylic halides, moderate-to-high yield conversions to the corresponding vinylic phosphonates are observed upon heating. Maintainance of stereochemistry about the olefinic linkage is observed upon reaction.

The reaction generating vinylic phosphonates is also observed to be in competition with a halide exchange reaction between the copper(I) halide and the vinylic halide. This halide exchange reaction has been investigated using copper(I) halide complexes of trivalent phosphorus reagents which are unable to yield phosphonate products. Maintainance of stereochemistry about the olefinic linkage is also observed in the halide exchange reaction.

Possible mechanisms of the phosphonation and the halide exchange reactions have been proposed.

FOR

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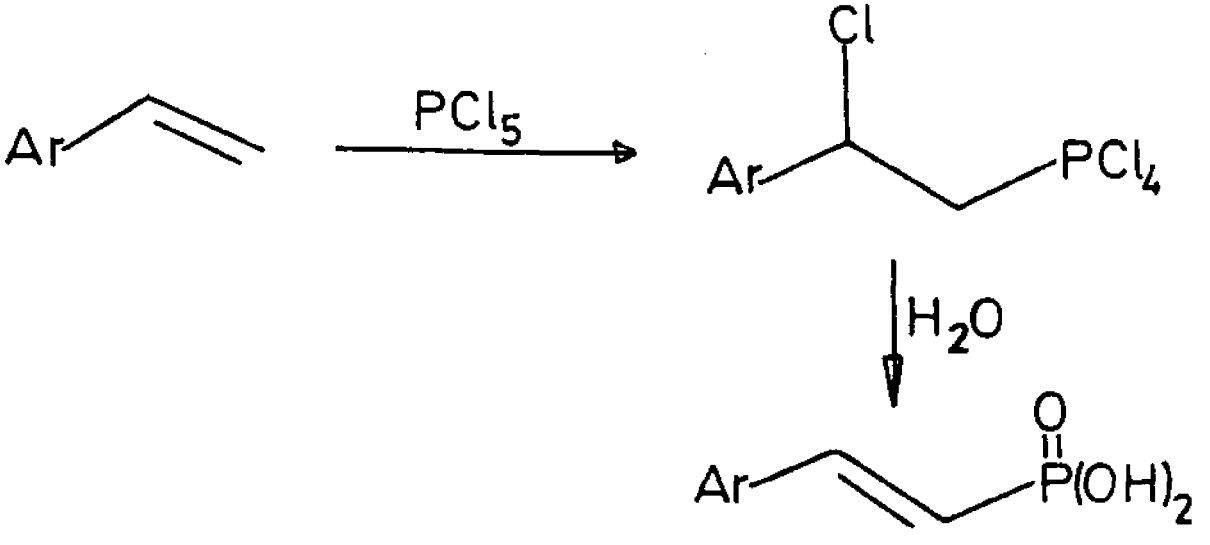
INTRODUCTION

PART I. SYNTHESES OF VINYLIC PHOSPHONATES.

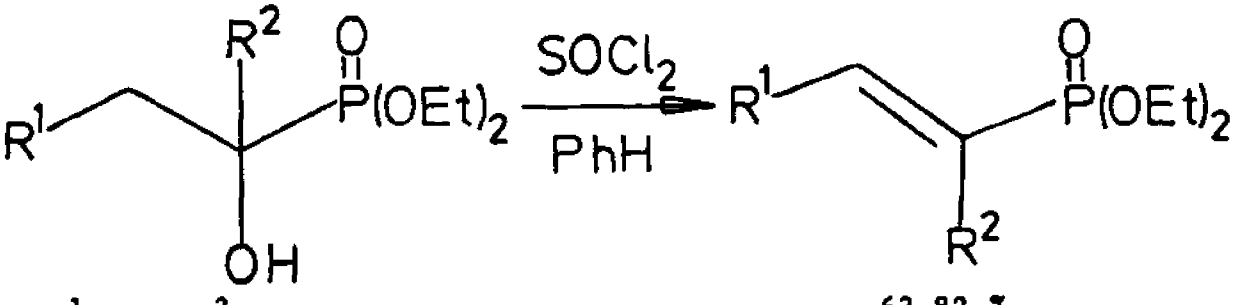
Vinylic phosphonates and their derivatives have received considerable attention in the past few decades due to their potential for industrial applications[1,2] and their utility in many organic syntheses.[3-14] That is, these compounds may be used as intermediates in the preparation of other materials for use in fire-proofing agents, surface-active agents, insecticides, and for reagents in organic synthetic procedures.

A number of multi-step synthetic methods are available. An early report on the synthesis of vinylic phosphonic acids by the addition of phosphorus pentachloride to unsymmetrical olefins followed by hydrolysis was made by J. Thiele[15] and was reinvestigated by Bergmann and Bondi[16](Scheme 1). This reaction has been



Scheme 1.

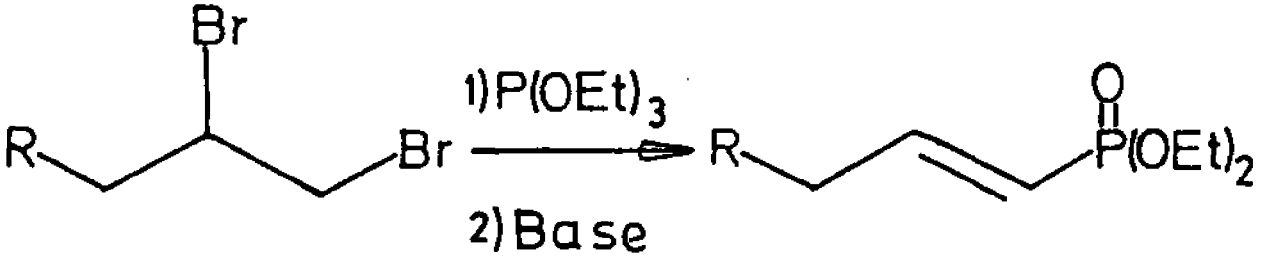
shown to proceed in a Markovnikov manner.[16-19] The yields from this reaction are quite good and it has been used for the synthesis of a variety of vinylic phosphonate derivatives from olefins.[17,18] Similarly, a number of diolefinic phosphonates[1,2,19-21] which are of use for the synthesis of rubber-like polymers,[1,2] have been prepared from phosphorus pentachloride and 1,3-diolefinic compounds. A series of vinylic phosphonates have also been prepared in good yield by the dehydration of α-hydroxyphosphonates[22] (Scheme 2).



a) R^1 = H, R^2 = Me
b) R^1 = R^2 = Me
c) R^1R^2 = $-(CH_2)_4-$
d) R^1R^2 = $-(CH_2)_3-$
e) R^1 = iPr, R^2 = Me

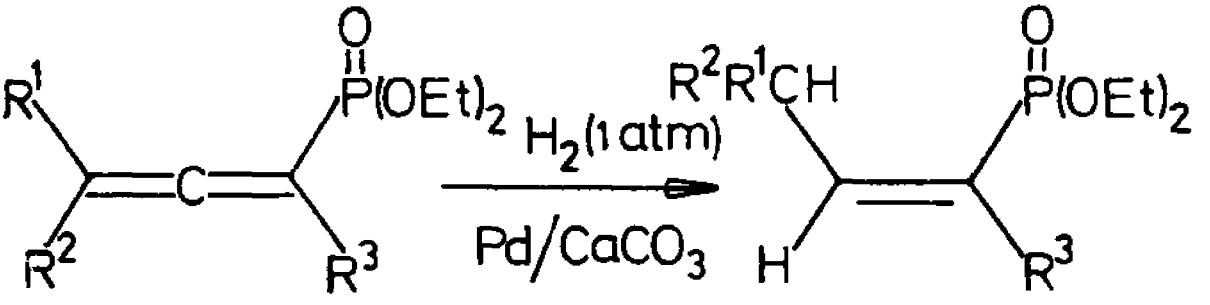
Scheme 2.

The Michaelis-Arbuzov reaction[23,24] of 1,2-dihalopropanes with trialkyl phosphites followed by dehydrohalogenation has also been found to be useful for the synthesis of vinylic phosphonates[25] (Scheme 3). However, the cis-isomers of vinylic phosphonates, which



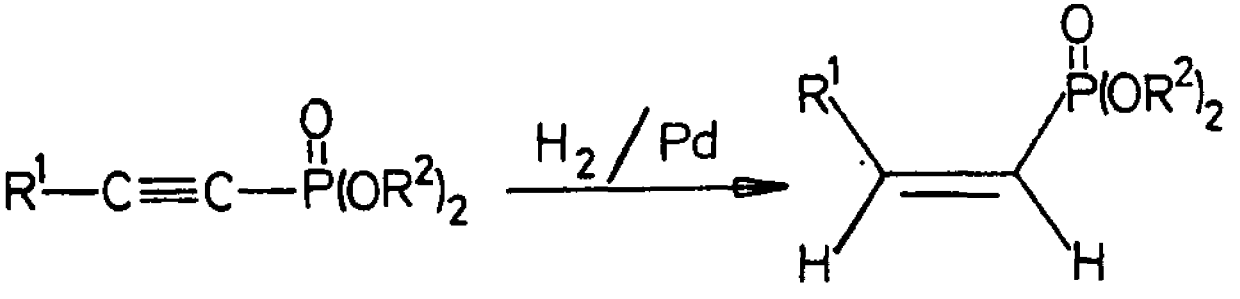
Scheme 3.

are considerably less available[26,27] than the trans-isomers, could best be obtained by the catalytic hydrogenation[14,28] of either 1,2-dienyl[14] or 1-alkynyl phosphonates[29,30](Schemes 4 and 5).



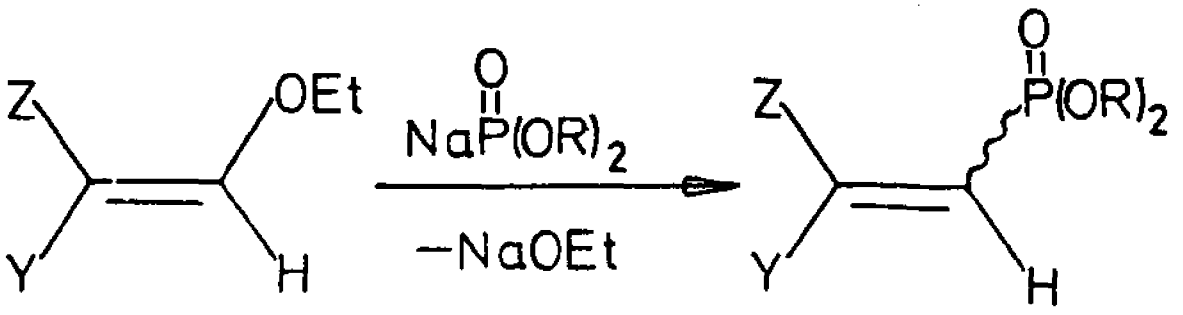
a) $R^1 = R^2 = R^3 = H$
b) $R^1 = Me$, $R^2 = R^3 = H$
c) $R^1 = R^2 = Me$, $R^3 = H$
d) $R^1 = R^2 = R^3 = Me$

Scheme 4.



Scheme 5.

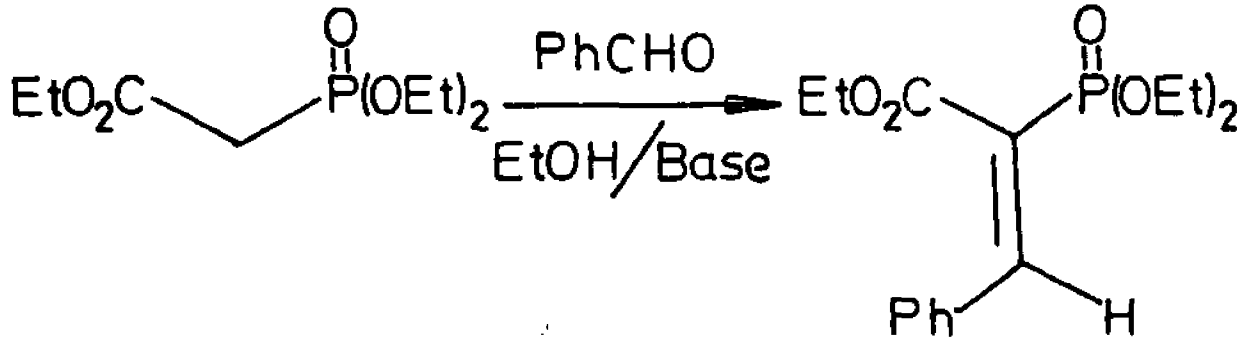
Reaction between sodium dialkylphosphites and ethoxymethylene derivatives of β-dicarbonyl compounds followed by elimination of sodium ethoxide to give α,β-unsaturated dicarbonyl phosphonates in good yield has also been reported[31](Scheme 6).



a) Y = Z = MeCO, R = Et
b) Y = Z = MeCO, R = n-Bu
c) Y = MeCO, Z = CO_2Et, R = Et
d) Y = CO_2Et, Z = CN, R = Et
e) Y = EtO_2CCO, Z = CO_2Et, R = Et

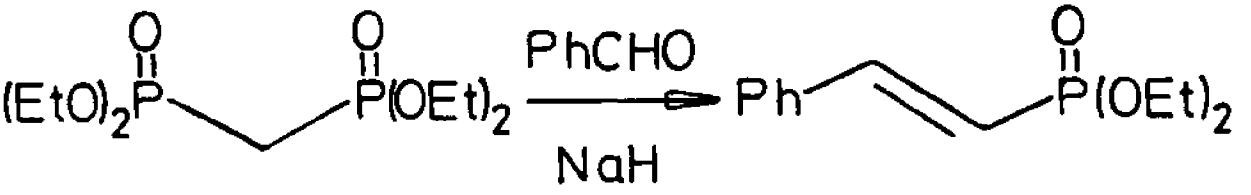
Scheme 6.

It is interesting to note that the reaction between triethyl phosphonoacetate and benzaldehyde has been reported to give triethylbenzylidenephosphonoacetate in the presence of a base and a protic solvent[32,33](Scheme 7). However, this procedure usually



Scheme 7.

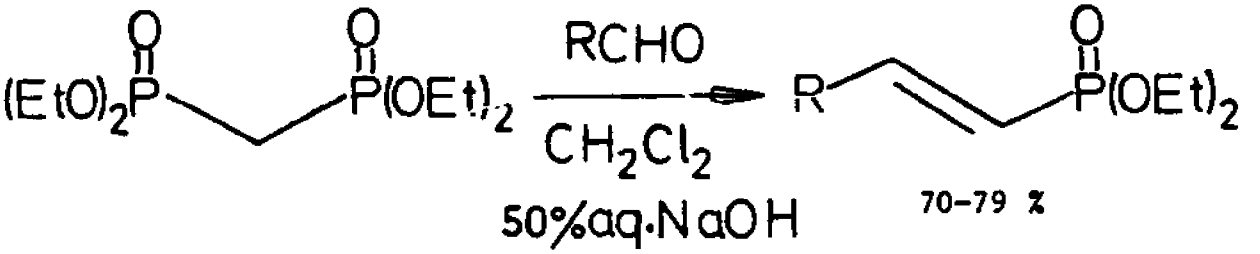
gives poor yields due to the formation of cinnamic acid. High yields of the vinylic phosphonates could be obtained by the reaction of tetraethyl methylenebisphosphonate and benzaldehyde in the presence of sodium hydride[34](Scheme 8).



Scheme 8.

Recently, Mikolajczyk et. al.[35] have used the Horner-Wittig reaction in a two-phase system to synthesize the vinylic phosphonates from tetraethyl methylenebisphosphonate and aldehydes. It should be noted that the reaction can proceed even in the absence of a typical phase-transfer catalyst since the starting phosphonate[36] contains two basic centers in the molecule as well as the relatively acidic methylene protons and acts in an autocatalytic manner(Scheme 9). Moreover, this reaction is convenient to perform and gives good yields of the pure E-isomers.

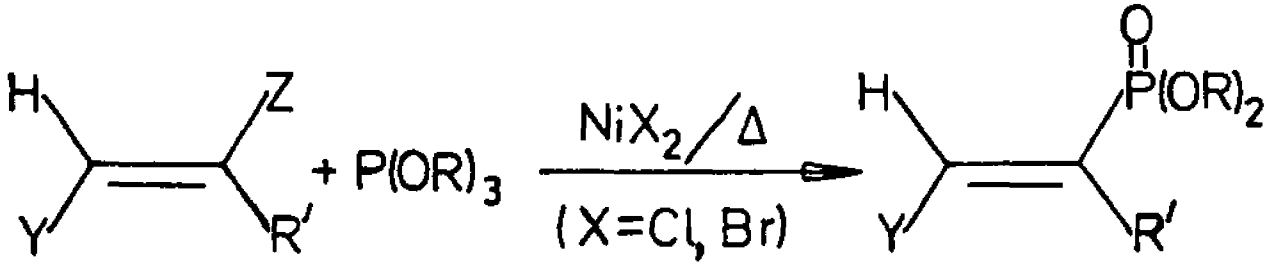
However, there are very few methods involving the direct synthesis of the vinylic phosphonates. These compounds can not be obtained easily by the typical Michaelis-Arbuzov reaction.[23,24]



R = Ph, 4-BrC_6H_4, p-$Me_2NC_6H_4$, PhCH=CH

Scheme 9.

The first direct synthesis of these vinylic phosphonates was reported by Tavs and Weitkamp.[37] On heating the mixture of a vinylic halide and trialkyl phosphite in the presence of a nickel halide complex at 150-190°C the vinylic phosphonates could be obtained in yields of 21-94%(Scheme 10). However, the typical yield of product from this reaction is low and the stereochemistry of the products still has not been clarified. Very recently, Hirao et. al.[38]

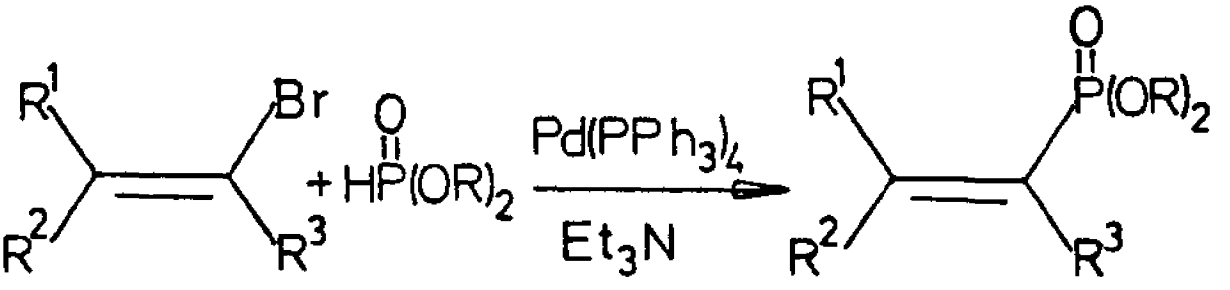


a) R' = H, Y = H, Z = Cl
b) R' = Ph, Y = H, Z = Br
c) R' = H, Y = Z = Cl
d) R' = H, Y = Ph, Z = Br

a) R' = Y = H, R = Et, iPr
b) R' = Ph, Y = H, R = Et
c) R' = H, Y = $PO(OR)_2$, R = Me, Et
d) R' = H, Y = Cl, R = Et
e) R' = H, Y = Ph, R = Et

Scheme 10.

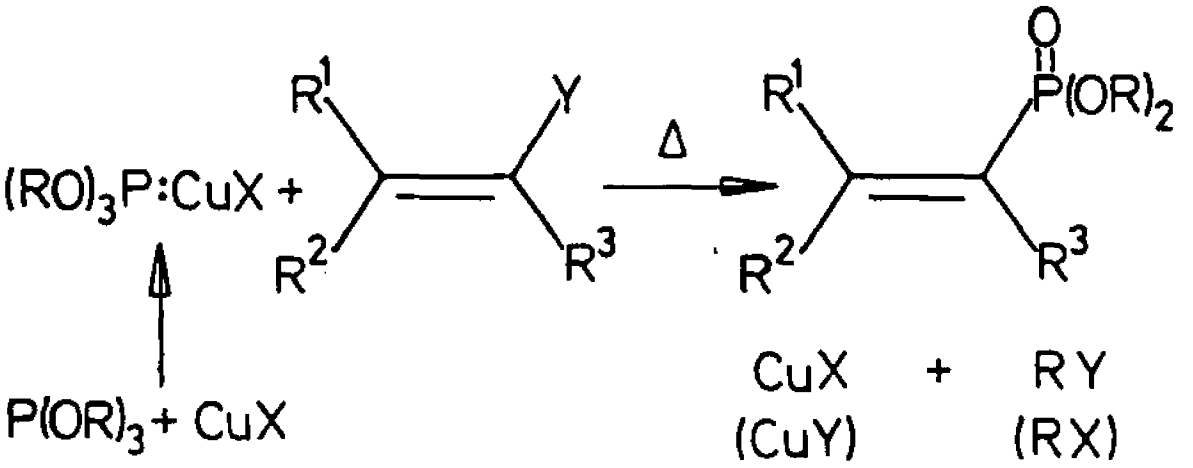
have found that the reaction of vinylic bromides with dialkyl phosphites in the presence of tetrakis(triphenylphosphine)palladium afforded the corresponding vinylic phosphonates in 66-98% yields. This reaction was also found to be stereoselective(Scheme 11). However, the reaction has been shown to work well only with the vinylic bromides.



a) R^1 = Ph, R^2 = R^3 = H, R^4 = Et
b) R^1 = R^2 = H, R^3 = Ph, R^4 = Et, iPr, n-Bu
c) R^1 = R^3 = H, R^2 = Ph, R^4 = Et
d) R^1 = R^2 = H, R^3 = Me, R^4 = Et, iPr
e) R^1R^2 = $-(CH_2)_4-$, R^3 = H, R^4 = Et

Scheme 11.

Thus, the direct phosphonation of vinylic halides by the use of transition metals as catalysts has to date found only limited success. However, direct phosphonation of aryl iodides by trialkyl phosphites have been reported to be effected by the use of CuCl,[39] $NiCl_2$,[40] $PdCl_2$,[39] Bronze[41] or Photolysis.[42] This led us to investigate the possibility of using trialkyl phosphite-copper(I) halide complexes[43-51] as reagents for the direct displacement of vinylic halides as shown in Scheme 12.



Scheme 12.

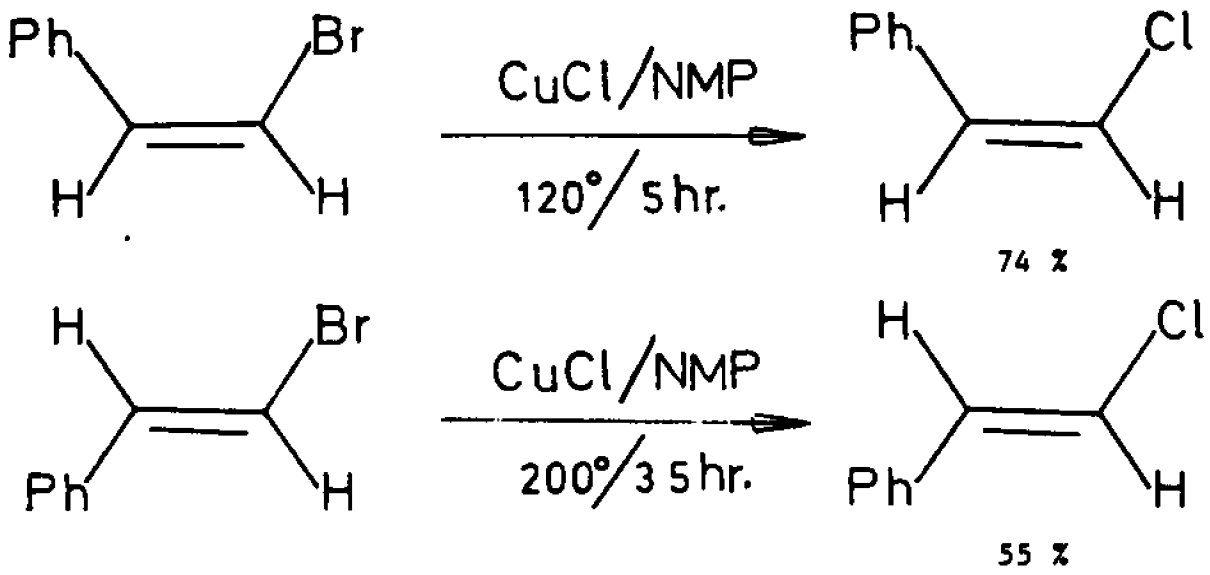
This reaction may be considered to be related to the Michaelis-Arbuzov reaction.[23,24] The use of these copper(I) complexes would allow the phosphonation to be performed in a homogeneous system, since copper(I) complexes are soluble in many organic solvents as well as the vinylic halides. Finally, it may be hoped that this method would be applicable to a wide variety of vinylic halides.

PART II. HALIDE EXCHANGE REACTIONS.

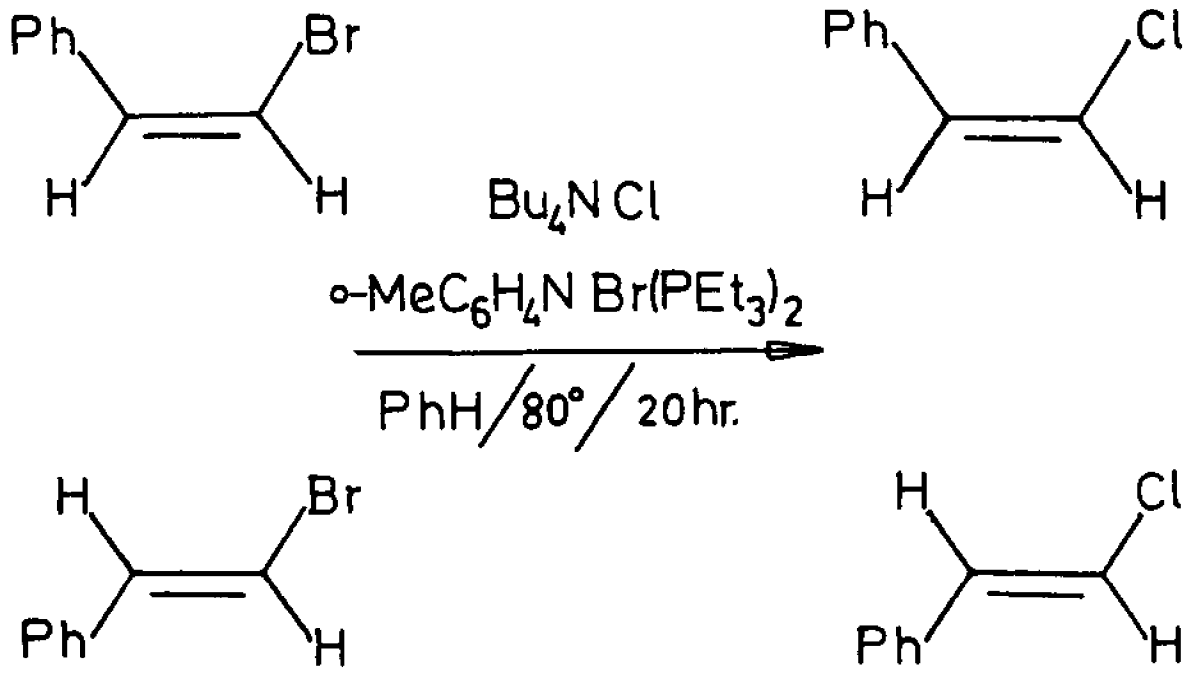
A large number of papers have been devoted to transition metal catalyzed halogen exchange reactions in aryl halides.[52-64] Particularly, complexes involving copper(I) have been investigated extensively for their catalysis of halide exchange reaction.[54,64] However, there have been relatively few reports on transition metal catalyzed halide exchange processes in vinylic systems.[52,65] Such exchange processes would be rather important in organic syntheses,[54-56,66,67] particularly for those conversions of readily available vinylic halides to the less available ones. Furthermore, these reactions are of significant potential for the direct synthesis of radioisotopic vinylic halides from the nonradioisotopic vinylic halide species. There is also the prospect of such processes being of use for carbon-carbon bond formation using carbon centered nucleophiles.[67]

A previous report on the replacement of bromide by chloride in a vinylic system has appeared.[65] This conversion was effected by the use of copper(I) chloride with N-methylpyrrolidone-2(NMP) as a complexing agent as well as solvent. The stereospecificity of the reaction was also observed(Scheme 13). It should be noted that the complex between copper(I) chloride and NMP is formed in situ.

Recently, Tsou and Kochi[52] have found that the reaction between chloride and β-bromostyrene catalyzed by certain nickel halide complexes affords β-chlorostyrene in high yields and with excellent stereospecificity(Scheme 14). Under the conditions employed there is no cis-trans isomerization observed.

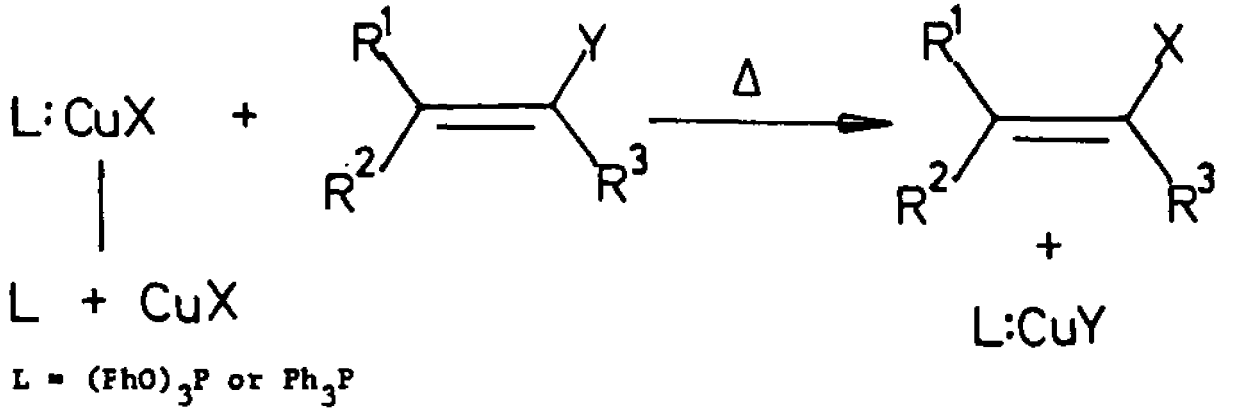


Scheme 13.



Scheme 14.

However, such halide exchange processes have been limited only to β-bromostyrene. Moreover, the halide exchange reaction catalyzed by copper(I) chloride-NMP system proceeded in only low yields even under the most drastic conditions. The use of nickel halidecomplexes, on the other hand, is considerably less convenient and requires extra reagents and excessive periods of time. Therefore, we have set out to investigate the possibility of using certain copper(I) halide complexes of trivalent phosphorus as catalysts for the halide exchange reaction in vinylic systems. Copper(I) halide complexes of triphenyl phosphite or triphenylphosphine seemed to be promising catalysts for this halide exchange reaction, since these complexes are analogous to those trialkyl phosphite-copper(I) halide complexes which have been prepared from trialkyl phosphite and copper(I) halides.[43-51] These complexes are quite stable under anhydrous and oxygen free conditions. More importantly, phosphorus ligands in these complexes are known not to undergo Michaelis-Arbuzov type reaction. It was expected that, these catalysts would be reasonably useful for halide replacement in various vinylic halides as shown in Scheme 15.



Scheme 15.

RESULTS AND DISCUSSION

PART I. PHOSPHONATION REACTIONS.

To investigate the phosphonation of vinylic halides, two phosphites, namely triethyl and triisopropyl phosphite, were used as phosphonating agents with a series of vinylic halides.

It was postulated that upon heating a vinylic halide with either the copper(I) chloride or bromide complex of triethyl or triisopropyl phosphite there would result the formation of the corresponding vinylic phosphonate. The result of this reaction would be a direct and convenient synthesis of vinylic phosphonates from vinylic halides as shown in Scheme 12.

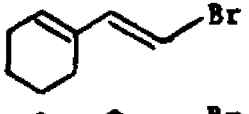
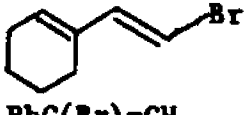
In actuality, the reaction proceeded smoothly when a copper(I) chloride complex of triethyl or triisopropyl phosphite was heated with a vinylic bromide under a nitrogen atmosphere at about 180-220°C(external oil bath) for 1-2 hours, the resultant ethyl or isopropyl chloride liberated being trapped by the use of a Dean-Stark trap. However, upon hydrolysis and extraction with ether there could not be obtained the expected pure vinylic phosphonate using a variety of isolation techniques, including column chromatography, gas liquid chromatography, high pressure liquid chromatography, and distillation. It was then found that the anticipated product vinylic phosphonates could form complexes with copper(I) chloride. This was evidenced in the following way: (1) a blue color appeared on the upper part of the column upon each attempt at column chromatographic separation; (2) distillation was found difficult to perform and

there was a considerable amount of copper salt remaining after each distillation; (3) the distillate upon injection into a gas liquid chromatographic column(2m/3mm column, silicon SE-30, oven temperature 180°C) resulted in the formation only of obvious decomposition materials; (4) finally, any material isolated using these methods always exhibited a blue color as a tail on thin layer chromatography.

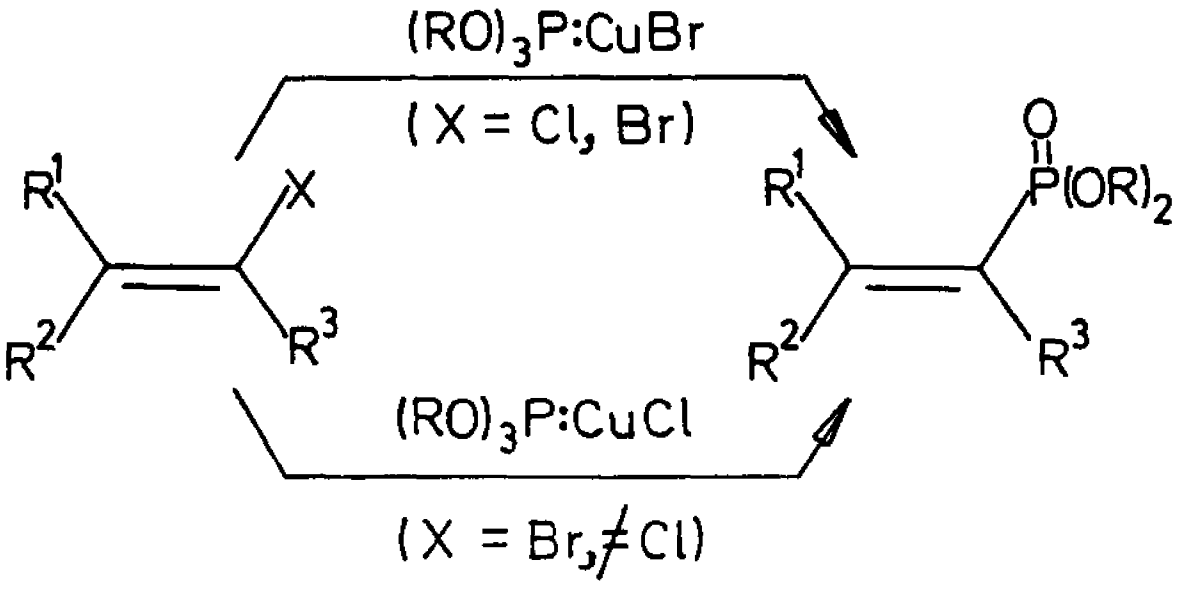
As a result of these observations it was concluded that removal of copper salts was necessary prior to product isolation. Thus, the vinylic phosphonate complex was treated with ethylenediamine in toluene or pentane to form a copper-amine complex[68,69] which was filtered leaving the free vinylic phosphonate. The phosphonate so obtained could be purified by using the standard methods as described above. By these procedures it was possible to obtain the pure vinylic phosphonates in high yields as shown in Table 1.

The vinylic chlorides seem to be unreactive toward the copper-(I) chloride complexes. Several vinylic chlorides were heated with the copper(I) chloride complexes of triethyl and triisopropyl phosphite under a nitrogen atmosphere at temperatures up to 220°C (external oil bath). None of the expected vinylic phosphonates were formed(Scheme 16). However, copper(I) bromide complexes were found to be effective in the conversions of the vinylic chlorides to the corresponding vinylic phosphonates. The effective temperature for these conversions was found to be in the range 160-210°C(external oil bath). Excellent yields resulted with these reactions(Table 2, entries 1-3). In the case of α-chlorostyrene, however, only a poor yield was found with the copper(I) bromide complexes(Table 2, entries

Table 1. Phosphonation of Vinylic Bromides with Copper(I) Chloride-Trialkyl Phosphite Complexes.

Entry	Vinylic Bromide	Phosphite Complex	Yield (%)*	
			Chloride	Phosphonate
1	PhCH=CHBr(E)	$(EtO)_3P$:CuCl	39(E)	52(E)
2	PhCH=CHBr(E)	$(iPrO)_3P$:CuCl	48(E)	48(E)
3	PhC(Me)=CHBr(Z/E=1/1.3)	$(EtO)_3P$:CuCl	34(Z/E=1.1/1)	52(Z/E=1.1/1)
4	PhC(Me)=CHBr(Z/E=1/1.3)	$(iPrO)_3P$:CuCl	43(Z/E=1.1/1)	39(Z/E=1.1/1)
5	PhC(Et)=CHBr(Z/E=2.8/1)	$(EtO)_3P$:CuCl	20(Z/E=1.7/1)	50(Z/E=1.5/1)
6	PhC(Et)=CHBr(Z/E=2.8/1)	$(iPrO)_3P$:CuCl	40(Z/E=1.7/1)	50(Z/E=1.5/1)
7	Ph_2C=CHBr	$(EtO)_3P$:CuCl	29	51
8	Ph_2C=CHBr	$(iPrO)_3P$:CuCl	46	44
9		$(EtO)_3P$:CuCl	28(E)	47(E)
10		$(iPrO)_3P$:CuCl	47(E)	44(E)
11	PhC(Br)=CH_2	$(iPrO)_3P$:CuCl	61	28

*Yield based on starting vinylic bromide.



Scheme 16.

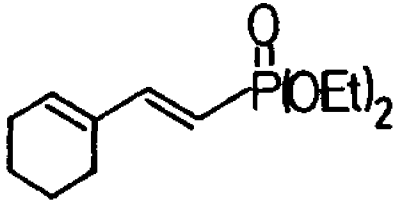
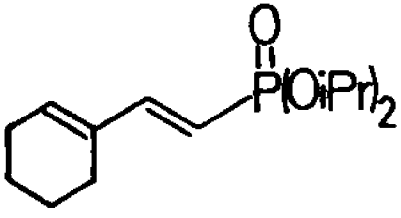
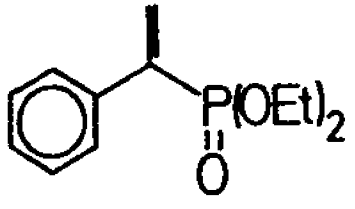
6 and 7). Large amount of unidentified colored products were obtained from this reaction beside the vinylic phosphonates. This caused some difficulties in separating those products. α-Chlorostyrene, unlike β-chlorostyrene, is quite unstable thermally as well as it is sensitive to moisture. The conversions of vinylic bromides to the corresponding vinylic phosphonates catalyzed by copper(I) bromide complexes were found to be quite efficient. These reactions were usually performed at 140-185°C(external oil bath) proceeding in high yields(Table 2, entries 4 and 5). All products and starting materials exhibited satisfactory ^{1}H-NMR, IR, UV, and elemental analyses(Tables 3 and 4).

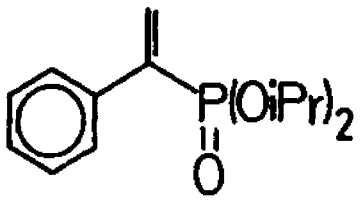
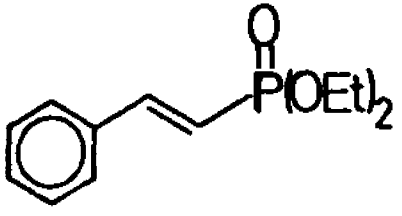
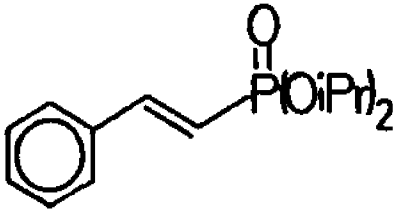
Table 2. Phosphonation of Vinylic Halides with Copper(I) Bromide-Trialkyl Phosphite Complexes.

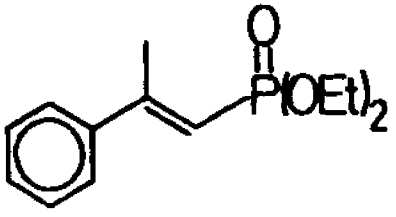
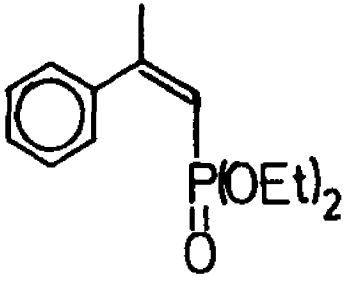
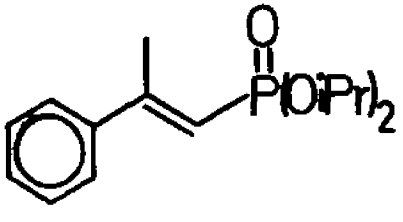
Entry	Vinylic Halide	Phosphite Complex	Yield (%) of Phosphonate*
1	PhCH=CHCl(E)	$(iPrO)_3P$:CuBr	76(E)
2	PhC(Me)=CHCl(Z/E=1/1.4)	$(EtO)_3P$:CuBr	85(Z/E=1/1.7)
3	PhC(Et)=CHCl(Z/E=1.7/1)	$(iPrO)_3P$:CuBr	82(Z/E=1/1)
4	Ph_2C=CHBr	$(EtO)_3P$:CuBr	95
5	Ph_2C=CHBr	$(iPrO)_3P$:CuBr	96
6	PhC(Cl)=CH_2	$(EtO)_3P$:CuBr	26
7	PhC(Cl)=CH_2	$(iPrO)_3P$:CuBr	49

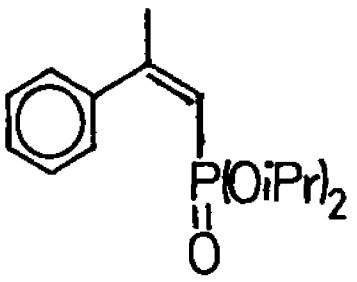
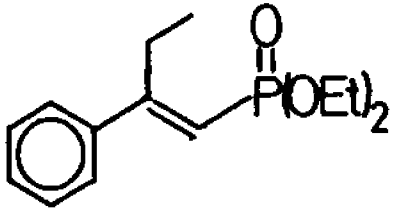
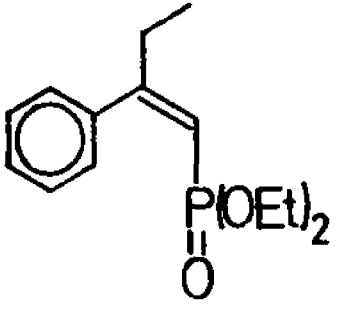
*Yield based on recovered vinylic halide.

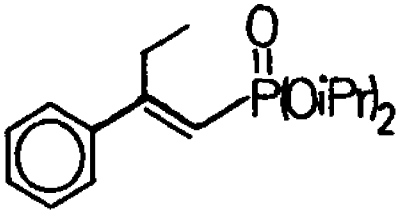
Table 3. Spectral Data of Some Vinylic Phosphonates.

Entry	Compound	^{1}H-NMR($CDCl_3$) δ(ppm)	IR(neat) ν(cm^{-1})	UV($CHCl_3$) λ_{max}(nm)
1.		1.30(t, J_{HH}=7.0Hz, 6H), 1.65(m, 4H), 2.17(m, 4H), 4.05(dt, J_{HH}=7.0Hz, J_{HP}=7.0Hz, 4H), 5.10-7.35(m, 3H).	3450(br), 3030, 1630 & 1595, 1235(br), 1035(br), 955(br).	236(shoulder), 251.
2.		1.35(d, J_{HH}=6.0Hz, 12H), 1.65(m, 4H), 2.15(m, 4H), 4.60(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 2H), 5.10-7.35(m, 3H).	3440(br), 3030, 1630 & 1595, 1385 & 1375, 1230(br), 1040-950.	236(shoulder), 252.
3.		1.30(t, J_{HH}=7.2Hz, 6H), 4.12(dq, J_{HH}=7.2Hz, J_{HP}=7.2Hz, 4H), 5.95(dd, J_{HH}=1.5Hz, J_{HP}=23Hz, 1H), 6.50(dd, J_{HH}=1.5Hz, J_{HP}=43Hz, 1H), 7.25-7.65(m, 5H).	3460(br), 3060 & 3020, 1620 & 1600, 1250(br), 1030(br), 975, 770, 700.	242.

4.		1.30(d, J_{HH}=6.0Hz, 12H), 4.70(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 4H), 5.95(dd, J_{HH}=1.5Hz, J_{HP}=24Hz, 1H), 6.50(dd, J_{HH}=1.5Hz, J_{HP}=43Hz, 1H), 7.15-7.20(m, 5H).	3450(br), 3060 & 3020, 1620 & 1600, 1385 & 1375, 1245(br), 1030-960, 770 & 700.	242.
5.		1.35(t, J_{HH}=7.0Hz, 6H), 4.10(dt, J_{HH}=7.0Hz, J_{HP}=7.0Hz, 4H), 6.25(dd, J_{HH}=18.0Hz, J_{HP}=18.0Hz, 1H), 7.52(dd, J_{HH}=18.0Hz, J_{HP}=22.0 Hz, 1H), 7.35(m, 5H).	3460(br), 3060 & 3020, 1615(d), 1235(br), 1035(br), 960(br), 750 & 690.	238(shoulder), 261.
6.		1.35(dd, J_{HH}=4.0 & 6.0Hz, 12H), 4.70(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 2H), 6.25(dd, J_{HH}=18.0Hz, J_{HP}=18.0Hz, 1H), 7.50(dd, J_{HH}=18.0Hz, J_{HP}=22.0 Hz, 1H), 7.35(m, 5H).	3460(br), 3060 & 3020, 1615(d), 1385 & 1375, 1240(br0, 1030-960, 745 & 690.	238(shoulder), 261.

7.		1.33(t, 7.0Hz, 6H), 2.20(d, J_{HP}=2.0Hz, 3H), 4.10(dq, J_{HH}=7.0Hz, J_{HP}=7.0Hz, 4H), 5.87(dd, J_{HH}=2.0Hz, J_{HP}=16.0Hz, 1H), 7.32(s, 5H).	3450(br), 3075 & 3055, 1600(m), 1235(br), 1035(br), 960(br), 760 & 700.	237(shoulder), 250.
		1.07(t, J_{HH}=7.0Hz, 6H), 2.50(dd, J_{HH}=2.0Hz, J_{HP}=3.0Hz, 3H), 3.80(dq, J_{HH}=7.0Hz, J_{HP}=7.0Hz, 4H), 5.70(dd, J_{HH}=2.0Hz, J_{HP}=16.0Hz, 1H), 7.31(s, 5H).	similar as above	similar as above
8.		1.35(d, J_{HH}=6.0Hz, 12H), 2.23(d, J_{HP}=2.0Hz, 3H), 4.65(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 2H), 5.88(dd, J_{HH}=2.0Hz, J_{HP}=16.0Hz, 1H), 7.33(s, 5H).	3470(br), 3055 & 3020, 1600(m), 1385 & 1375, 1240(br), 1030-960, 760 & 700.	235(shoulder), 249.

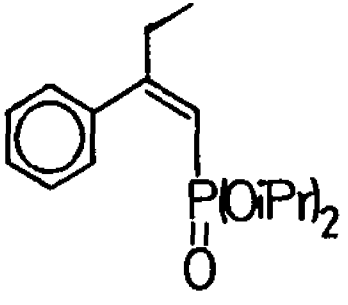
		1.11(dd, J_{HH}=6.0 & 6.0Hz, 12H), 2.50(dd, J_{HH}=2.0Hz, J_{HP}=3.0Hz, 3H), 4.53(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 2H), 5.70(dd, J_{HH}=2.0Hz, J_{HP}=16.0Hz, 1H), 7.32(s, 5H).	similar as above	similar as above
9.		1.02(t, J_{HH}=7.0Hz, 3H), 1.34(t, J_{HH}=7.0Hz, 6H), 2.49(dq, J_{HH}=7.0Hz, J_{HP}=2.0Hz, 2H), 4.10(dq, J_{HH}=7.0Hz, J_{HP}=7.0Hz, 4H), 5.75(dd, J_{HH}=2.0Hz, J_{HP}=16.0Hz, 1H), 7.33(s, 5H).	3470(br), 3055 & 3020, 1600(m), 1240(br), 1025(br), 955(br), 750 & 700.	237(shoulder), 245.
		1.02(t, J_{HH}=7.0Hz, 3H), 1.06(t, J_{HH}=7.0Hz, 6H), 3.02(ddq, J_{HH}=7.0 & 2.0 Hz, J_{HP}=3.0Hz, 2H), 3.79(dq, J_{HH}=7.0, J_{HP}=7.0Hz, 4H), 5.69(dd, J_{HH}=2.0Hz, J_{HP}=16.0Hz, 1H), 7.30(s, 5H).	similar as above	similar as above

10. 

1.01(t, J_{HH}=7.0Hz, 3H),
1.33(d, J_{HH}=6.0Hz, 12H),
2.49(dq, J_{HH}=7.0Hz, J_{HP}=2.0Hz, 2H),
4.65(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 2H),
5.73(dd, J_{HH}=2.0Hz, J_{HP}=16.0Hz, 1H), 7.31(s, 5H).

3470(br),
3055 & 3020,
1600(m),
1385 & 1375,
1240(br),
1030-965,
770 & 700.

237(shoulder),
245.



1.01(t, J_{HH}=7.0Hz, 3H),
1.13(dd, J_{HH}=6.0 & 6.0Hz, 12H),
3.05(ddq, J_{HH}=7.0 & 2.0Hz, J_{HP}=3.0Hz, 2H),
4.55(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 2H),
5.67(dd, J_{HH}=2.0Hz, J_{HP}=16.0Hz, 1H),
7.31(s, 5H).

similar as above

similar as above

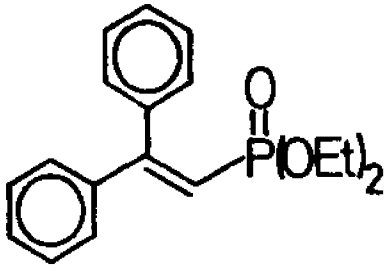
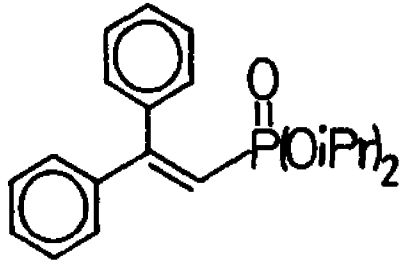
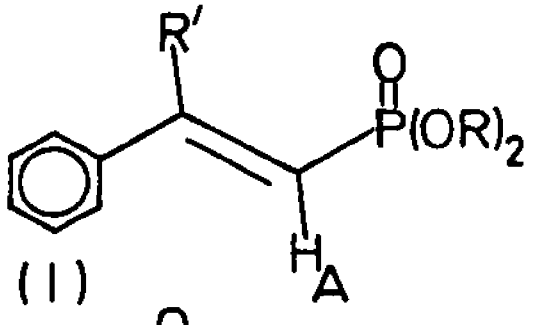
11.		1.12(t, J_{HH}=7.0Hz, 6H), 3.86(dq, J_{HH}=7.0Hz, J_{HP}=7.0Hz, 4H), 6.18(d, J_{HP}=16.0Hz, 1H), 7.25(s, 5H), 7.35(s, 5H).	3470(br), 3055 & 3020, 1604 & 1593, 1240(br), 1065-1010, 980-935, 760 & 700.	237(shoulder), 265.
12.		1.21(dd, J_{HH}=6.0 & 6.0Hz, 12H), 4.55(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 2H), 6.14(d, J_{HP}=16.0Hz, 1H), 7.25(s, 5H), 7.35(s, 5H).	3460(br), 3055 & 3020, 1604 & 1593, 1385 & 1375, 1245(br), 1030-960, 770 & 700.	237(shoulder), 265.

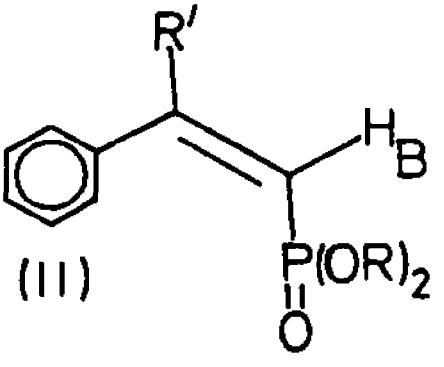
Table 4. Elemental Analyses of Some Vinylic Phosphonates.

Entry	Compound	Found		Calculated	
		C(%)	H(%)	C(%)	H(%)
1.	$C_{12}H_{21}O_3P$	58.96	9.03	59.00	8.67
2.	$C_{14}H_{25}O_3P$	61.83	9.51	61.75	9.25
3.	$C_{12}H_{17}O_3P$	60.15	7.35	60.00	7.13
4.	$C_{14}H_{21}O_3P$	62.57	7.89	62.68	7.89
5.	$C_{13}H_{19}O_3P$	61.68	7.52	61.40	7.53
6.	$C_{15}H_{23}O_3P$	63.53	8.02	63.82	8.21
7.	$C_{14}H_{21}O_3P$	62.88	7.88	62.68	7.89
8.	$C_{16}H_{25}O_3P$	64.65	8.50	64.85	8.50
9.	$C_{18}H_{21}O_3P$	68.60	6.98	68.34	6.69
10.	$C_{20}H_{25}O_3P$	69.63	7.63	69.75	7.32

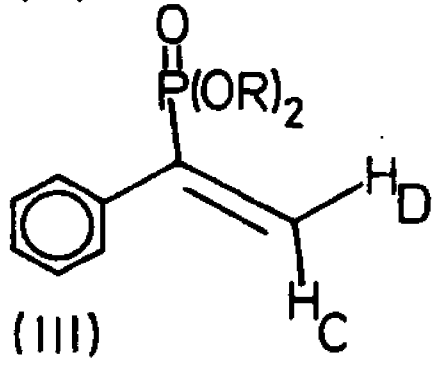
A rather important feature of this reaction is its stereoselectivity, as the stereochemistry of the vinylic halides was observed to be principally retained during the course of the reaction. Determination of the stereochemistry of all compounds was based on ^{1}H-NMR analysis. The spin coupling constants of trans, cis, and geminal protons have been observed to be: J_{HH} trans greater than J_{HH} cis; J_{HP} trans greater than J_{HP} cis; and J_{HP} cis greater than J_{HP} geminal.[70] Typical values for J_{HH} trans is 14-18 Hz, J_{HH} cis is 8-12 Hz, J_{HP} trans is 20-50 Hz, J_{HP} cis is 10-30 Hz, and J_{HP} geminal is 10-27 Hz.[26,37,71,72] All chemical shifts of the vinylic phosphonates were assigned according to the previous work[9,19,28,35,38] and by using additive increments[72] compared to the starting vinylic halides (Tables 3 and 5). The E-β-styryl system(I) exhibits chemical shifts of the β-proton(H_A) over the range 5.73-6.25 ppm. The α-proton(I, R' = H) appears at 7.50-7.52 ppm, downfield from the β-proton,



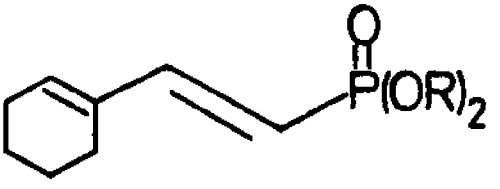
(I)



(II)

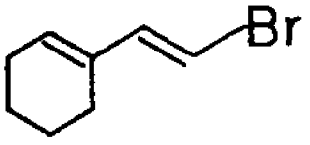
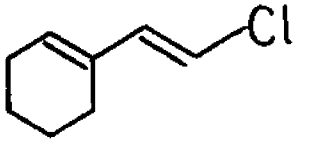
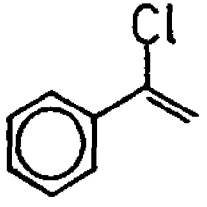
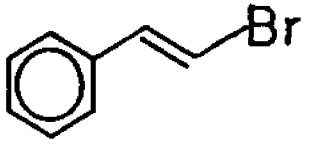
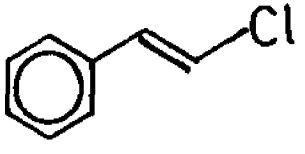


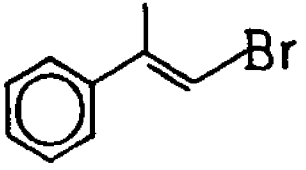
(III)



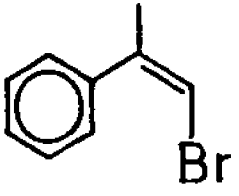
(IV)

Table 5. ^{1}H-NMR Spectral Data of Some Vinylic Halides.

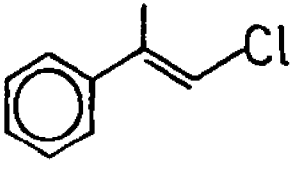
Entry	Compound	δ(ppm) in $CDCl_3$
1.		1.57(t, J=4.0Hz, 2H), 1.68(t, J=3.0Hz, 2H), 2.55-1.95(m, 4H), 6.80-5.65(m, 3H).
2.		1.63(m, 4H), 2.62-1.95(m, 4H), 6.59-5.60(m, 3H).
3.		5.44(d, J=2.0Hz, 1H), 5.66(d, J=2.0Hz, 1H), 7.64-7.13(m, 5H).
4.		6.55(d, J=14.0Hz, 1H), 6.75(d, J=14.0Hz, 1H), 7.13(s, 5H).
5.		6.45(d, J=14.0Hz, 1H), 6.75(d, J=14.0Hz, 1H), 7.18(s, 5H).

6. 

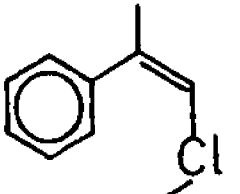
2.15(d, J=1.5Hz, 3H), 6.34(d, J=1.5Hz, 1H), 7.21(s, 5H).



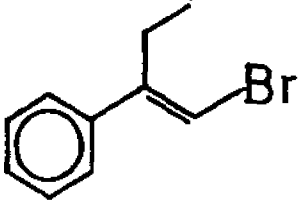
2.02(d, J=1.5Hz, 3H), 6.10(d, J=1.5Hz, 1H), 7.26(s, 5H).

7. 

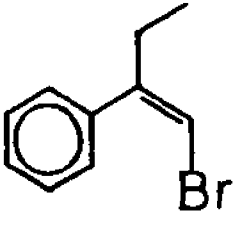
2.15(d, J=1.5Hz, 3H), 6.20(d, J=1.5Hz, 1H), 7.20(s, 5H).



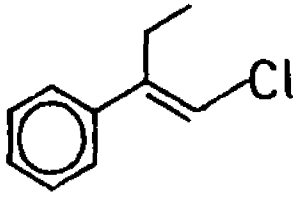
1.98(d, J=1.5Hz, 3H), 5.98(d, J=1.5Hz, 1H), 7.25(s, 5H).

8. 

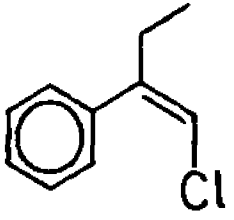
1.04(t, J=7.0Hz, 3H), 2.55(dq, J=7.0 & 2.0Hz, 2H),
6.41(d, J=2.0Hz, 1H), 7.19(s, 5H).



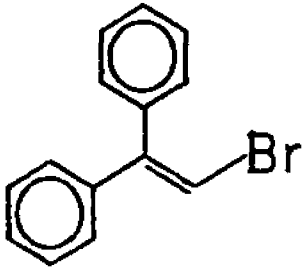
0.96(t, J=7.0Hz, 3H), 2.43(dq, J=7.0 & 2.0Hz, 2H),
6.20(d, J=2.0Hz, 1H), 7.29(s, 5H).

9. 

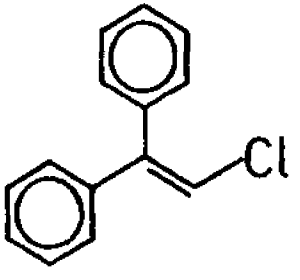
1.05(t, J=7.0Hz, 3H), 2.68(dq, J=7.0 & 2.0Hz, 2H),
6.14(d, J=2.0Hz, 1H), 7.20(s, 5H).



0.92(t, J=7.0Hz, 3H), 2.40(dq, J=7.0 & 2.0Hz, 2H),
6.02(d, J=2.0Hz, 1H), 7.26(s, 5H).

10. 

6.68(s, 1H), 7.17(s, 5H), 7.30(s, 5H).

11. 

6.15(s, 1H), 7.20(s, 5H), 7.30(s, 5H).

probably due to the anisotropic effect. Compound I(R' = H) shows J_{HH} = 18 Hz, J_{HP} cis = 22 Hz, and J_{HP} geminal = 18 Hz while I(R' = Me, Et, and Ph) show J_{HP} geminal = 16 Hz. The methyl and Methylene protons of I(R' = Me and Et) both show spin coupling with H_A, J_{HH} being about 2 Hz, which is the same as J_{HP}.

The Z-ß-styryl system(II, R' = Me and Et) shows a chemical shift of the ß-proton, H_B, at 5.67-5.88 ppm as a double of doublets, J_{HH} = 2 Hz and J_{HP} = 16 Hz, whereas the methyl and methylene protons show J_{HH} about 2 Hz and J_{HP} = 3 Hz. Similarly, H_D in the α-styryl system(III) appears as a double of doublets, J_{HH} about 1.5 Hz and J_{HP} = 23-24 Hz, at 5.59 ppm. The H_C also appears as a double of doublets, J_{HH} about 1.5 Hz, J_{HP} about 43 Hz, appearing at 6.50 ppm. However, the dieneic system(IV) gives the chemical shifts of the vinylic protons as a multiplet at 5.10-7.35 ppm.

The methylene and methine protons of the alkoxyl group which is attached to the phosphorus atom are also split by the phosphorus atom. All the spectral data, ^{1}H-NMR, IR, and UV are summarized in Tables 3, 5, 6, and 7.

Finally, the vinylic halides recovered from the reaction between vinylic bromides and copper(I) chloride complexes of trialkyl phosphites were solely the vinylic chlorides. Therefore, the halogen replacement has been found to compete effectively with the phosphonation process. The exchange reaction which is occuring, however, may be circumvented by the use of the copper(I) bromide

Table 6. Spectral Data of Some Copper(I) Halide-Trivalent Phosphorus Complexes.

Entry	Compound		Spectroscopic Data
1.	$(EtO)_3P$:CuCl	^{1}H-NMR(CCl_4)	1.30(t, J_{HH}=7.0Hz, 9H),
		δ(ppm)	4.02(dq, J_{HH}=7.0Hz, J_{HP}=10.0Hz, 6H).
		IR(neat)	2980, 2930, 2900, 1025(br), 940(br), 800-740.
		ν(cm^{-1})	
		UV(pentane)	214.
		λ_{max}(nm)	
2.	$(iPrO)_3P$:CuCl	^{1}H-NMR(CCl_4)	1.25(d, J_{HH}=6.0Hz, 18H),
		δ(ppm)	4.70(dh, J_{HH}=6.0Hz, J_{HP}=10.0Hz, 3H).
		IR(CCl_4)	2980, 2930, 2900, 1385 & 1375, 1020-930, 875,
		ν(cm^{-1})	775.
		UV(pentane)	214.
		λ_{max}(nm)	

3.	$(PhO)_3P:CuCl$	^1H-NMR δ(ppm)	7.10(s, 15H).
		IR(parafin oil) $\nu(cm^{-1})$	2950, 2920, 2850, 1585, 1185, 930, 905, 885, 760 & 690.
		UV($CHCl_3$) λ_{max}(nm)	236, 263.
4.	$Ph_3P:CuCl$	^1H-NMR($CDCl_3$) δ(ppm)	7.70-7.00(m, 15H).
		IR(parafin oil) $\nu(cm^{-1})$	2940, 2910, 2840, 1470, 1450, 1430, 1080, 740 & 690.
		UV($CHCl_3$) λ_{max}(nm)	237, 252.
5.	$(EtO)_3P:CuBr$	^1H-NMR($CDCl_3$) δ(ppm)	1.30(t, J_{HH}=7.0Hz, 9H), 4.09(dq, J_{HH}=7.0Hz, J_{HP}=10.0Hz, 6H).
		IR(neat) $\nu(cm^{-1})$	2980, 2930, 2900, 1025(br), 940(br), 800-740.
		UV(pentane) λ_{max}(nm)	214.

6.	$(iPrO)_3P$:CuBr	^{1}H-NMR($CDCl_3$) δ(ppm)	1.30(d, J_{HH}=6.0Hz, 18H), 4.78(dh, J_{HH}=6.0Hz, J_{HP}=10.0Hz, 3H).
		IR(parafin oil) ν(cm^{-1})	2910(m), 1385 & 1375, 1020-930, 880, 775.
		UV(pentane) λ_{max}(nm)	214.
7.	$(PhO)_3P$:CuBr	^{1}H-NMR($CDCl_3$) δ(ppm)	7.08(s, 15H).
		IR(parafin oil) ν(cm^{-1})	2940, 2910, 2840, 1580, 1180, 1155, 910, 885, 760 & 685.
		UV($CHCl_3$) λ_{max}(nm)	237, 263.
8.	Ph_3P:CuBr	^{1}H-NMR($CDCl_3$) δ(ppm)	7.50-6.90(m, 15H).
		IR(parafin oil) ν(cm^{-1})	2940, 2910, 2840, 1470, 1455, 1430, 1080, 740 & 690.
		UV($CHCl_3$) λ_{max}(nm)	238, 260(shoulder).

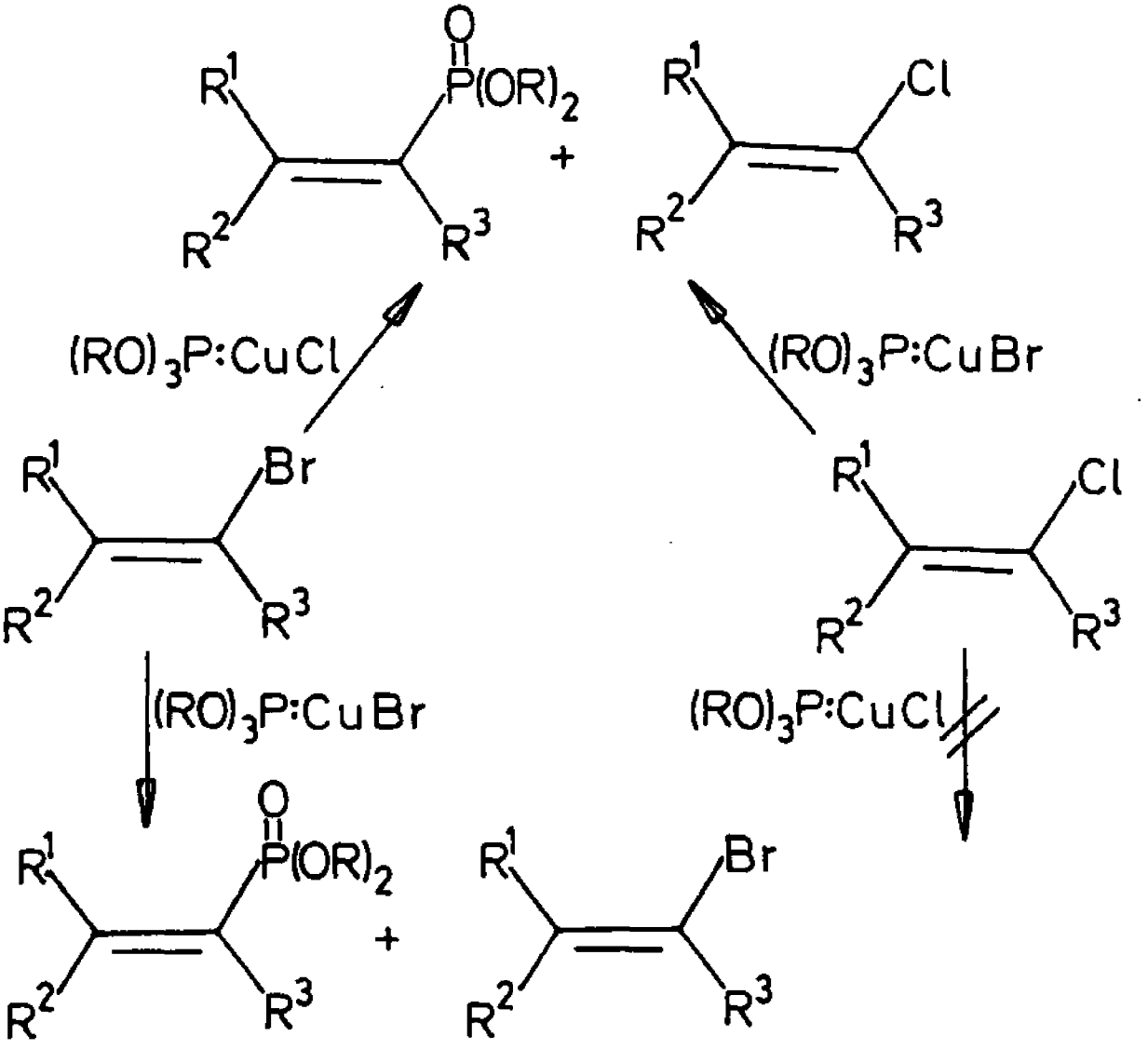
Table 7. ^{1}H-NMR Spectral Data of Some Trivalent Phosphorus Compounds.

Entry	Compound	δ(ppm) in $CDCl_3$
1.	$P(OEt)_3$	1.25(t, J_{HH}=7.0Hz, 9H), 3.84(dq, J_{HH}=7.0Hz, J_{HP}=8.0Hz, 6H).
2.	$P(OiPr)_3$	1.25(d, J_{HH}=6.0Hz, 18H), 4.33(dh, J_{HH}=6.0Hz, J_{HP}=8.0Hz, 3H).
3.	$P(OPh)_3$	7.10(s, 15H).
4.	PPh_3	7.22(s, 15H).

complexes. This poses a difficulty in that the vinylic chlorides appear to be unreactive in this process using copper(I) chloride complexes of the phosphites. This difficulty can be overcome by the use of the corresponding copper(I) bromide complexes (vide supra). The details of the halogen exchange process will be discussed in the next section.

PART II. HALIDE EXCHANGE REACTIONS.

In the course of the above described studies of the direct synthesis of vinylic phosphonates from vinylic halides with copper-(I) halide complexes of trialkyl phosphites, there was uncovered an accompanying facile halide exchange reaction as shown in Scheme 17. This prompted a further examination of this exchange reaction



Scheme 17.

employing a series of copper(I) halide complexes of triphenyl phosphite and triphenylphosphine(Scheme 15).

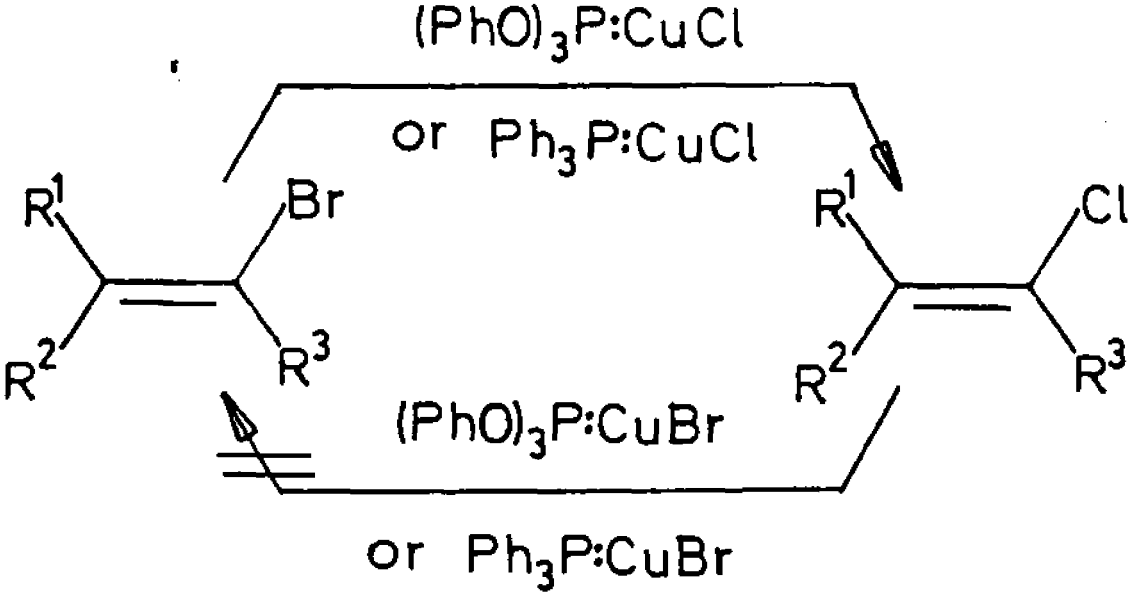
As noted, a halide exchange reaction takes place when a mixture of vinylic bromide and a copper(I) chloride complex of either triphenyl phosphite or triphenylphosphine is heated under a nitrogen atmosphere at about 150-180°C(external oil bath) for 1-2 hours. The yields of products obtained from this reaction are very high (Table 8). Moreover, the exchange reaction of these vinylic bromides catalyzed by the copper(I) chloride complexes is highly stereoselective as demonstrated by ^{1}H-NMR measurements. Use of higher temperatures with prolonged heating results in some isomerization. This was demonstrated by heating a mixture of 1-chloro-2-phenylpropene (E/Z = 1.4) and a slight excess of triphenyl phosphite-copper(I) chloride complex under a nitrogen atmosphere at 190°C(external oil bath) for over 2 hours. The vinylic chloride resulting from this reaction was observed to have the stereochemical distribution E/Z = 3.3.

The copper(I) species which is ligated with a strong electron donor for catalyzing this reaction is considerably important. This This was further demonstrated by heating a mixture of 1-bromo-2,2-diphenylethene and copper(I) chloride with or without a solvent which is incapable of complexation with the copper(I) species under a nitrogen atmosphere. No reaction could be observed and starting material could be recovered quantitatively.

Table 8. Halide Exchange Reaction Catalyzed by Copper(1) Chloride Complexes of Triphenyl Phosphite and Triphenylphosphine.

Entry	Vinylic Bromide	Copper(I) Chloride Complex	Yield (%) of Vinylic Chloride
1.	PhCH=CHBr(E)	$(PhO)_3P$:CuCl	94(E)
2.	PhCH=CHBr(E)	Ph_3P:CuCl	98(E)
3.	Ph(Me)C=CHBr(E/Z = 1.4)	$(PhO)_3P$:CuCl	85(E/Z = 1.4)
4.	Ph(Me)C=CHBr(E/Z = 1.4)	Ph_3P:CuCl	98(E/Z = 1.3)
5.	Ph(Et)C=CHBr(Z/E = 4.2)	$(PhO)_3P$:CuCl	89(Z/E = 4.2)
6.	Ph_2C=CHBr	$(PhO)_3P$:CuCl	95
7.	Ph_2C=CHBr	Ph_3P:CuCl	96

Furthermore, all attempts to exchange bromide for chloride by this approach with vinylic chlorides resulted in the isolation of unchanged vinylic chlorides(Scheme 18). Although the proper thermodynamic data is not available for the complexes concerned, such a result might be anticipated in light of considerations of free energy data available for the vinylic halides and the copper(I) halides.



Scheme 18.

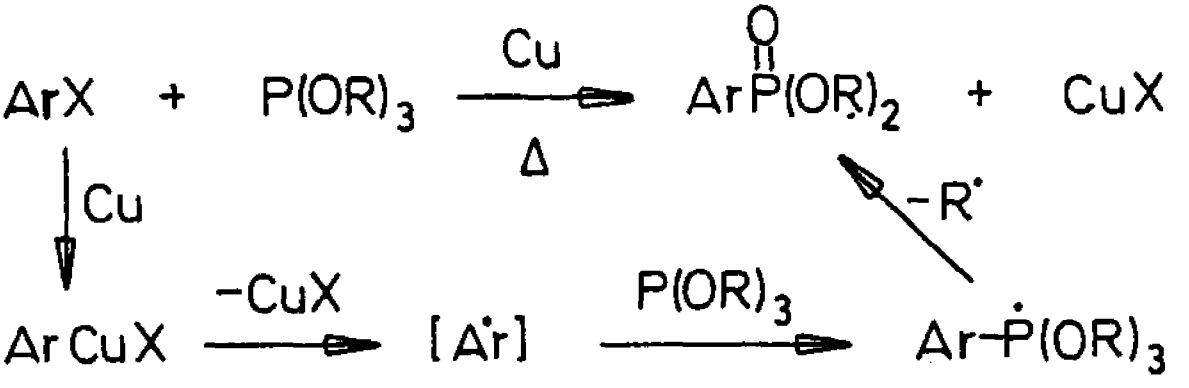
PART III. MECHANISMS OF COPPER(I) COMPLEX-CATALYZED REACTION OF VINYLIC HALIDES.

Copper(I) reagents have been known to catalyze many replacement reactions of aromatic and vinylic halides, particularly for those reactions involving copper(I) halides which are related to the well known Ullmann reaction.[74-84] In recent years the mechanism of the Ullmann reaction has been intensively reviewed[58,63,80-86] and interpreted in different ways. In general, a concerted reaction involving a four-center transition state has been considered as the mechanism for a copper-assisted nucleophilic displacement reaction.[54,55,61,84,87,88] An alternative stepwise reaction involving a radical species as an intermediate has also been proposed.[74,82,84,89,90] This rationalization was made on the basis that the reactions are generally performed at elevated temperature. Recently, Cohen et. al.[62,63,83,91] have proposed organocopper compounds as intermediates in these reactions. However, all the mechanisms which have been proposed so far give no definitive answers.

The phosphonation and halide exchange reactions of vinylic halides as observed in the present systems have a close relationship to the Ullmann reaction in many respects. Firstly, these reactions are usually performed at high temperature.[74-79] Secondly, the rates of reactions for vinylic halides are usually of the order: vinylic bromides are usually faster than vinylic chlorides.[63] Thirdly, these reactions usually proceed with high stereospecificity when applied to the vinylic halides.[65,91,92] Finally, the

Ullmann reaction can also be performed in a homogeneous system by using a copper(I) salt in a complexing solvent.[85] In contrast, homogeneity in the present system is due to the miscible nature of those vinylic halides with copper(I) complexes.[45-51]

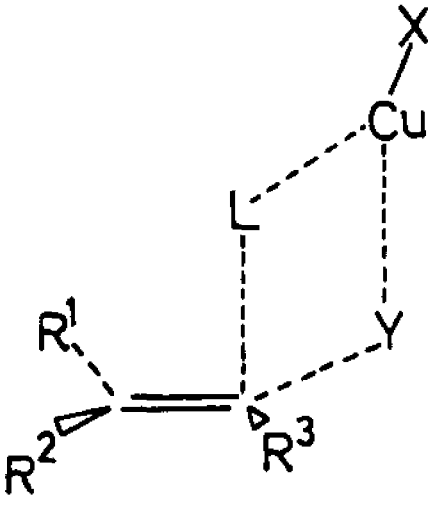
Phosphonation of aryl halides by trialkyl phosphites in the presence of copper powder as a catalyst has generally been rationalyzed as a radical process[41,93-95] as shown in Scheme 19.



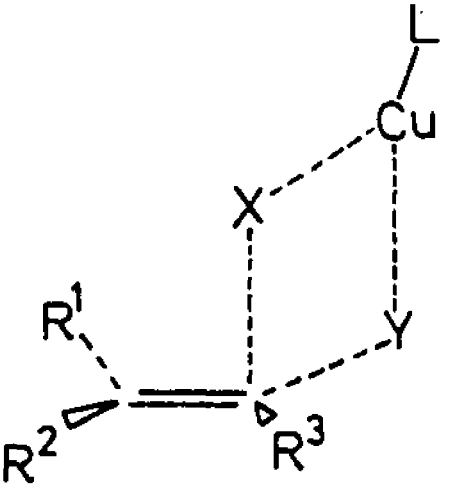
Scheme 19.

However, this stepwise reaction is not consistent with some previous observations.[42] When this reaction has been applied to vinylic halides the retention of stereochemistry[65,91,92] which resulted very likely rules out the radical reaction. Furthermore, Cohen et. al.[63] have shown that aryl radicals are not intermediates for the reaction of aryl bromides and copper(I) salts. It has been found that added tetrahydrofuran has no effect on this reaction.

The concerted reactions involving four-center transition states(V and VI) are also less likely. In the present work it has been found that under the same conditions copper(I) chloride does not react with vinylic bromides in the absence of complexing agents. In contrast, copper(I) chloride-trialkyl phosphite complexes do react readily with the vinylic bromides. In fact, an increase in electron density on the copper(I) by complexation should increase the enthalpy of activation of these transition states. Instead, as in many similar reactions, the catalyzing ability of copper(I) halides is promoted by strong electron donor ligands.[54,55,85,86,96-98] Furthermore, compelling evidence has been found to support the formation of an organocopper compound as an intermediate in these reactions.[62,86]



(V)



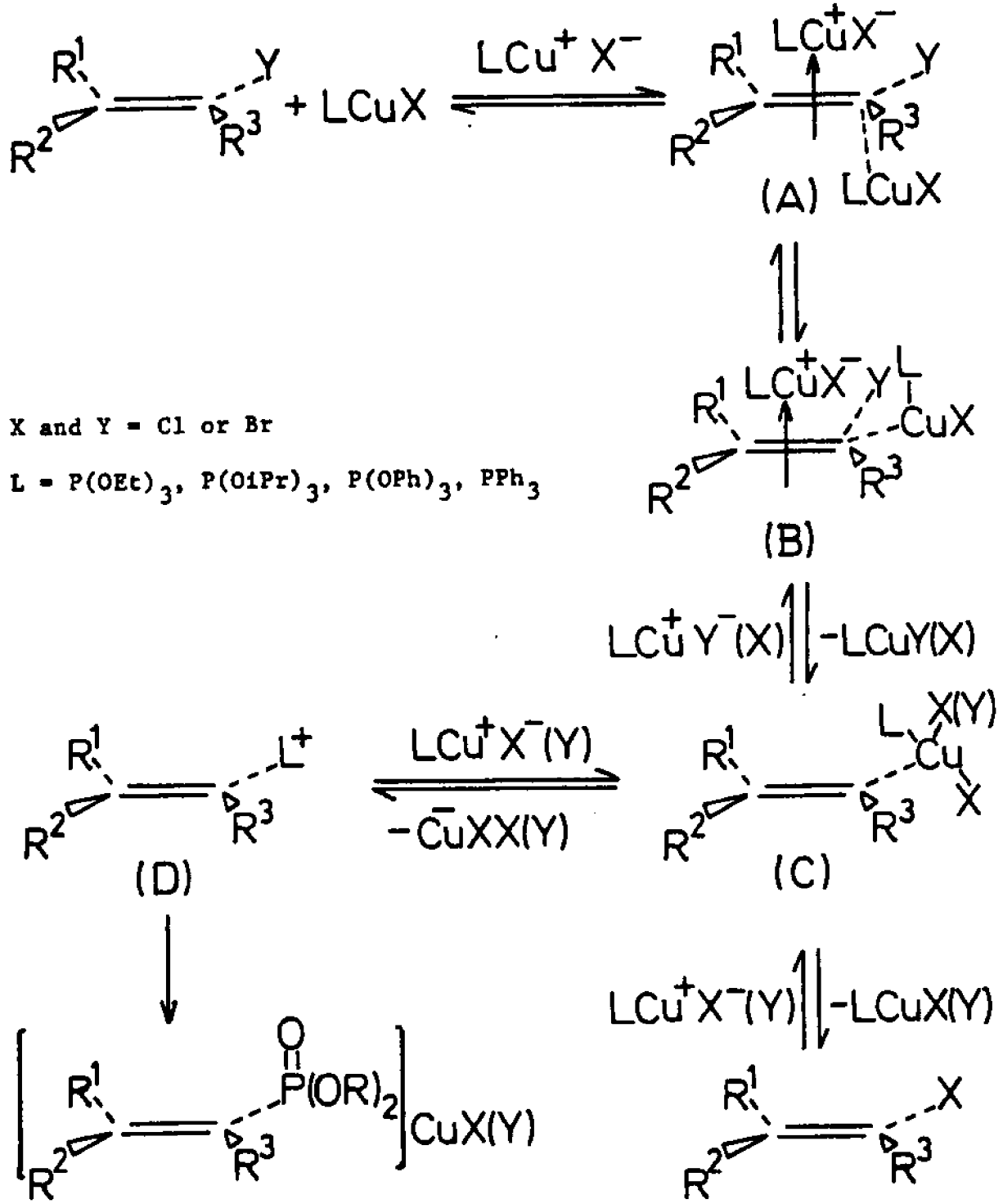
(VI)

Phosphonation reactions in the present system are found to be effective for vinylic bromides with those copper(I) chloride and copper(I) bromide complexes. It is also observed that reactions occur with vinylic chlorides and copper(I) bromide complexes. However, no reactions could be observed with vinylic chlorides and copper(I) chloride complexes. Furthermore, replacement of bromide for chloride also fails in this system as well as in others.[52-65] The latter is readily understandable on the grounds of thermodynamic data[60,99-102] which is available for vinylic halides and copper(I) halides. The low enthalpy and high entropy barriers found for these exchange processes is characteristic of a number of oxidative addition reactions.[99-102] In turn, the formation of C-Cl bond is favored over the formation of C-Br bond. In fact, it has been reported that C-Br bond is much more reactive than the corresponding C-Cl bond.[103,104] Of course, thermodynamic control in the formation of vinylic halides is not the only factor in these reactions. The structures of the copper(I) halide complexes would play an important role in these reactions. It has been found that copper(I) halide complexes of trivalent phosphorus show quite different structures.[105-110] However, these structural differences of the copper(I) halide complexes do not throw much light on the mechanism of these reactions.

Recently, a few copper(III) complexes have been proposed as intermediates in several reaction systems.[111-114] This copper(III) is also believed to be an intermediate in many copper(I)-assisted replacement reactions.[56,62,63,85] Thus, copper(III) would also be a reasonable intermediate species for consideration in the present system. These copper(III) species presumably result from the so-called oxidative addition reaction.[115] This type of reaction requires nonbonding electron density on the metal, in agreement with the present observations and many others.[56,62,85,115-117] A mechanistic scheme which could accommodate the presentexperimental data is shown in Scheme 20.

The complexes LCuX, which are tetrameric in the solid state, would be partially dissociated and in equilibrium under the reaction conditions(Scheme 21). This may be demonstrated in the reaction of β-bromostyrene with copper(I) chloride in the presence of 10% triphenylphosphine in dry diglyme. The halide exchange occurs readily whereas under the same conditions without triphenylphosphine added, only the starting β-bromostyrene was recovered. This would be rationalized as halide exchange between the copper(I) halide complex and the copper(I) halide or ligand exchange process as shown in Schemes 22 and 23.

Thus, the first step would involve a nucleophilic attack of the π-complex[116,117](A) by a LCuX at the sp^2 carbon bearing the halogen.[118,119] This nucleophile approaches perpendicularly to the plane of the olefin but opposite of LCu^+X^- as shown in structure

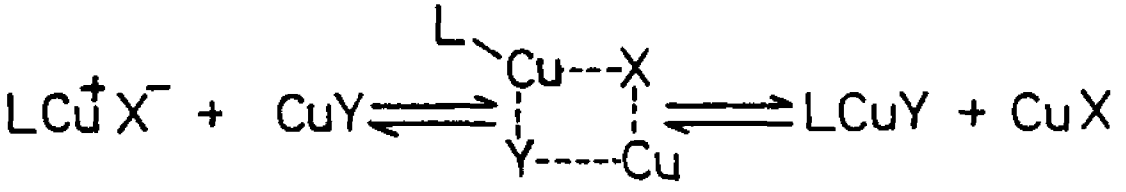


X and Y = Cl or Br

L = $P(OEt)_3$, $P(OiPr)_3$, $P(OPh)_3$, PPh_3

Scheme 20.

Scheme 21.



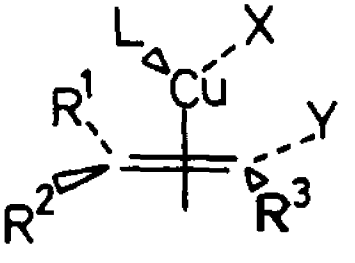
Scheme 22.

Scheme 23.

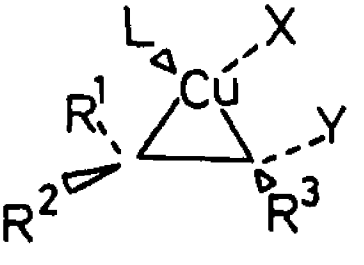
(A). Then the entering and the leaving groups begin to rotate together while maintaining partial overlap of the orbitals of both the forming and breaking bonds with the p orbital of the trigonal carbon as shown in structure (B). Finally, the leaving group Y leaves perpendicularly to the plane of the olefin while the entering group now is on the same plane of the olefin as shown in structure (C). The organocopper(III) compound (C) so formed would then collapse to give either the vinylic halide or

the phosphonium intermediate (D) which further undergoes the Arbuzov reaction to give the phosphonate which is in the form of copper(I) complex.

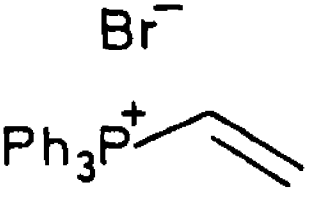
By analogy with the organocuprates,[120-124] these complexes LCuX would act as nucleophiles[116,117] rather than Lewis acids by forming π-complexes(VII).[125-133] Though some copper(I) halides are known to form complexes with some normal olefins,[134-136] it is noted in the present work that no π-complexes resulted from vinylic halides with either copper(I) halides or copper(I) halide complexes. Alternatively, oxidative addition of vinylic halide to LCuX across the π-bond (VIII)[116,117] would be unlikely for copper(I) halide complexes. Only a few organometallic compounds of these type of complexes are known, and only those with Pt(0)[120] and Pd(0).[116,117] This type of complex would be subjected to nucleophilic attack at the carbon bearing the halogen by another LCuX. This could lead to several possible products and retention of the configuration of the expected products would not be expected. Finally, all steps of the mechanism shown should be written as equilibria, except for the last step when the displacement portion of the



(VII)



(VIII)



(IX)

Michaelis-Arbuzov reaction occurs. This is demonstrated in the treatment of vinyl triphenylphosphonium bromide (IX) with either copper(I) chloride or bromide in dry diglyme at reflux. Neither vinyl chloride or bromide was detected from the reaction but the starting phosphonium salt (IX) was recovered. On the other hand, under the same reaction conditions this vinyl phosphonium salt (IX) does react with LCuCl to give vinyl chloride.

The failure of reactions between vinylic chlorides and LCuCl is probably due to the leaving ability and bond polarizability of chloride being less than that of bromide. It has also been observed here that the catalytic activity of LCuBr species are better than that of the corresponding LCuCl. This conclusion is drawn from the fact that the reaction using LCuBr as a catalyst requires less drastic reaction conditions and gives better yields. This is in agreement with the report[137] that LCuBr species are more reactive than LCuCl in the oxidative addition reactions. Finally, these catalytic reactions of vinylic halides by LCuX are governed by thermodynamic considerations.

EXPERIMENTAL.

General:

All solvents were commercial materials and distilled prior to use except anhydrous diethyl ether(Mallinckrodt), 95% ethanol(Mallinckrodt), ethyl acetate(J. T. Baker Chem. Co. and Fisher Scientific Co.), and hexanes(J. T. Baker Chem. Co. and Mallinckrodt) which were used without further purification.

Triethyl phosphite(Aldrich Chem. Co. and Matheson Coleman & Bell), triisopropyl phosphite(Aldrich Chem. Co.), triphenyl phosphit(Aldrich Chem. Co.), 1-bromo-2-cyclohexenylethene(Aldrich Chem. Co.), β-bromostyrene(Aldrich Chem. Co.), acetophenone(J. T. Baker Chem. Co.), propiophenone(Aldrich Chem. Co.), piperidine (J. T. Baker Chem. Co. and Fisher Scientific Co.), and thionyl chloride(J. T. Baker Chem. Co.) were distilled prior to use.

Triphenylphosphine(Aldrich Chem. Co.), benzophenone(Fisher Scientific Co.), and paraformaldehyde(trioxymethylene)(Fisher Scientific Co.) were dried in vacuo prior to use.

Phenylacetylene(Aldrich Chem. Co.), bromine(J. T. Baker Chem. Co.), phosphorus tribromide(Aldrich Chem. Co.), phosphorus pentachloride(Aldrich Chem. Co.), and phosphorus oxychloride(Matheson Coleman & Bell) were used without further purification.

tert-Butyllithium was commercially available from Aldrich Chem. Co.

Anhydrous hydrogen chloride and hydrogen bromide(Union Carbide) technical grade were used without further purification.

Copper(I) chloride and copper(I) bromide were freshly prepared by a standard method[138,139] and dried in vacuo prior to use.

Neutral alumina(Act. I, 80-200 mesh) was commercially available from Fisher Scientific Co.

Silica gel(60-200 mesh) was commercially available from J. T. Baker Chem. Co.

Melting point were determined on an electrothermal melting point apparatus(Mel-Temp) and were uncorrected.

^{1}H-NMR spectra were recorded on a Varian EM 360 spectrometer.

IR spectra were recorded on a Perkin-Elmer 598 spectrophotometer.

UV spectra were recorded on a Cary 14 spectrophotometer.

Elemental analyses were performed by Guelph Chem. Lab., Ontario, Canada, and Galbraith Lab., Knoxville, Tennessee.

PART I. PHOSPHONATION REACTIONS.

1) Diethyl (E)-2-Phenylvinylphosphonate.

To a 50-mL, one-necked flask equipped with a short Vigreaux column, a Dean Stark trap, a condenser, and topped with a gas inlet tube was placed copper(I) chloride complex of triethyl phosphite(10.75g, 0.05mol) and β-bromostyrene(6.40g, 0.035mol). The mixture was then heated under a nitrogen atmosphere at 200-220°C (external oil bath) and the volatile material, ethyl halide, was collected in the Dean Stark trap, meanwhile, there were considerable amounts of solids, copper(I) halide, formed in the reaction mixture. The heating was performed for 1 hr(or until there was no more volatile material collected in the trap) and the reaction mixture was allowed to cool to room temperature. The reaction mixture was poured into 60 mL of toluene and the solids were washed well with toluene. Then ethylenediamine(5 mL) was added to the solution dropwise while stirring. The solids formed were filtered off and washed well with toluene. The filtrate was acidified with 10% HCl and extracted with ether. The organic phase was washed with water. The combined aqueous phase was extracted with ether. The organic phase was dried(anhy. $MgSO_4$), and concentrated. The crude product 6.11g was chromatographed on silica gel and eluted with hexanes-ethyl acetate(100:0 to 3:1) to give β-chlorostyrene 1.90g(39%) and the vinylic phosphonate as a thick, colorless liquid 4.40g(52%). The phosphonate has a bp 135-6°C/0.45-0.50mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.40.

2) Diisopropyl (E)-2-Phenylvinylphosphonate.

(a) The mixture of copper(I) chloride complex of triisopropyl phosphite(13.80g, 0.045mol) and β-bromostyrene(5.48g, 0.03mol) were placed in a 50-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 180-200°C for 2 hr and then at 200-220°C for 30 min and allowed to cool to room temperature. The reaction mixture was poured into 50 mL of pentane and the solids were washed well with pentane. Then 7 mL of ethylenediamine was added to the solution with stirring. The solids formed were filtered and washed well with pentane. The filtrate was acidified with 10% HCl and extracted with ether as described above. The organic phase was dried and concentrated to give the crude product which was distilled in vacuo to give β-chlorostyrene 2.00g(48%) and the vinylic phosphonate(145-50°C/1.2mm) 3.91g(48%) as a thick, colorless liquid. The phosphonate has a bp 132-3°C/0.45-0.50mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.40.

(b) The mixture of copper(I) bromide complex of triisopropyl phosphite(5.0g, 0.014mol) and β-chlorostyrene(1.40g, 0.01mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 180-90°C for 2 hr and was worked-up as described in 2(a). The filtrate was acidified with 10% HCl and extracted with pentane. The organic phase was washed with water. The combined aqueous phase was extracted with

ether. The combined organic phase was dried(anhy. $MgSO_4$), and concentrated. The crude product 2.11g was chromatographed on silica gel and eluted with hexanes-ethyl acetate(100:0 to 3:1) to give β-chlorostyrene 0.60g and the vinylic phosphonate 1.17g(76% based on recovered β-chlorostyrene).

3) Diethyl 2-Phenylprop-1-enylphosphonate.

(a) A mixture of copper(I) chloride complex of triethyl phosphite(4.30g, 0.02mol) and 1-bromo-2-phenylpropene(3.00g, 0.015mol) were placed in a 25-mL, one-necked equipped in the manner described in (1). The reaction mixture was heated at 200-220°C for 2 hr and allowed to cool to room temperature. The reaction mixture was poured into 50 mL of pentane and the solids were washed well with pentane. Then 6.6 mL(about 5 equivalents) of ethylenediamine was added to the solution with stirring. The solids formed were filtered and washed well with pentane. The filtrate was acidified with 10% HCl and extracted with pentane. The organic phase was washed with water. The combined aqueous phase was extracted with ether. The combined organic phase was dried(anhy. $MgSO_4$), and concentrated. The crude product 3.26g was chromatographed on silica gel and eluted with hexanes-ethyl acetate(100:0 to 3:1) to give 1-chloro-2-phenylpropene 0.80g(34%) and the vinylic phosphonate 2.00g(52%) as a thick, colorless liquid. The phosphonate has a bp 130-2°C/0.40mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.37.

(b) A mixture of copper(I) bromide complex of triethyl phosphite (1.86g, 0.006mol) and 1-chloro-2-phenylpropene(0.99g, 0.005mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 180-90°C for 2.5 hrs and 190-200°C for 1 hr and allowed to cool to room temperature. The reaction mixture was worked-up as described in 3(a) and the crude product was chromatographed on neutral alumina(Act. I) and eluted with hexanes-ethyl acetate(100:0 to 3:1) to afford 1-chloro-2-phenylpropene 0.37g and the vinylic phosphonate 0.88g(85% based on recovered 1-chloro-2-phenylpropene) as a thick, colorless liquid.

4) Diisopropyl 2-Phenylprop-1-enylphosphonate.

A mixture of copper(I) chloride complex of triisopropyl phosphite(6.15g, 0.02mol) and 1-bromo-2-phenylpropene(3.00g, 0.015mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 190-200°C for 2 hrs and allowed to cool to room temperature. The reaction mixture was worked-up as described in 3(a) and the crude product, 4.48g, was chromatographed as described in 3(a) to give 1-chloro-2-phenylpropene 0.95g(43%) and the vinylic phosphonate 2.08g(39%) as a thick, colorless liquid. The phosphonate has a bp 125-7°C/0.4mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.44.

5) Diethyl 2-Phenylbut-1-enylphosphonate.

A mixture of copper(I) chloride complex of triethyl phosphite (4.30g, 0.02mol) and 1-bromo-2-phenylbut-1-ene(1.90g, 0.009mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 205-210°C for 1.5 hrs and worked-up as described in 3(b) to give 1-chloro-2-phenylbut-1-ene 0.31g(20%) and the vinylic phosphonate 1.20g(50%) as a thick, coloeless liquid. The phosphonate has a bp 129-31°C/0.45-0.50mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.34.

6) Diisopropyl 2-Phenylbut-1-enylphosphonate.

(a) A mixture of copper(I) chloride complex of triisopropyl phosphite(6.15g, 0.02mol) and 1-bromo-2-phenylbut-1-ene(1.90g, 0.009mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 195-200°C for 2 hrs and worked-up as described in 3(b). Upon chromatographic separation on neutral alumina(Act. I)-hexanes-ethyl acetate system it gave 1-chloro-2-phenylbut-1-ene 0.61g(40%) and the vinylic phosphonate 1.22g(50%) as a thick, colorless liquid. The phosphonate has a bp 127-9°C/0.45-0.50mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.45.

(b) A mixture of copper(I) bromide complex of triisopropyl phosphite(3.09g, 0.01mol) and 1-chloro-2-phenylbut-1-ene(0.83g, 0.005mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 160-80°C for 8 hrs and worked-up as described in 3(b) to give 1.42g of the crude product. Upon chromatographic separation on neutral alumina (Act. I)-hexanes-ethyl acetate system to afford 1-chloro-2-phenyl-but-1-ene 0.48g and the vinylic phosphonate 0.52g(82% based on recovered 1-chloro-2-phenylbut-1-ene) as a thick, colorless liquid.

7) Diethyl 2,2-Diphenylvinylphosphonate.

(a) A mixture of copper(I) chloride complex of triethyl phosphite(4.30g, 0.02mol) and 1-bromo-2,2-diphenylethene(2.85g, 0.01 mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 200-220°C for 2 hrs and worked-up as described in 3(b) to give 1-chloro-2,2-diphenylethene 0.73g(29%) and the vinylic phosphonate 1.83g(51%) as a thick, colorless liquid. The phosphonate has a bp 173-4°C/0.45-0.50mm and R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.31.

(b) A mixture of copper(I) bromide complex of triethyl phosphite(3.70g, 0.012mol) and 1-bromo-2,2-diphenylethene(2.00g, 0.0077 mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 180-5°C

for 2 hrs and worked-up as described in 3(b) to give 1-bromo-2,2-diphenylethene 0.68g and the vinylic phosphonate 1.53g(95% based on recovered 1-bromo-2,2-diphenylethene).

8) Diisopropyl 2,2-Diphenylvinylphosphonate.

(a) A mixture of copper(I) chloride complex of triisopropyl phosphite(6.15g, 0.02mol) and 1-bromo-2,2-diphenylethene(2.85g, 0.011mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 190-200°C for 2 hrs and worked-up as described in 3(b) to give 1-chloro-2,2-diphenylethene 1.12g(46%) and the vinylic phosphonate 1.70g (44%) as a thick, colorless liquid. The phosphonate has a bp 168-9°C/0.45-0.50mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.34.

(b) A mixture of copper(I) bromide complex of triisopropyl phosphite(1.45g, 0.0047mol) and 1-bromo-2,2-diphenylethene(0.60g, 0.0023mol) were placed in a 25-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 140-60°C for 7 hrs and worked-up as described in 3(b) to give 0.88 g of the crude product. Upon chromatographic separation on neutral alumina(Act. I)-hexanes-ethyl acetate system, 1-bromo-2,2-diphenylethene 0.39g and the vinylic phosphonate 0.26g(96% based on recovered 1-bromo-2,2-diphenylethene) were obtained.

9) Diethyl 2-Cyclohexenylvinylphosphonate.

A mixture of copper(I) chloride complex of triethyl phosphite (4.30g, 0.02mol) and 1-bromo-2-cyclohexenylethene(2.80g, 0.015mol) was heated at 200-215°C for 1 hr as described in (1). The reaction mixture was worked-up in the manner described in 3(a) to give the crude product(2.55g). Upon chromatographic separation on silica gel-pentane-ethyl acetate system, 1-chloro-2-cyclohexenylethene 0.55g(28%) and the vinylic phosphonate 1.72g(47%) were obtained. The phosphonate has a bp 129-35°C/0.65-0.60mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.40.

10) Diisopropyl 2-Cyclohexenylvinylphosphonate.

A mixture of copper(I) chloride complex Of triisopropyl phosphite(6.15g, 0.02mol) and 1-bromo-2-cyclohexenylethene(2.80g, 0.015 mol) was heated at 180-95°C for 1 hr as described in (1). The reaction mixture was worked-up in the manner described in 3(a) to give the crude product(3.77g). Upon chromatographic separation on silica gel-pentane-ethyl acetate system, 1-chloro-2-cyclohexenylethene 1.00g(47%) and the vinylic phosphonate 1.80g(44%) were obtained. The phosphonate has a bp 135-43°C/0.55-0.60mm and R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.49.

11) Diethyl 1-Phenylvinylphosphonate.

A mixture of copper(I) bromide complex of triethyl phosphite (15.40g, 0.05mol) and α-chlorostyrene(4.85g, 0.035mol) was heated at 180-85°C for 4.5 hrs and then at 200-210°C for 0.5 hr and worked-up as described in 3(b) to give 4.07g of the crude product. Upon chromatographic separation on silica gel-hexanes-ethyl acetate system there was obtained α-chlorostyrene 0.94g, unidentified products 1.46g, and the vinylic phosphonate(2.10g). The impure phosphonate was further chromatographed on neutral alumina(Act. I) and eluted with hexanes-ethyl acetate to give the product 1.75g(26% based on recovered α-chlorostyrene). The phosphonate has a bp 175-7°C/3.00mm and R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.46

12) Diisopropyl 1-Phenylvinylphosphonate.

(a) A mixture of copper(I) chloride complex of triisopropyl phosphite(17.58g, 0.05mol) and α-chlorostyrene(4.85g, 0.035mol) was heated at 180-85°C for 4.5 hrs and then at 200-210°C for 0.5 hr and worked-up as described in 3(b) to give 7.08g of the crude product. Upon chromatographic separation on silica gel-hexanes-ethyl acetate system there was obtained α-chlorostyrene 1.28g, unidentified products 0.71g, and the vinylic phosphonate(4.05g). The impure phosphonate was further chromatographed on neutral alumina(Act. I), eluting with hexanes-ethyl acetate to give the phosphonate 3.36g(49% based on recovered α-chlorostyrene) as a

thick, light yellow liquid. The phosphonate has a bp 158-9°C/3.00 mm and a R_f(silica gel, hexanes-ethyl acetate in 1:1) of 0.48.

(b) A mixture of copper(I) chloride complex of triisopropyl phosphite(5.54g, 0.018mol) and α-bromostyrene(2.92g, 0.016mol) were placed in a 50-mL, one-necked flask equipped in the manner described in (1). The reaction mixture was heated at 160-80°C for 3 hrs and worked-up as described in 3(b) to give α-chlorostyrene 1.34g(61%) and the vinylic phosphonate 1.20g(28%) as a light yellow liquid.

PART II. HALIDE EXCHANGE REACTIONS.

1. (a) Reaction of β-Bromostyrene and Triphenyl Phosphite-Copper(I) Chloride Complex.

To a 25-mL, one-necked flask equipped with a condenser and a gas inlet tube was placed triphenyl phosphite-copper(I) chloride complex(8.20g, 0.02mol) and β-bromostyrene(3.70g, 0.018mol). The resulting mixture was heated under a nitrogen atmosphere at 160-90°C(external oil bath) for 1.5 hrs. Pentane(about 25 mL) was gradually added while the reaction mixture was cooling. The solids were filtered and washed well with pentane, then redissolved in ether and filtered to give a solid 0.45g(mp greater than 360°C, identified as CuBr). The volume of the ether solution was reduced to about one half, the solids crystallized from the solution was filtered and dried in vacuo to give 5.81g of product(mp 74-6°C) which was identified as triphenyl phosphite-copper(I) bromide complex(compared to an authentic sample). The pentane solution was concentrated to give 7.31g of the crude product. Upon chromatographic separation on silica gel(or neutral alumina, Act. I) and eluting with hexanes, 2.28g(94%) of β-chlorostyrene was obtained. Further elution of the column with hexanes-ethyl acetate(100:0 to 1:1) gave triphenyl phosphite(2.15g).

(b) Reaction of β-Bromostyrene and Triphenylphosphine-Copper(I) Chloride Complex.

To a 25-mL, one-necked flask equipped with a condenser and a gas inlet tube was placed triphenylphosphine-copper(I) chloride complex(4.70g, 0.013mol) and β-bromostyrene(1.83g, 0.01mol). The reaction mixture was heated under a nitrogen atmosphere at 180°C for 1.5 hrs. Pentane(about 25 mL) was added to the reaction mixture upon cooling. The solids were filtered and washed well with pentane. The filtrate was concentrated and chromatographed on neutral alumina(Act. I) eluted with hexanes to give β-chlorostyrene 1.37g(98%).

2. (a) Reaction of 1-Bromo-2-phenylpropene and Triphenyl Phosphite-Copper(I) Chloride Complex.

A mixture of triphenyl phosphite-copper(I) chloride complex (3.27g, 0.008mol) and 1-bromo-2-phenylpropene(1.18g, 0.006mol) was heated under a nitrogen atmosphere at 180-90°C for 1 hr. The reaction mixture was worked-up as described in 1(b) to give 1-chloro-2-phenylpropene 0.77g(85%).

(b) Reaction of 1-Bromo-2-phenylpropene and Triphenylphosphine-Copper(I) Chloride Complex.

A mixture of triphenylphosphine-copper(I) chloride complex (2.89g, 0.008mol) and 1-bromo-2-phenylpropene(1.18g, 0.006mol) was heated under a nitrogen atmosphere at 180°C for 1 hr. The reaction

mixture was worked-up as described in 1(b) to give 1-chloro-2-phenylpropene 0.90g(98%).

3. Reaction of 1-Bromo-2-phenylbutene and Triphenyl Phosphite-Copper(I) Chloride Complex.

A mixture of triphenyl phosphite-copper(I) chloride complex (0.82g, 0.002mol) and 1-bromo-2-phenylbutene(0.30g, 0.0014mol) was heated under a nitrogen atmosphere at 180°C for 2 hrs. The reaction mixture was worked-up as described in 1(b) to give 1-chloro-2-phenylbutene 0.21g(89%).

4. (a) Reaction of 1-Bromo-2,2-diphenylethene and Triphenyl Phosphite-Copper(I) Chloride Complex.

A mixture of triphenyl phosphite-copper(I) chloride complex (0.61g, 0.0015mol) and 1-bromo-2,2-diphenylethene(0.30g, 0.0012mol) was heated under a nitrogen atmosphere at 180°C for 1.5 hrs. The reaction mixture was worked-up as described in 1(b) to give 1-chloro-2,2-diphenylethene 0.236g(95%).

(b) Reaction of 1-Bromo-2,2-diphenylethene and Triphenylphosphine-Copper(I) Chloride Complex.

A mixture of triphenylphosphine-copper(I) chloride complex was heated under a nitrogen atmosphere at 180°C for 1 hr. Thr reaction mixture was worked-up as described in 1(b) to give 1-chloro-2,2-diphenylethene 0.24g(96%).

PART III. SYNTHESIS.

1) Copper(I) Chloride-Triethyl Phosphite Complex.[43-51]

In a dried, one-necked flask equipped with a Claisen head, a rubber septum, and a gas inlet tube was placed 5.0g(0.05mol) of freshly prepared copper(I) chloride and 100 mL of dry pentane. Triethyl phosphite(8.31g, 0.05mol) was slowly added to the suspension at room temperature. After the addition, the solution became clear(if it is not clear, the solution should be allowed to stir for another 10 min) and the trace of unreacted material was filtered off and concentrated. Thick, colorless liquid was dried in vacuo. The yields were 90-97%. The purity was checked by ^{1}H-NMR.

2) Copper(I) Chloride-Triisopropyl Phosphite Complex.[43-51]

The complex was prepared in the manner described in (1) to give a pure white solid(checked by ^{1}H-NMR) in 88-96% yield (mp 112-4°C).

3) Copper(I) Bromide-Triethyl Phosphite Complex.[45-51]

The complex was prepared in the manner described in (1) as a colorless, thick liquid at room temperature. The pure complex (checked by ^{1}H-NMR) was obtained in 80-90% yield

4) Copper(I) Bromide-Triisopropyl Phosphite Complex.[43-51]

The complex was prepared in the manner described in (1) as a pure white solid(checked by ^{1}H-NMR) in 80-93% yield(mp 146-8°C).

5) Copper(I) Chloride-Triphenyl Phosphite Complex.

In a 250-mL, one-necked flask equipped with a Claisen head, a rubber septum, and a gas inlet tube was placed freshly prepared copper(I) chloride(7.25g, 0.073mol) and dry pentane 175 mL. Triphenyl phosphite(23.2g, 0.075mol) was added dropwise to the suspension at room temperature and the resulting reaction mixture was refluxed for 1 hr. The solution became clear after stirring at room temperature for 3 hrs. The unreacted solid materials were filtered off and concentrated. The solids were recrystallized in pentane-methylene chloride to give the complex(mp 85-8^{o}C) 75-90% yield.

6) Copper(I) Chloride-Triphenylphosphine Complex.

To a 1L, two-necked flask equipped with a condenser topped with a gas inlet tube and a rubber septum was suspended freshly prepared copper(I) chloride(9.90g, 0.10mol) in 450 mL of pentane. The refluxing mixture was stirred under a nitrogen atmosphere at room temperature for 30 min. Triphenylphosphine(26.23g, 0.10mol) was added in portions and the reaction mixture was allowed to stir for 3 hrs. The white solids were filtered and washed with pentane. The solids were redissolved in hot methylene chloride and filtered while hot. Crystallization of the solids afforded the pure complex (checked by ^{1}H-NMR) 33.60g(93%) as white crystals. The mp of the complex was 120-30^{o}C(dec.).

7) Copper(I) Bromide-Triphenyl Phosphite Complex.

Freshly prepared copper(I) bromide(21.5g, 0.15mol) and dry pentane(400 mL) were suspended in a 1L, one-necked flask equipped in the manner described in (5). Triphenyl phosphite(46.5g, 0.15mol) was added slowly to the suspension at room temperature. A slight excess of copper(I) bromide was added and heated to reflux for 1 hr. Methylene chloride was added to dissolve the white solids formed in the reaction mixture and the undissolved materials were filtered off. The solvent was evaporated and the solids were recrystallized in pentane to give the pure complex(checked by ^{1}H-NMR) mp 72-4^{o}C in 65-80% yield.

8) Copper(I) Bromide-Triphenylphosphine Complex.

To a suspension of copper(I) bromide(7.17g, 0.05mol) and pentane(200 mL) in a 500-mL, two-necked flask equipped in the manner described in (6) was added slowly triphenylphosphine(13.15 g, 0.05mol) at room temperature. The small amount of copper(I) bromide was added to maintain the copper(I) bromide in excess. The suspension was refluxed for 1 hr and the solids formed were dissolved in hot methylene chloride and filtered. The solution was concentrated to half of its original volume and ether was added. The solids formed were filtered and washed with ether to give the pure complex(checked by ^{1}H-NMR) 19.66g(97%), mp 167-9^{o}C.

9) Hydroxymethyltriphenylphosphonium Chloride.[140]

A 1L, 3-necked flask equipped with a mechanical stirrer, a drying tube, and connected to a hydrogen chloride tank was introduced triphenylphosphine(196.5g, 0.75mol), paraformaldehyde(trioxymethylene)(24.75g, 0.28mol), and ether(750 mL). The suspension was vigorously stirred and hydrogen chloride gas was bubbled through for 2-3 hrs(or until no further precipitation occured). The solids were filtered and washed with ether(several times). The solids were dried in vacuo overnight(or at least 12 hrs). The filtrate from the ether-washed solution was concentrated and recrystallized from ethanol(95%) to give triphenylphosphine(about 37-43g). The salt obtained from this reaction was 180-230g(90-99%, based on recovered starting triphenylphosphine).

10) Chloromethyltriphenylphosphonium Chloride.[140]

A 1L, 3-necked flask equipped with a mechanical stirrer, a reflux condenser, and an addition funnel was introduced hydroxymethyltriphenylphosphonium chloride(230g, 0.70mol) and methylene chloride(400 mL) was added. Thionyl chloride(104.25mL, 1.45mol) was slowly added to the vigorously stirred phosphonium salt and the resulting solution was refluxed for 2.5 hrs. A second portion of thionyl chloride(14.0mL, 0.20mol) was added and refluxed for another 1 hr. The reaction mixture was evaporated to dryness and dried in vacuo overnight(or at least 15 hrs). The solids(almost white)

were boiled with methylene chloride(425 mL) and the white solids which remain insoluble were filtered to give 121.15g of the product. The filtrate was boiled with charcoal(10g) and filtered. To the filtrate was gradually added ether until a white turbidity appeared and it was then refrigerated. The total product recrystallized from the last portions were 38.40g, 22.00g, and 9.40g. The overall yield of the product was 191.60g(79%), mp 258-60°C(dec.).

11) Bromomethyltriphenylphosphonium Bromide.[140]

A 1L, 3-necked flask equipped with a mechanical stirrer, a reflux condenser, and an addition funnel was placed phosphorus tribromide(55mL, 0.57mol) and methylene chloride(100 mL) was added. Bromine(28mL, 0.55mol) was slowly added to the solution. The reaction mixture(a solution with a solid phosphorus pentabromide) was allowed to cool to room temperature. Hydroxymethyltriphenylphosphonium chloride(164.50g, 0.50mol), dissolved in methylene chloride (400 mL), was slowly added to the phosphorus pentabromide solution. After the addition, the reaction mixture was refluxed for 5 hrs and allowed to cool. To the reaction mixture was added ethyl acetate (650 mL). The precipitate formed was filtered and washed well with ethyl acetate and ether. The solids were recrystallized from ether-ethanol to give colorless crystals of the phosphonium salt 130.45g, to 148.00g(60% to 68%), mp 239.5-241.5°C(dec.).

12) 1-Bromo-2-phenylpropene.

A sample of bromomethyltriphenylphosphonium bromide(43.6g, 0.1mol) was placed in a 1L, 3-necked flask equipped with a mechanical stirrer, a condenser, and a gas inlet tube. After the air in the system had been displaced with nitrogen, ether(200 mL) was added followed by piperidine(7.9g, 0.09mol) at room temperature. tert-Butyllithium in pentane(49.0mL, 0.09mol) was slowly added to the vigorously stirred suspension at this stage, the white suspension gradually changing to a yellow solution. After the solution was stirred for 30 min, acetophenone(10mL, 0.085mol) was added dropwise. After the addition, the reaction mixture was refluxed for 30 min and allowed to stand at room temperature for 30 min or longer. The solids were filtered and washed several times with ether. The filtrate was shaken with 2x100 mL 2N H_2SO_4 and washed with $NaHCO_3$ solution, dired, and concentrated to give the crude product. The solids from the reaction were washed well with acetone to give the starting phosphonium salt(checked by ^{1}H-NMR) 13.0g. The crude product from the reaction was chromatographed on neutral alumina(Act. I) and on eluting with hexanes gave a mixture of both cis- and trans-1-bromo-2-phenylpropene present in almost equal amounts(calculated from ^{1}H-NMR). The yield was 4.68g(34% based on recovered starting phosphonium bromide).

Other conversions carried out in a similar manner were: propiophenone to 1-bromo-2-phenylbutene(24%), benzophenone to 1-bromo-2,2-diphenylethene(39%).

13) 1-Chloro-2-phenylpropene.[141]

In a 1L, 3-necked flask equipped in the manner described in (12) was introduced chloromethyltriphenylphosphonium chloride (52.10g, 0.15mol). After the air in the system had been displaced with nitrogen, ether(600 mL) was added and the suspension was stirred at 0-5°C(ice-bath) for 30 min. tert-Butyllithium in pentane(88.70mL, 0.165mol) was added rapidly and stirred for another 30 min while the temperature was raised at room temperature. Acetophenone(21.24mL, 0.18mol) was added dropwise and the reaction mixture was refluxed for 2 hrs. Another portion of acetophenone (11.80mL, 0.10mol) was added and refluxed for further 15 hrs. Ether was slowly distilled off, the pot temperature rising slowly. The solids were filtered and washed with ether several time. The The filtrate was evaporated to dryness and chromatographed on silica gel eluting with hexanes to give a mixture of both cis- and trans-1-chloro-2-phenylpropene(present in almost equal amounts, based on ^{1}H-NMR) in 7.45g(33%).

14) α-Chlorostyrene.[142-145]

To 175g(0.84mol) of phosphorus pentachloride in a 500-mL flask was added acetophenone(88.2mL, 0.67mol) dropwise at 0-5°C (ice-bath). The reaction mixture was allowed to stir at room temperature for overnight. The reaction mixture was then heated at reduced pressure at 50-60°C and allowed to cool to room

temperature. The reaction mixture was poured into ice water and extracted with ether. The organic layer was washed with $NaHCO_3$ solution and water, dried and concentrated. The crude product was distilled to give 16.6g of α-chlorostyrene(contaminated with some acetophenone), and 44.0g of acetophenone(contaminated with some α-chlorostyrene). The yield of the product was about 40%(based on recovered starting acetophenone).

15) α-Bromostyrene.

In a 200-mL, 3-necked flask equipped with an addition funnel, hydrogen bromide conducting tube, and a condenser topped with a drying tube was placed phenylacetylene(3.06g, 0.03mol) in dry ether(60 mL). The solution was saturated with hydrogen bromide gas and triphenylphosphine(7.87g, 0.03mol) in dry ether(20 mL) was added concurrently. The resulting mixture was refluxed for 30 hrs and the solids were filtered to give triphenylphosphine hydrobromide. The filtrate was distilled at 68.5-69.0°C/2.8mm to give α-bromostyrene 4.59g(85%).

References:

1. Kosolapoff, G. M. U. S. Patent (1945), 2389576, ; Chem. Abstr. (1946), 1535.
2. Vivaut, G. Chem. Abstr. (1979), 91, 20709.
3. Hullar, T. L. Tetrahedron Lett. (1967), 4921.
4. Hunger, K. Chem. Abstr. (1968), 101, 3530.
5. Griffin, C. E. and Kundu, S. K. J. Org. Chem. (1969), 34, 1532.
6. Johnson, B. F. G.; Lewis, J. and Postle, S. R. J. Organomet. Chem. (1976), 121, C7.
7. Postle, S. R. and Whitham, G. H. J. Chem. Soc. Perkin I (1977), 2084.
8. Slates, H. L. and Wendler, N. L. Chem. & Ind.(London) (1978), 430.
9. Daniewski, W. M. and Griffin, C. E. J. Org. Chem. (1966), 31, 3236.
10. Gareev, R. D.; Longinova, G. M.; and Pudovik, A. N. J. Org. Chem. USSR (Engl. Transl.) (1979), 49, 433.
11. Gareev, R. D. and Pudovik, A. N. J. Org. Chem. USSR (Engl. Transl.) (1979), 49, 442.
12. Khusainova, N. G.; Bredikhina, Z. A.; and Pudovik, A. N. J. Org. Chem. USSR (Engl. Transl.) (1979), 49, 451.
13. Kutyrev, G. A.; Vinokurov, A. I.; Ishmaeva, E. A.; Shakirov, I. Kh.; Shagidullin, R. R.; Cherkasov, R. A.; and Pudovik, A. N. J. Org. Chem. USSR (Engl. Transl.) (1979), 49, 458.

14. Glamkowski, E. J.; Gal, G.; Purick, R.; Davidson, A. J.; and Sletzinger, M. J. Org. Chem. (1970), 35, 3510.

15. Thiele, J. Chem. Ztg. (1912), 36, 657.

16. Bergmann, E. and Bondi, A. Ber. (1930), 63, 1158; ibid (1931), 64, 1455; ibid (1933), 66, 278; ibid (1933), 66, 286.

17. Kosolapoff, G. M. and Huber, W. F. J. Amer. Chem. Soc. (1946), 68, 2540.

18. Kosolapoff, G. M. and McCullough, J. F. J. Amer. Chem. Soc. (1951), 73, 855.

19. Mashlyakovskii, L. N.; Ionin, B. I.; Okhrimenko, I. S.; and Petrov, A. A. J. Org. Chem. USSR (Engl. Transl.) (1967), 37, 1237.

20. Pudovik, A. N. and Konovalova, I. V. J. Org. Chem. USSR (Engl. Transl.) (1961), 31, 1580.

21. Mashlyakovskii, L. N. and Ionin, B. I. J. Org. Chem. USSR (Engl. Transl.) (1965), 35, 1582.

22. Hasserodt, U. and Korte, F. W. A. G. K. Chem. Abstr. (1964), 10718.

23. Arbuzov, A. E. and Kushkova, N. P. J. Gen. Chem. Russia (1936), 6, 283.

24. Kosolapoff, G. M. J. Amer. Chem. Soc. (1944), 66, 1511.

25. Ford-Moore, A. H. and Williams, J. H. J. Chem. Soc. (1947), 1465.

26. Kenyon, G. L. and Westheimer, F. H. J. Amer. Chem. Soc. (1966), 88, 3557.

27. Agiar, A. M. and Daigle, D. J. Org. Chem. (1965), 30, 2826.

28. Petrov, A. A.; Ionin, B. I.; and Ignatyev, V. M. Tetrahedron Lett. (1968), 15.

29. Coover,Jr., H. W. U. S. Patent (1958), 2827475; Chem. Abstr. (1958), 11472.

30. Christensen, B. G.; Leanza, W. J.; Beattie, T. R.; Patchett, A. A.; Arison, B. H.; Ormond, R. E.; Kuehl,Jr., F. A.; Schonberg, G. A.; and Jardetzky, O. Science (1969), 166, 123.

31. Kreutzkamp, N. and Schindler, H. Chem. Ber. (1959), 92, 1695.

32. Pudovik, A. N. and Lebedeva, N. M. Chem. Abstr. (1956), 2429.

33. Patai, S. and Schwartz, A. J. Org. Chem. (1960), 25, 1232.

34. Wadsworth,Jr., W. S. and Emmons, W. D. J. Amer. Chem. Soc. (1961), 83, 1733.

35. Mikolajczyk, M.; Grzejszczak, S.; Midura, W.; and Zatorski, A. Synthesis (1976), 396.

36. Kosolapoff, G. M. J. Amer. Chem. Soc. (1953), 75, 1500.

37. Tavs, P. and Weitkamp, H. Tetrahedron (1970), 26, 5529; U. S. Patent (1970), 3493639.

38. Hirao, T.; Masunaga, T.; Oshiro, Y.; and Agawa, T. Tetrahedron Lett. (1980), 21, 3595.

39. Kukhar, V. P. and Sagina, E. I. J. Org. Chem. USSR (Engl. Transl.) (1977), 47, 1523.

40. Tavs, P. Ber. (1970), 103, 2428.

41. Tavs, P. and Korte, F. Tetrahedron (1967), 23, 4677.

42. Plumb, J. B. and Griffin, C. E. J. Org. Chem. (1962), 27, 4711.

43. Wulfman, D. S.; Thinh, N. van; McDaniel, R. S.; and Peace, B. W. J. Chem. Soc. Dalton (1975), 523.

44. Moser, W. R. J. Amer. Chem. Soc. (1969), 91, 1135 & 1141.

45. Nishizawa, Y. Bull. Chem. Soc. Japan (1961), 34, 1170.

46. Beriger, E. U. S. Patent (1960), 2931826.

47. Arbuzov, A. E. Ber. (1905), 38, 1171.

48. Arbuzov, A. E. J. Russ. Phys. Chem. (1906), 38, 161, 193, and 687.

49. Wulfman, D. S.; Peace, B. W.; and Steffen, E. K. J. Chem. Soc. Chem. Commun. (1971), 1360.

50. Peace, B. W.; Carman, F. C.; and Wulfman, D. S. Synthesis (1971), 658.

51. Verkade, J. G. and Coskran, J. K.,"Organic Phosphorus Compounds", Vol. 2, Ed. by Kosolapoff, G. M. and Maier, L., Wiley-Interscience, New York, N. Y., (1972), p. 77.

52. Tsou, T. T. and Kochi, J. K. J. Org. Chem. (1980), 45, 1930.

53. Takagi, K.; Hayama, N.; and Okamoto, T. Chem. Lett.(1978), 191.

54. Hardy, W. B. and Fortenbaugh, R. B. J. Amer. Chem. Soc. (1958), 80, 1716.

55. Burdon, J.; Coe, P. L.; Marsh, C. R.; and Tatlow, J. C. J. Chem. Soc. Perkin I (1972), 763.

56. Lewin, A. H. and Goldberg, N. L. Tetrahedron Lett. (1972), 491.

57. Posner, G. H. Org. Reaction (1975), 22, 253.

58. Jukes, E. A. Adv. Organomet. Chem. (1974), 12, 215.

59. Belf, I. J.; Buxton, M. W.; and Fuller, G. J. Chem. Soc. (1965), 3372.

60. Liedholm, B. Acta Chem. Scand. (1969), 23, 3175.

61. Liedholm, B. Acta Chem. Scand. (1971), 25, 113.

62. Cohen, T.; Wood, J.; and Dietz,Jr., A. G. Tetrahedron Lett. (1974), 3555.

63. Cohen, T. and Cristea, I. J. Amer. Chem. Soc. (1976), 98, 748.

64. Koten, G. van; Jastrzebski, J. T. B. H.; and Noltes, J. G. Tetrahedron Lett. (1976), 223.

65. Lapouyade, R.; Daney, M.; Lapenue, M.; and Bouas-Laurent, H. Bull. Soc. Chim. France (1973), 720.

66. Suzuki, H. and Hanafusa, T. Synthesis (1974), 53.

67. Kochi, J. K.,"Organometallic Mechanisms and Catalysis", Academic Press., N. Y. (1978), Chap. 16.

68. Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; and Chiesi-Villa, A. J. Amer. Chem. Soc. (1978), 100, 4918.

69. Cotton, F. A. and Wilkinson, G.,"Advanced Inorganic Chemistry", 4th. Ed., Wiley-Interscience, New York, N. Y. (1980), p. 801.

70. Pople, J. A.; Schneider, W. G.; and Bernstein, H. J.,"High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., New York, N. Y., (1959), p. 238 ff.

71. Benezra, C. and Ourisson, G. Bull. Soc. Chim. France (1966), 1825.

72. Anderson, W. A.; Freeman, R.; and Reilly, C. A. J. Chem. Phys. (1963), 39, 1518.

73. Matter, U. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; and Sternhell, S. Tetrahedron (1969), 25, 691.

74. Bachmann, W. E. and Clarke, H. T. J. Amer. Chem. Soc. (1927), 49, 2089.

75. Weston, P. E. and Adkins, H. J. Amer. Chem. Soc.(1928), 50, 859.

76. Adams, R. and Teeter, H. H. J. Amer. Chem. Soc.(1940), 62, 2188.

77. Adkins, H. Org. Syn. (1946), 26, 51.

78. Bachmann, W. E. and Hoffman, R. A. Org. Reaction (1944), 2, 243.

79. Allen, C. F. H. Org. Syn. (1940), 20, 45.

80. Fanta, P. E. Chem. Rev. (1946), 38, 139.

81. Fanta, P. E. Chem. Rev. (1964), 64, 613.

82. Goshaev, M.; Otroshchenko, O. S.; and Sadykov, A. S. Russ. Chem. Rev. (Engl. Transl.) (1972), 41, 1046.

83. Fanta, P. E. Synthesis (1974), 9.

84. Bacon, R. G. R. and Hill, H. A. O. Quart. Rev. (1965), 19, 95.

85. Cohen, T. and Tirpak, J. G. Tetrahedron Lett. (1975), 143.

86. Lewin, A. H. and Cohen, T. Tetrahedron Lett. (1965), 4531.

87. Nilsson, M. Acta Chem. Scand. (1958), 12, 537.

88. Stephens, R. D. and Castro, C. E. J. Org. Chem.(1963), 28, 3313.

89. Gragerov, I. P. and Kasukhim, L. F. J. Org. Chem. USSR (Engl. Transl.) (1969), 5, 2.

90. Toda, F. and Takehira, Y. J. Chem. Soc. Chem. Commun. (1975), 174.

91. Cohen, T. and Poeth, T. J. Amer. Chem. Soc. (1972), 94, 4363.

92. Jennen, J. Bull. Soc. Chim. Belges (1973_, 46, 199.

93. Ramirez, F. and McKelvie, N. J. Amer. Chem. Soc.(1957), 79, 5829.

94. Griffin, C. E. Chem. & Ind.(London) (1957), 415.

95. Cadogan, J. I. G. and Foster, W. R. J. Chem. Soc. (1961), 3071.

96. Cohen, T. and Schambach, R. A. J. Amer. Chem. Soc. (1970), 92, 3189.

97. Cairncross, A.; Roland, J. R.; Henserson, R. M.; and Sheppard, W. A. J. Amer. Chem. Soc. (1970), 92, 3187.

98. Bacon, R. G. R.; Seeterram, S. G.; and Stewart, O. J. Tetrahedron Lett. (1967), 2003.

99. Liedholm, B. Acta Chem. Scand. (1971), 25, 106.

100. Sato, M.; Motoyama, I.; and Hata, K. Bull. Chem. Soc. Japan (1970), 43, 2972.

101. International Critical Tables, V, p. 187.

102. Gould, E. S.,"Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N. Y. (1959), p. 37.

103. Davis, A. J. H. and Graham, W. A. G. Inorg. Chem. (1971), 10, 1653.

104. Ugo, R.; Pasini, A.; Fusi, A.; and Cenini, S. J. Amer. Chem. Soc. (1972), 94, 7364.

105. Raston, C. L. and White, A. H. J. Chem. Soc. Dalton (1976), 2153.

106. Bowmaker, G. A.; Clark, G. R.; and Yuen, D. K. P. J. Chem. Soc. Dalton (1976), 2329.

107. Axtell, D. D. J. Amer. Chem. Soc. (1973), 95, 4555.

108. Jardine, F. J. Adv. Inorg. Chem. Radiochem.(1975), 17, 116.

109. Taylor,Jr., L. F.; Weininger, M. S.; and Amma, E. L. Inorg. Chem. (1974), 13, 2835.

110. Gill, J. T.; Mayerle, J. J.; Welcker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; and Lippard, S. J. Inorg. Chem. (1976), 15, 1155.

111. Meyerstein, D. Inorg. Chem. (1971), 10, 638.

112. Magee,Jr., J. S. and Wood, R. H. Can. J. Chem. (1965), 43, 1234.

113. Lister, M. W. Can. J. Chem. (1953), 31, 638.

114. Cotton, F. A. and Wilkinson, G.,"Advanced Inorganic Chemistry", 4th. Ed., Wiley-Interscience, New York, N. Y. (1980), p. 818.

115. Cotton, F. A. and Wilkinson, G., ibid, (1980), p. 1237.

116. Klein, J. and Levine, R. J. Amer. Chem. Soc. (1972), 94, 2520.

117. Klein, J. and Levine, R. Tetrahedron Lett. (1974), 2935.

118. Fitton, P. and McKeon, J. E. J. Chem. Soc. Chem. Commun.(1968), 4.

119. Semmelhack, M. F.; Helquist, P. M.; and Gorzynski, J. D. J. Amer. Chem. Soc. (1972), 94, 9234.

120. Cotton, F. A. and Wilkinson, G.,"Advanced Inorganic Chemistry", 4th. Ed., Wiley-Interscience, New York, N. Y. (1980), p. 808.

121. House, H. O. Acc. Chem. Res. (1976), 9, 59.

122. Yamamoto, Y.; Yatagai, H.; Sonoda, A.; and Murahashi, S.-I. J. Chem. Soc. Chem. Commun. (1976), 452.

123. Fillipo,Jr., J. S. Inorg. Chem. (1978), 17, 275.

124. Ashby, E. C. and Watkins, J. J. J. Amer. Chem. Soc. (1977), 99, 5312.

125. Semmelhack, M. F. and Yamashita, A. J. Amer. Chem. Soc.(1980), 102, 5924.

126. Semmelhack, M. F.; Seufert, W.; and Keller, L. J. Amer. Chem. Soc. (1980), 102, 6584.

127. Evitt, E. R. and Bergman, R. G. J. Amer. Chem. Soc. (1980), 102, 7003.

128. Kurosawa, H.; Majima, T. and Asada, N. J. Amer. Chem. Soc. (1980), 102, 6996.

129. Lennon, P. J. Amer. Chem. Soc. (1980), 102, 7033.

130. Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. J. Amer. Chem. Soc. (1980), 102, 5930.

131. Bäckvall, J.-E.; Nordberg, R. E.; Björkman, E. E.; and Moberg, C. J. Chem. Soc. Chem. Commun. (1980), 943.

132. Petal, B. A.; Kao, L. C.; Cortese, N. A.; Minkiewicz, J. V. and Heck, R. F. J. Org. Chem. (1979), 44, 918.

133. Eisenstein, O. and Hoffmann, R. J. Amer. Chem. Soc. (1980), 102, 6148.

134. Baenziger, N. C.; Richards, G. F.; and Doyle, J. R. Inorg. Chem. (1964), 3, 1529.

135. Haight, H. I.; Doyle, J. R.; Baenziger, N. C.; and Richards, G. F. Inorg. Chem. (1963), 2, 1301.

136. van den Hende, J. H. and Baird, W. C. J. Amer. Chem. Soc. (1963), 85, 1009.

137. Cotton, F. A. and Wilkinson, G.,"Advanced Inorganic Chemistry", 4th. Ed., Wiley-Interscience, New York, N. Y. (1980), p. 1240.

138. Vogel, A. I.,"A Text-Book of Practical Organic Chemistry", 3rd. Ed., Longmans, Green & Co., New York, N. Y. (1956), p.190.

139. Vogel, A. I., ibid, (1956), p. 191.

140. Kobrich, G.; Trapp, H.; Flory, K.; and Drischel, W. Chem. Ber. (1966), 99, 689; Chem. Abstr. (1966), 12709.

141. Seyferth, D.; Grim, S. O.; and Read, T. O. J. Amer. Chem. Soc. (1960), 82, 1510; ibid, (1961), 83, 1617.

142. Nikilenko, L. N. and Popov, S. I. J. Org. Chem. USSR (Engl. Transl.) (1962), 32, 29.

143. Newman, M. S.; Fraenkel, G.; and Kirn, W. N. J. Org. Chem. (1963), 28, 1851.

144. Rapoport, Z.; Shulman, P.; and Thuval, M. J. Amer. Chem. Soc. (1978), 100, 7041.

145. McCullough, J. J. and Manning, C. J. Org. Chem. (1978), 43, 2839.