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An Easy Access to Trisubstituted Vinyl Chlorides and Improved Synthesis of Chloro/ Bromostilbenes

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***Abstract*:** The α-chlorophosphonates $(OCH_2CMe_2CH_2O)P(O)CHCl\text{-}C_6H_4\text{-}4\text{-}R$ [R=H (**4**), Me (**5**), OMe (**6**)], which are now readily accessible, react with ketones R'C(O)R" in the presence of NaH (without recourse to the more expensive *t*-BuLi) to afford trisubstituted vinyl halides $R'C(R'')=CCl(C_6H_4\text{-}4\text{-}R)$ in good yields. The corresponding α-bromophosphonates [R=H (**7**), Me (**8**)] failed to react with ketones and gave the symmetrical acetylenes $4\text{-}R\text{-}C_6H_4\text{-}C{\equiv}C\text{-}C_6H_4\text{-}4\text{-}R$ as isolable products in low yield. We have found that K_2CO_3 in refluxing xylene is a good base for the synthesis of chlorostilbenes; using this base the bromostilbenes $ArCH=CBr(C_6H_4\text{-}4\text{-}R)$ can be prepared in significantly higher yields than by using NaH. The stereochemistry of two of the trisubstituted vinyl chlorides is unambiguously proven by X-ray structure determination. Thus for (Cl)PhC=CPh(Me), the isomer with the upfield NMR shift for the CH_3 protons and for $(Cl)PhC=C(Ph)(C_6H_4\text{-}4\text{-}Me)$, the isomer with the downfield NMR shift for the $\text{-}C_6H_4\text{-}4\text{-}CH_3$ protons have *Z* stereochemistry.

We have recently reported a convenient route to aryl substituted chloro and bromo olefins from α-chloro/bromophosphonates and aldehydes by the Wadsworth-Emmons reaction.[1] However, literature is scarce on the use of ketones to obtain tetrasubstituted olefins (trisubstituted vinyl chlorides) by this method.[2,3] Obvious practical difficulties such as steric bulk and lower reactivity of ketones have largely been responsible for this, thereby necessitating the use of very strong and expensive bases;[2a, 3a] in addition, an easy access to suitable α-chloro/ bromophosphonates was not available.[3] We now report a simple and practical method to obtain trisubstituted vinyl chlorides from α-chlorophosphonates and ketones. We also describe a comparative study of the efficacy of different bases and solvents in the reaction of α-chloro/ bromophosphonates with aldehydes. An interesting reaction of α-bromophosphonates with NaH to yield a symmetrical acetylene is also noted. Finally, we report the stereochemistry of two of the trisubstituted vinyl chlorides as determined unambiguously by X-ray crystallography.

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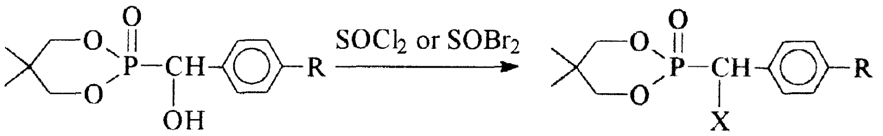
The α-chloro/ bromophosphonates **4-8** used in the present study were synthesized[4] as shown in Scheme 1. Details of the reactions of the chlorophosphonates **4-6** with ketones are shown in Scheme 2 and Table 1.

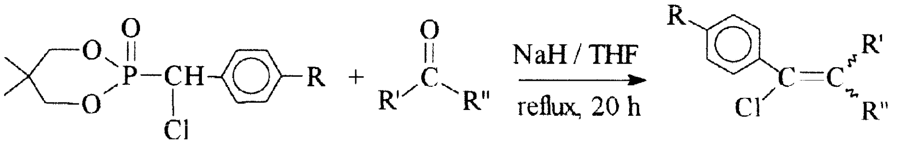
Scheme 1



R = H (**1**), Me (**2**), OMe (**3**)

X = Cl; R = H (**4**), Me (**5**), OMe (**6**)
X = Br; R = H (**7**), Me (**8**)

Scheme 2



4 - 6

9 - 11 (65-96 % yield)

Table 1. Details on the reactions of phosphonates with ketones

R'	R"	Yield (%)[a]	*E*/*Z* ratio	R'	R"	Yield (%)[a]	*E*/*Z* ratio
9 (R = H)				**10** (R = Me)			
a Ph	Ph	85	-------	**a** Ph	Ph	85	------
b Ph	4-Me-C_6H_4	86	40:60	**b** Ph	4-Me-C_6H_4	85	50:50
c Ph	4-OMe-C_6H_4	81	33:67	**c** Ph	4-OMe-C_6H_4	82	50:50
d Ph	Me	65	75:25	**d** 4-OMe-C_6H_4	Me	66	40:60
e 4-OMe-C_6H_4	Me	65	67:33	**e** Ph-C(O)	Ph	65	50:50
f 4-Me-C_6H_4	Me	69	67:33	**11** (R = OMe)			
g 3-NO_2-C_6H_4	3-NO_2-C_6H_4	95	-------	**a** Ph	Ph	80	-------
h -$(CH_2)_5$-		65	-------	**b** Ph	4-Me-C_6H_4	83	50:50
i -$(CH_2)_6$-		70	-------	**c** 3-NO_2-C_6H_4	3-NO_2-C_6H_4	96	------

[a] Yields of *E*/*Z* mixtures (based on available X-ray structures as well as ^{1}H and ^{13}C NMR spectroscopy as appropriate).

In an earlier paper by Crenshaw and Zimmer[2a] on the synthesis of trisubstituted vinyl chlorides of the type **9-11**, the authors used the strong base *t*-BuLi (which is also expensive) to obtain good yields of the products.[5] In our reactions with α-chlorophosphonates **4-6**, we found that NaH is very effective as a base and the yields are better. In addition, since our chlorophosphonates are very readily prepared in high yields,[4] we believe that our route to trisubstituted vinyl chlorides is superior to earlier methods. Furthermore, we have also found that the vinyl chloride Ph(Cl)C=C(C_6H_4-3-NO_2)$_2$ can be obtained in 43% yield even when reacting **4** with a weak base such as K_2CO_3 in acetonitrile. Thus it appears that the cyclic phosphonates **4-6** show an enhanced reactivity as compared to the acyclic ones.[6]

In the reaction of **4** with acetophenone/NaH, although the reaction mixture on distillation showed a *Z E* ratio of *ca* 1:8, the initial reaction mixture showed the Z/E isomeric ratio to be *ca* 1:3. We have isolated the *minor Z*-isomer of (Cl)PhC=CPh(Me) (**9d**) as a crystalline solid which shows the *upfield* ^{1}H NMR spectroscopy chemical shift for the CH_3 protons. The structure has been proven by X-ray crystallography (Fig. 1); this is the predominant isomer claimed by Crenshaw and Zimmer using the phosphonate $(MeO)_2P(O)CHCl(Ph)$.[2a] Since the chloro and methyl groups are similar in size, their positions in this structure are readily interchanged without affecting crystal packing; this type of disorder has been discussed elsewhere.[7]

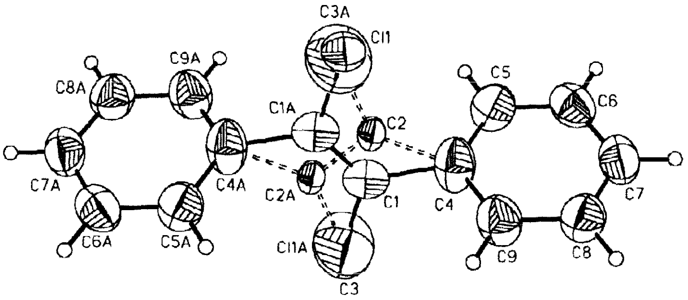


Fig. 1. Molecular structure of the *Z* isomer of **9d**. Selected bond distances: C(1)- C(1A) 1.289(6); C(1)-Cl(1A) 1.686(4); C(1)-C(3) 1.5305 (10); C(2)-Cl(1) 1.7097 (10) Å

Since unambiguous assignment of stereochemistry for the isomers in the above system is difficult, we characterized the isomer of **9b** which has the *downfied* ^{1}H NMR spectroscopy shift for the -C_6H_4-4-CH_3 protons by X-ray crystallography. This isomer has the two phenyl groups positioned *cis* to each other [Fig. 2]

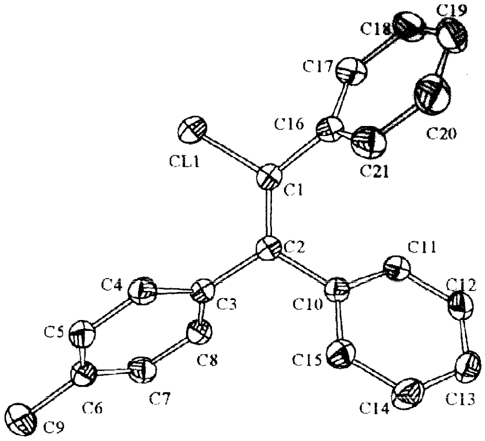
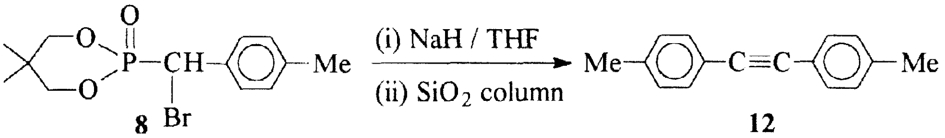


Fig. 2. Molecular structure of the *Z* isomer of **9b** (phenyl groups on the same side). Selected bond distances: C(1)-C(2) 1.340(3); C(1)-Cl(1) 1.752(8); C(1)-C(16) 1.482 (3); C(2)-C(3) 1.490(4); C(2)-C(10) 1.489(7) Å.

The *E*/*Z* ratios for **9e**, **9f** and **10d** are ascertained by comparing their NMR spectra with **9d**; the ^{13}C NMR signal of =C-CH_3 for the *Z*-isomer appears upfield to that of the *E*-isomer. Assignment of *E*/*Z* ratios for **10b** and **11b** is done by comparing their ^{1}H NMR spectra with that of **9b**; for **9c** assignement is made by assuming a similar trend in its spectrum.

We have also tried several reactions of ketones with the α-bromophosphonates 7 and **8** using NaH. We observed an olefinic compound (^{1}H NMR spectroscopy, see experimental) that did not contain the ketonic residue; the same result was obtained when no ketone was added. However, the only product that we could isolate in a pure state was the symmetrical acetylene (Scheme 3).

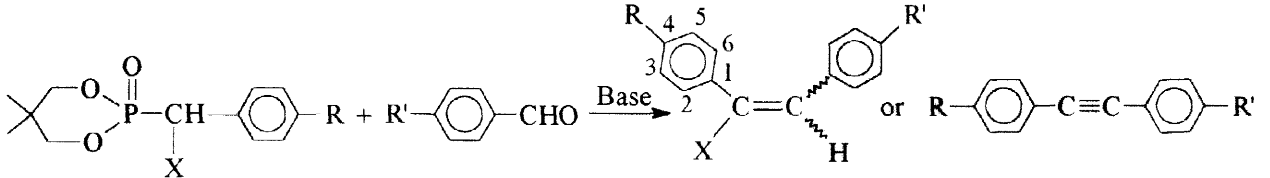
Scheme 3



8 **12**

The second aspect of the present study deals with the effect of reaction conditions on the nature and yield of the products. Since aldehydes are more reactive than ketones, the reaction of the former with the phosphonates has been checked in detail using different bases and solvents (Scheme 4, Table 2). As can be seen from Scheme 4, *Z*-olefins are also formed in significant quantities; this is in line with the observation made by Larsen and Aksnes that cyclic phosphonates increase *Z*-stereoselectivity.[6] The *E*/*Z* ratio is based on the δ(^{1}H) value for C_6H_4-OCH_3 or C_6H_4-CH_3 protons and the well separated δ(^{13}C) values for the *ipso*-carbon labelled as C(1) in Scheme 4 and diagram in Table 2; the *E*-isomer always showed the downfield chemical shift for C(1) in ^{13}C NMR spectroscopy.

Scheme 4



13 (a, b) (X = Cl)
14 (a, b) (X = Br)
15

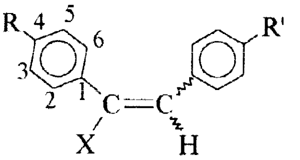
Table 2. Details on the reactions of phosphonates with aldehydes using different bases

Sl. No.	Phosph-onate	Aldehyde (R'=)	Base	Solvent/ Temp/ Time	Product	Yield, % (*E Z* ratio[a])
1	**4**	4-OMe	NaH[b]	THF/0→20°C/13 h	**13a**	98 (65:35)
2	**4**	4-OMe	NaH[b]/ DMSO (1:3)	THF/0°C/8 h	**13a**	65 (65:35)
3	**4**	4-OMe	NaH[c]/ DMSO	DMSO/0→20°C/9 h	**13a,15**	50 (total): 10% alkene (75:25); 40% alkyne
4	**4**	4-OMe	NaH[c]/ DMSO	DMSO/75°C/8 h	**15**	53 (alkyne only)
5	**4**	4-OMe	CsF[c]	MeCN/reflux/3 d	**13a**	52 (40:60)
6	**4**	4-OMe	K_2CO_3[c]	MeCN/reflux/3 d	**13a**	83 (55:45)
7	5	H	K_2CO_3[c]	MeCN/reflux/3 d	**13b**	88 (60:40)
8	7	4-OMe	K_2CO_3[c]	MeCN/reflux/5 d	**14a**	50 (50:50)[d]
9	**8**	H	K_2CO_3[c]	MeCN/reflux/5 d	**14b**	52 (30:70)
10	**4**	4-OMe	K_2CO_3[c]	Neat/150°C/1 h	**13a**	68 (55:45)
11	**4**	4-OMe	KF or $HN(i\text{-}Pr)_2$	MeCN/reflux or neat/ 24 h	No reaction	

[a] Based on ^{1}H and ^{13}C NMR spectroscopy.
[b] 1.5 mole eq.
[c] 3 mole eq.
[d] Ph(Br)C=CPh(H) (6%) was obtained as a side product.

It can be noted that NaH in THF gives the best yield of the chloro olefin. Use of DMSO resulted in the formation of the alkyne in addition to the olefin.[8] There is a reversal of stereochemistry when CsF is used, but we have not been able to increase the yield of the predominant isomer. The reaction under neat conditions using K_2CO_3 is attractive, but for phosphonates with m.p. >160°C heating at higher temperatures may be required. What attracted our attention more was the use of cheap K_2CO_3 in a suitable solvent.[9] We have further explored the effect of different solvents using K_2CO_3 as a base in the reaction of **4** with *p*-anisaldehyde. Of the several solvents tried, xylene gives the best yield. In DMF the reaction did not work. The yields are in the order THF (reflux, 3d, 33%) < acetone (reflux, 3d, 53%) < DMSO (80°C, 1d, 60%; 20% alkyne is also present) < CH_3CN + TMEDA (reflux, 3d, 80%) < CH_3CN (reflux, 3d, 83%) < xylene (reflux, 1d, 90%).

Table 3. Synthesis of chloro/ bromo stilbenes using K_2CO_3 as a base



Sl. No.	Phosphonate	Aldehyde (R')	Product	Yield, % (*E*/*Z* ratio)[a]
1	**4**	OMe	**13a** (X = Cl)	90 (40:60)
2	**4**	Me	**13c** (X = Cl)	97 (65:35)
3	**5**	Cl	**13d** (X = Cl)	81(50: 50)
4	**6**	Cl	**13e** (X = Cl)	89 (30:70)
5	**6**	Me	**13f** (X = Cl)	90 (35:65)
6	**6**	H	**13g** (X = Cl)	92 (50:50)
7	**7**	OMe	**14a** (X = Br)	65 (60:40)
8	**8**	Cl	**14c** (X = Br)	73 (60:40)
9	**8**	OMe	**14d** (X = Br)	69 (50:50)

[a] Isomer ratio (by ^1H NMR and ^{13}C NMR spectroscopy) given in parentheses.

Since xylene as the reaction medium afforded the best results, we have used the K_2CO_3/ xylene method to synthesize other chloro- and bromostilbenes. As can be seen from Table 3, excellent yields are obtained under these conditions. Noteworthy is the dramatic improvement in the yields of bromostilbenes over the NaH/THF method previously reported by us.[1]

In summary we have developed a convenient and practical synthesis of trisubstituted vinyl chlorides as well as bromostilbenes in addition to elucidating the stereochemistry of two of the vinyl chlorides.

Experimental Section

Chemicals were purchased from Aldrich/ Fluka or local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[10] Reactions were performed under dry nitrogen atmosphere unless otherwise specified. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker 200 MHz spectrometer in $CDCl_3$ with chemical shifts (ppm) measured against $(CH_3)_4Si$. IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer. Mass spectra were recorded on a CEC-21-110B double focussing mass spectrometer. Elemental analyses were obtained from the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta.

The α-chloro/ bromophosphonates **4-8** were prepared by the procedure described earlier.[4] Only typical procedures are given below.

(a) Synthesis of $Ph(Cl)C{=}CPh_2$ (9a)

To a stirred suspension of NaH (previously washed with hexane) (0.119 g, 4.94 mmol) in THF (20 mL) at 0°C was added phosphonate **4** (0.90 g, 3.29 mmol) in THF (10 mL). After 0.5 h, benzophenone (0.60 g, 3.29 mmol) in THF (20 mL) was added dropwise during 15 min. and the mixture heated under reflux for 20 h. After cooling and quenching with cold water (30 mL), the mixture was extracted with ether (3 × 10 mL). The ether layer was dried (Na_2SO_4) and the solvent removed to obtain a semisolid which was purified by column chromatography (silica gel, hexane) to obtain colourless needles (0.81 g, 85%), m.p. 118-119°C (lit.[2a] m.p. 117.5-119°C). IR: 966, 1028, 1074, 1493, 1595 cm^{-1}. ^{1}H NMR: 6.80-7.45 (m). ^{13}C NMR: 127.0, 127.5, 127.9, 128.1, 129.8, 130.0, 130.6.

Data for compounds **9-11** prepared similarly, is given below.

9b (mixture): ^{1}H NMR: 2.24, 2.38 (2s, *E* and *Z* isomers respectively; ratio 2:3, 3H, $ArCH_3$), 6.89-7.39 (m, 14H, Ar*H*). ^{13}C NMR: 21.2 (*E*), 21.3 (*Z*), 127.0, 127.5, 127.9, 128.1, 128.7, 128.9, 129.7, 130.0, 130.5, 130.6, 136.8, 137.4, 139.1, 139.6, 140.3, 141.3, 142.2.

Pure *Z* isomer obtained by crystallization from hexane. M.p. 98-100°C. IR: 966, 1020, 1074, 1508, 1591 cm^{-1}. ^{1}H NMR: 2.38 (s, 3H, CH_3), 6.89-7.39 (m, 14H, Ar*H*). ^{13}C NMR: 21.3, 126.9, 127.9, 128.8, 129.7, 130.0, 130.6, 137.3, 139.1, 139.6, 141.3. Anal. Calcd. for $C_{21}H_{17}Cl$: C, 82.73; H, 5.63. Found; C, 82.65; H, 5.61.

9c (mixture, liquid): IR: 968, 1034, 1074, 1153, 1248, 1510, 1607 cm^{-1}. ^{1}H NMR: 3.75, 3.87 (2s, ratio 1:2, 3H, OCH_3), 6.69-7.77 (m, 14H, Ar*H*). ^{13}C NMR: 55.1, 55.3, 113.5, 113.6, 126-148 (many lines), 158.9, 159.1. MS: 320, 322 $[M]^+$ ($^{35,37}Cl$), 286, 270, 253, 239,226, 215, 202, 178, 165, 152. Anal. Calcd. for $C_{21}H_{17}ClO$: C, 78.60; H, 5.35. Found; C, 78.65; H, 5.25.

9d (mixture, liquid, b.p. 125°C/0.5mm, lit.^{2a} b.p. 115°C/0.55mm): **IR**: 893, 1028, 1074, 1215, 1491, 1599 cm^{-1}. ^{1}H NMR: 2.09, 2.40 (2s, ratio 1:8, 3H, CH_3), 7.00-7.60 (m, 10H, Ar*H*). ^{13}C NMR: 23.5, 126.8, 127.6, 127.8, 128.1, 128.3, 128.9, 130.0, 135.4, 139.3, 141.8. Anal. Calcd. for $C_{15}H_{13}Cl$: C, 78.76; H, 5.74. Found; C, 78.82; H, 5.78.

Pure *Z* isomer (crystallized from the mixture from hexane after several days, m.p. 120-122°C). ^{1}H NMR: 2.09 (s, 3H, CH_3), 7.20-7.60 (m, 10H, Ar*H*).

9e (mixture, liquid): IR: 1034, 1074, 1111, 1248, 1510, 1607 cm^{-1}. ^{1}H NMR: 2.07, 2.38 (2s, ratio 1:2, 3H, CH_3), 3.75, 3.87 (2s, ratio 2:1, 3H, OCH_3), 6.70-7.00 (AB qrt, 4H, Ar*H*), 7.10-7.60 (m, 5H, Ar*H*). ^{13}C NMR: 23.1 (*Z*), 23.5 (*E*), 55.2, 55.3, 113.5, 113.6, 127.4-139.5 (many lines), 158.4, 158.5. Anal. Calcd. for $C_{16}H_{15}ClO$: C, 74.26; H, 5.85. Found; C, 74.30; H, 5.92.

9f (mixture, liquid): IR: 893, 1020, 1072, 1512, 1599 cm^{-1}. ^{1}H NMR: 2.10, 2.30 (2s, ratio 1:2, 3H, CH_3), 2.40, 2.44 (2s, ratio 2:1, ArCH_3), 6.90-7.60 (m, 9H, Ar*H*). ^{13}C NMR: 21.1 (*Z*), 21.3 (*E*), 23.1, 23.5, 127.5-139.5 (many lines). MS: 242, 244 [M]$^+$ (^{35,37}Cl)., 227, 207, 192, 189, 165, 129, 115, 105. Anal. Calcd. for $C_{16}H_{15}Cl$: C, 79.15; H, 6.24. Found; C, 79.20; H, 6.25.

9g (m.p. 126-127°C, lit.^{2a} m.p. 126-127.5°C): IR: 993, 1084, 1346, 1523, 1591 cm^{-1}. ^{1}H NMR: 7.30-8.40 (m). ^{13}C NMR: 122.6, 123.1, 124.9, 125.2, 129.3, 129.7, 135.9, 136.3, 137.6, 141.5, 142.0.

9h (liquid): IR: 991, 1070, 1489, 1608 cm^{-1}. ^{1}H NMR: 1.57-1.67 (m, 6H, CH_2), 2.17-2.20 (m, 2H, $=CCH_2$), 2.50-2.60 (m, 2H, $=CCH_2$), 7.40 (s, 5H, Ar*H*). ^{13}C NMR: 26.3, 27.2, 27.9, 31.9, 32.0, 122.7, 127.8, 128.1, 129.3, 137.9, 139.3. MS: 206, 208 [M]$^+$ (^{35,37}Cl), 171, 159, 138, 129, 115, 105, 91. Anal. Calcd. for $C_{13}H_{15}Cl$: C, 75.52; H, 7.32. Found; C, 75.60; H, 7.33.

9i (liquid): IR: 935, 1026, 1070, 1450, 1601 cm^{-1}. ^{1}H NMR: 1.50-1.70 (m, 8H, CH_2), 2.20-2.30 (m, 2H, $=CCH_2$), 2.50-2.60 (m, 2H, $=CCH_2$), 7.40 (s, 5H, Ar*H*). ^{13}C NMR: 22.7, 26.4, 28.3, 29.9, 32.7, 33.8, 125.6, 127.7, 128.1, 129.2, 139.7. Anal. Calcd. for $C_{14}H_{17}Cl$: C, 76.16; H, 7.77. Found; C, 77.19; H, 8.40.

10a (m.p. 127-130°C): IR: 943, 999, 1028, 1076, 1449, 1597 cm^{-1}. ^{1}H NMR: 2.30 (s, 3H, ArCH_3), 6.90-7.40 (m, 14H, Ar*H*). ^{13}C NMR: 21.2, 126.9, 127.4, 127.9, 128.1, 128.6, 127.8, 129.9, 130.5, 136.5, 138.0, 142.1. Anal. Calcd. for $C_{21}H_{17}Cl$: C, 82.73; H, 5.63. Found: C, 81.92, H, 5.86.

10b (m.p. 108-110°C): IR: 966, 1020, 1072, 1508, 1604 cm^{-1}. ^{1}H NMR: 2.10, 2.15, 2.16, 2.29 (4s of equal intensity, 6H, ArCH_3), 7.30-7.90 (m, 13H, Ar*H*). ^{13}C NMR: 21.2, 126.8-142.4 (many lines). Anal. Calcd for $C_{22}H_{19}Cl$: C, 82.86; H, 6.01. Found: C, 82.45; H, 5.96.

10c (m.p. 72-74°C): IR: 968, 1034, 1072, 1111, 1248, 1510, 1605 cm^{-1}. ^{1}H NMR: 2.38, 2.39 (2s, ratio 1:1, 3H, ArCH_3), 3.48, 3.60 (2s, 3H, OCH_3), 6.50-7.30 (m, 13H, Ar*H*). ^{13}C NMR: 21.4, 55.2, 55.3, 113.5, 113.6, 113.8, 114.2, 127.0-142.6 (many lines), 158.7, 159.0. Anal. Calcd. for $C_{22}H_{19}ClO$: C, 78.90; H, 5.73. Found: C, 78.65; H, 5.68.

10d (m.p. 128-130°C): IR: 1032, 1074, 1109, 1242, 1512, 1606 cm^{-1}. ^{1}H NMR: 2.05, 2.27 (2s, ratio 3:2, 3H, C*H*$_3$), 2.35-2.40 (2s, ratio 2:3, 3H, ArC*H*$_3$), 3.75-3.85 (2s, ratio 2:3, 3H, OC*H*$_3$), 6.70-7.40 (m, 8H, Ar*H*). ^{13}C NMR: 21.1, 21.2, 23.0, 23.4, 55.1, 55.2, 113.5, 113.6, 126.0-140.0 (many lines), 158.6, 159.4, 163.6. Anal. Calcd. for $C_{17}H_{17}ClO$: C, 74.84; H, 6.29. Found; C, 74.64; H, 6.40.

10e (liquid): IR: 812, 1022, 1059, 1597, 1668 cm^{-1}. ^{1}H NMR: 2.23, 2.34 (2s, ratio 1:1, 3H, C*H*$_3$), 6.98-8.15 (m, 14H, Ar*H*). ^{13}C NMR: 21.3, 128.0-134.0 (many lines). MS: 332, 334 $[M]^+$ (^{35,37}Cl), 192. Anal. Calcd. for $C_{22}H_{17}ClO$: C, 79.38; H, 5.15. Found; C, 79.45; H, 5.15.

11a (m.p. 119-120°C): IR: 999, 1030, 1076, 1277, 1506, 1597 cm^{-1}. ^{1}H NMR: 3.75 (s, 3H, OC*H*$_3$), 6.70-7.40 (m, 14H, Ar*H*). ^{13}C NMR: 55.2, 113.4, 126.8, 127.4, 127.9, 128.1, 129.8, 130.5, 131.4, 131.8, 139.5, 141.8, 142.2, 159.3. Anal. Calcd. for $C_{21}H_{17}ClO$: C, 78.62; H, 5.34. Found: C, 78.21; H, 5.55.

11b (m.p. 96-98°C): IR: 966, 1028, 1111, 1251, 1504, 1602 cm^{-1}. ^{1}H NMR: 2.25, 2.29 (2s, ratio 1:1, 3H, ArC*H*$_3$), 3.77, 3.79 (2s, ratio 1:1, 3H, OC*H*$_3$), 6.70-7.38 (m, 13H, Ar*H*). ^{13}C NMR: 21.1, 55.2, 113.3, 126.8-142.4 (many lines), 159.2. Anal. Calcd. for $C_{22}H_{19}ClO$: C, 78.90; H, 5.73. Found: C, 78.67; H, 5.70.

11c (m.p. 174-176°C): IR: 1032, 1097, 1253, 1300, 1506, 1529, 1602 cm^{-1}. ^{1}H NMR: 3.79 (s, 3H, OC*H*$_3$), 6.74-8.24 (m, 12H, Ar*H*). ^{13}C NMR: 55.3, 113.9, 122.4, 123.0, 125.0, 125.3, 129.3, 129.6, 131.4, 136.0, 136.5, 142.2, 160.2. MS: 410, 412 $[M]^+$(^{35,37}Cl), 375, 239, 128. Anal. Calcd. for $C_{21}H_{15}ClN_2O_5$: C, 61.39; H, 3.68; N, 6.82. Found; C, 61.24; H, 3.75, N, 6.75.

(b) Formation of the acetylene 4-Me-C_6H_4-C≡C-C_6H_4-4-Me (12)

To a stirred suspension of NaH (previously washed with hexane) (0.108 g, 4.5 mmol) in THF (20 mL) at 0° C was added the α-bromophosphonate **8** (1.0 g, 3.0 mmol) in THF (20 mL), and the reaction mixture heated under reflux for 24 h. It was then cooled, quenched with water (30 mL) and extracted with ether (2 × 25 mL). The organic layer was dried (Na_2SO_4) and the volatiles removed to yield a semisolid (^{1}H NMR: 2.26, 2.38, 2.39 (3s, 6H, ArC*H*$_3$), 6.90-7.70 (m, 8H, Ar*H*). Column chromatography (silica gel, hexane) afforded the acetylene **12** (0.050 g, 8%), m.p. 135-137°C (lit.[10] m.p. 138-138.8°C). ^{1}H NMR: 2.40 (s, 3H, ArC*H*$_3$), 7.20 (AB d, 2H, Ar*H*), 7.45 (AB d, 2H, Ar*H*).

When an equimolar quantity of 4,4'-dimethoxybenzophenone was added after the formation of the phosphonate anion and the reaction mixture refluxed and worked up as before, again the acetylene **12** was obtained.

A similar result was obtained using the bromophosphonate 7.

(c) Preparation of the chloro/bromo stilbenes 13/14 and the acetylene 15

Typical procedure for 13a

To a mixture of the α-chlorophosphonate **4** (0.50 g, 1.82 mmol) and anhydrous K_2CO_3 (0.75 g, 5.43 mmol) in xylene (5 mL) at 20°C was added 4-methoxybenzaldehyde (0.25 g, 1.82 mmol) and the mixture heated under reflux for 24 h. Then, xylene was removed, water (25 mL) added, and the mixture extracted with ether under reflux for 24 h. Then, xylene was removed, water (25 mL) added, and the mixture extracted with ether (3 × 20 mL). The organic layer was dried (Na_2SO_4), solvent removed, and the residue chromatographed over silica gel (3% CH_2Cl_2 in hexane) to afford **13a** (liquid, 0.40 g, 90%). IR: 908, 1033, 1113, 1252, 1510, 1606 cm^{-1}. ^{1}H NMR: 3.76, 3.86 (2s, ratio 2:3, 3H, OCH_3), 6.70-7.90 (10H, Ar*H*, C=C*H*). ^{13}C NMR: 55.2, 55.3, 113.8, 125.7, 126.7, 128.0, 128.5, 128.6, 128.8, 129.3, 130.1, 131.1, 138.2 and 139.7 (*ipso* carbon at (Ar)(Cl)C=, ratio 2:3, *Z* and *E*-isomers respectively), 159.0, 159.5. MS: 244, 246 [M]$^+$(^{35,37}Cl), 208, 165. Anal. Calcd. for $C_{15}H_{13}ClO$: C, 73.60; H, 5.36. Found; C, 73.38; H, 5.45.

Data for the other compounds prepared similarly, is given below.

13b (liquid): IR: 927, 1030, 1076, 1508, 1606 cm^{-1}. ^{1}H NMR: 2.30, 2.36 (2s, ratio 3:2, 3H, CH_3), 6.85-7.85 (m, 10H, Ar*H*, C=C*H*). ^{13}C NMR: 21.2, 21.4, 125.3, 126.7, 127.3, 127.9, 128.3, 128.6, 128.8, 129.2, 129.3, 129.5, 132.3, 132.4, 134.9, 135.5, 135.6, 136.6, 138.8 (*Z*), 138.9 (*E*). Anal. Calcd. for $C_{15}H_{13}Cl$: C, 78.70; H, 5.70. Found; C, 78.68; H, 5.71.

13c (liquid): IR: 947, 1032, 1074, 1510, 1597 cm^{-1}. ^{1}H NMR: 2.30, 2.45 (2s, ratio 2:3, 3H, CH_3), 6.80-7.85 (m, 10H, Ar*H* + C=C*H*). ^{13}C NMR: 21.1, 21.3, 125.8, 126.1, 126.7, 128.4, 128.6, 128.8, 129.0, 129.3, 131.4, 132.3, 132.6, 137.3, 138.0 (*Z*), 139.6 (*E*). Anal. Calcd. for $C_{15}H_{13}Cl$: C, 78.70; H, 5.70. Found; C, 78.46; H, 5.26.

13d (m.p. 56-58°C): IR: 914, 1010, 1086, 1487, 1618 cm^{-1}. ^{1}H NMR: 2.37, 2.39 (2s, ratio 1:1, 3H, CH_3), 6.80-7.80 (m, 9H, Ar*H* + C=C*H*). ^{13}C NMR: 21.1, 21.2, 124.0, 126.6, 127.2, 128.4, 129.0, 129.3, 129.9, 130.7, 133.0, 134.1, 139.0 (*Z* + *E*). MS: 262, 264, 266 [M]$^+$ (^{35,37}Cl), 227, 192. Anal. Calcd. for $C_{15}H_{12}Cl_2$: C, 68.46; H, 4.59. Found; C, 68.73; H, 4.80.

13e (liquid): IR: 1030, 1086, 1138, 1250, 1510, 1605 cm^{-1}. ^{1}H NMR: 3.80, 3.82 (2s, ratio 7:3, 3H, OCH_3), 6.80-7.80 (m, 9H, Ar*H* + C=C*H*). ^{13}C NMR: 55.3, 114.0, 128.6, 128.7, 131.8, 132.6, 133.0. Anal. Calcd. for $C_{15}H_{12}Cl_2O$: C, 64.50; H, 4.30. Found; C, 64.23; H, 4.37.

13f: Already reported by us[1] (IR: 1116, 1172, 1284, 1508, 1610 cm^{-1}).

13g (liquid): IR: 927, 1030, 1111, 1257, 1510, 1601 cm^{-1}. ^{1}H NMR: 3.80, 3.85 (2s, 1:1, 3H, CH_3), 6.85-7.85 (m, 10H, Ar*H* + C=C*H*). ^{13}C NMR: 55.4, 113.7, 113.9, 116.2, 120.2, 124.4, 127.2, 127.7, 128.0, 128.2, 128.7, 129.3, 130.6, 131.9, 132.5, 135.6, 138.1, 140.7, 141.9, 141.9, 144.6, 149.7. Anal. Calcd. for $C_{15}H_{13}ClO$: C, 73.60; H, 5.36. Found; C, 73.51; H, 5.30.

14a (liquid): IR: 966, 1030, 1109, 1249, 1510, 1605 cm^{-1}. ^{1}H NMR: 3.75, 3.85 (2s, ratio 2:3, 3H, OCH_3), 6.65-7.80 (m, 10H, Ar*H* + C=C*H*). ^{13}C NMR: 55.2, 55.3, 113.7, 121.1, 122.1, 127.8, 128.3, 128.7, 129.3, 129.5, 130.0, 130.8, 132.6, 139.8 (*Z*), 141.4 (*E*), 159.5. MS: 290, 288 [M]$^+$ (^{79,81}Br), 209. Anal. Calcd. for $C_{15}H_{13}BrO$: C, 62.30; H, 4.50. Found; C, 62.60; H, 4.40.

14b (liquid): IR: 814, 903, 1014, 1095, 1510, 1606 cm^{-1}. ^{1}H NMR: 2.35, 2.40 (2s, ratio 3:7, 3H, Ar-CH_3), 7.00-7.80 (m, 10H, Ar*H* + C=C*H*). ^{13}C NMR: 21.1, 21.3, 124.3, 127.4, 127.7, 127.9, 128.2, 128.7, 129.0, 129.2, 131.6, 132.7, 136.5, 138.3 (*Z*), 138.8 (*E*). MS: 290, 288 $[M]^+$ (^{79,81}Br), 209, 165. Anal. Calcd. for $C_{15}H_{13}Br$: C, 65.90; H, 4.79. Found; C, 66.31; H, 4.95.

14c (liquid): IR: 903, 1009, 1086, 1487, 1608 cm^{-1}. ^{1}H NMR: 2.35, 2.40, (2s with ratio 2:3, 3H, Ar-C*H*$_3$), 6.90-7.70 (m, 9H, Ar*H* + C=C*H*). ^{13}C NMR: 20.9, 21.1, 127.6, 128.4, 129.0, 129.4, 129.8, 130.5, 138.2 (*Z*), 138.8 (*E*). MS: 310,308, 306 $[M]^+$ (^{79,81}Br; ^{35,37}Cl), 229, 227 $[M\text{-}Br]^+$, 192 [M-Br-Cl]. Anal. Calcd. for $C_{15}H_{12}BrCl$: C, 58.59; H, 3.92. Found; C, 58.43; H, 4.07.

14d (liquid): Mixture of isomers. IR: 905, 1024, 1252, 1510, 1608 cm^{-1}. ^{1}H NMR: 2.40, 2.42 (2s, ratio 1:1, 3H, Ar-C*H*$_3$), 3.77, 3.87 (2s, 3H, OC*H*$_3$), 6.69-7.80 (m, 9H, Ar*H* + C*H*=CBr). ^{13}C NMR: 21.2, 21.4 (2C-*C*H$_3$), 55.2, 55.3 (2s, O*C*H$_3$), 113.7, 113.8, 122.0, 122.3, 127.7, 128.7, 129.0, 129.1, 129.3, 129.4, 130.0, 130.8, 132.2, 133.0, 136.9, 138.5 (*Z*), 138.6 (*E*), 138.7, 158.5, 158.8 (Ar*C* + *C*H=*C*Br).

MS: 302,304 $[M]^+$(^{79,81}Br), 223, 179, 178, 165, 115. Anal. Calcd. for $C_{16}H_{15}BrO$: C, 63.34; H, 4.90. Found; C, 63.42; H, 4.99.

15 (obtained from the reaction of **4** with *p*-anisaldehyde in DMSO at 75°C for 8h, m. p. 56-58°C): IR 2216 cm^{-1} (ν(C≡C)). ^{1}H NMR: 3.80 (s, 3H, C*H*$_3$), 6.80-7.60 (m, Ar*H*). ^{13}C NMR: 55.3, 88.3, 89.7, 114.2, 115.5, 123.8, 128.0, 128.5, 131.6, 133.2, 159.8. Anal. Calcd. for $C_{15}H_{12}O$: C, 86.50; H, 5.80. Found; C; 86.55; H, 5.85.

X-ray data:

Crystals of the isomers of both compounds **9b** and **9d** were grown from hexane. Data were collected on an Enraf-Nonius Mach3 diffractometer.

Crystal data: **9b**: Empirical formula: $C_{21}H_{17}Cl$. Formula wt. 304.80. Monoclinic; $P2_1/c$. a = 8.9609 (12), b = 9.14 (4), c = 20.174 (5)Å. β = 90.771 (17)°. V = 1653 (7)Å^3. Z = 4. Density (calc.) 1.225Mgm^{-3}. MoKα (λ = 0.71073 Å) μ = 0.225mm^{-1}. θ range: 2.0-25°. Data/ restraints/ parameters 2899/0/200. Goof 1.043. R1 ($I > 2\sigma(I)$) = 0.0383; wR2 = 0.1012.[12] Largest diff. peak and hole 0.270 and -0.281 eÅ^{-3}.

9d: Empirical formula: $C_{15}H_{13}Cl$. Formula wt. 228.72. Monoclinic; $P2_1/c$. a = 5.8100 (5), b = 17.2620 (10), c = 20.174 (5)Å. β = 119.439 (5)°. V = 601.87 (8)Å^3. Z = 2. Density (calc.) = 1.262 Mgm^{-3}. MoK$_\alpha$ (λ = 0.71073 Å). μ = 0.285 mm^{-1}. θ range: 2.30-27.5°. Data/ restraints/ parameters 1378/2/92. Goof: 1.101. R1 ($I > 2\sigma(I)$) = 0.0532; wR2 = 0.1458.[12] Largest diff. peak and hole 0.291 and -0.305 eÅ^{-3}. Methyl hydrogens were not included in the refinement since the chloro-methyl exchange is observed (also see Fig. 1).[7]

A complete set of X-ray data on compounds **9b** and **9d** (11 pages) is available from the authors.

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References

1. Kumaraswamy, S.; Kumara Swamy, K. C. *Tetrahedron Lett.* **1997**, *38*, 2183.
2. a) Crenshaw, M. D.; Zimmer, H. *J. Org. Chem.* **1983**, *48*, 2782. b) Tsai, H. J. *Tetrahedron Lett.* **1996**, *37*, 629.
3. a) Petrova, J.; Coutrot, P.; Drefux, M.; Savignac, P. *Synthesis* **1975**, 658. b) Gajda, T. *Synthesis* **1990**, 717. (A good method using PPh_3/CCl_4, but removal of by-products is not very convenient in case of non-volatile phosphonates.) c) Morise, X.; Savignac, P.; Denis, M. *J. Chem. Soc., Perkin Trans.1* **1996**, 2179.
4. Kumaraswamy, S.; Selvi, R. S.; Kumara Swamy, K. C. *Synthesis* **1997**, 207.
5. Even in the synthesis of fluoro-olefins (ref. 2b) and 1-chlorovinyl sulfoxides by the Horner-Wadsworth reaction, a more expensive base, LDA is used. Otten, P. A.; Davies, H. M.; van der Gen, A. *Tetrahedron Lett.* **1995**, *36*, 781.
6. Larsen, R. O.; Aksnes, G. *Phosphorus Sulfur* **1983**, *16*, 339.
7. Desiraju, G. R.; Sarma, J. A. R. P. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1986**, *96*, 599.
8. A similar result was obtained by Zimmer, *et al.* Zimmer, H.; Hickey, K. R.; Schumaker, R. J. *Chimia* **1974**, *28*, 656.
9. Although the use of K_2CO_3 as a base in the Horner-Wadsworth reaction is reported, it has not been used for the synthesis of chlorostilbenes. See Texier-Boulett, F.; Foucaud, A. *Synthesis* **1979**, 884.
10. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, Pergamon, Oxford, **1986**.
11. Sioda, R. E.; Cowan, D. O.; Koski, W. S. *J. Am. Chem. Soc.* **1967**, *89*, 230.
12. SHELX-97, *A package for structure solution and refinement*, Sheldrick, G. M., University of Göttingen, Göttingen, Germany.