

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

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Abstract: The α -chlorophosphonates $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{O})\text{CHCl}-\text{C}_6\text{H}_4-4-\text{R}$ [$\text{R}=\text{H}$ (4), Me (5), OMe (6)], which are now readily accessible, react with ketones $\text{R}'\text{C}(\text{O})\text{R}''$ in the presence of NaH (without recourse to the more expensive *t*-BuLi) to afford trisubstituted vinyl halides $\text{R}'\text{C}(\text{R}'')=\text{CCl}(\text{C}_6\text{H}_4-4-\text{R})$ in good yields. The corresponding α -bromophosphonates [$\text{R}=\text{H}$ (7), Me (8)] failed to react with ketones and gave the symmetrical acetylenes $4-\text{R}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-4-\text{R}$ 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 $\text{ArCH}=\text{CBr}(\text{C}_6\text{H}_4-4-\text{R})$ 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 $(\text{Cl})\text{PhC}=\text{CPh}(\text{Me})$, the isomer with the upfield NMR shift for the CH_3 protons and for $(\text{Cl})\text{PhC}=\text{C}(\text{Ph})(\text{C}_6\text{H}_4-4-\text{Me})$, the isomer with the downfield NMR shift for the $-\text{C}_6\text{H}_4-4-\text{CH}_3$ protons have *Z* stereochemistry. © 1998 Elsevier Science Ltd. All rights reserved.

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.

The α -chloro/ bromophosphonates **4-8** used in the present study were synthesized⁴ as shown in Scheme 1. Details of the reactions of the chlorophosphonates **4-6** with ketones are shown in Scheme 2 and Table 1.

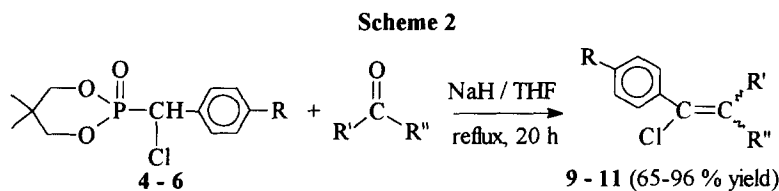
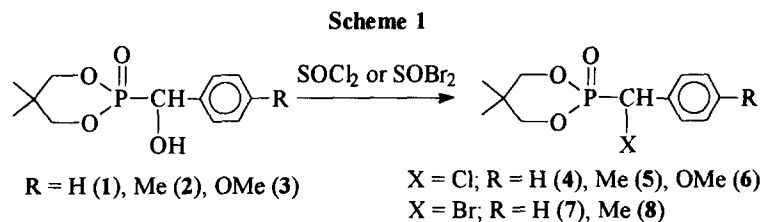


Table 1. Details on the reactions of phosphonates with ketones

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 ₆ H ₄	86	40:60	b Ph	4-Me-C ₆ H ₄	85	50:50
c Ph	4-OMe-C ₆ H ₄	81	33:67	c Ph	4-OMe-C ₆ H ₄	82	50:50
d Ph	Me	65	75:25	d 4-OMe-C ₆ H ₄	Me	66	40:60
e 4-OMe-C ₆ H ₄	Me	65	67:33	e Ph-C(O)	Ph	65	50:50
f 4-Me-C ₆ H ₄	Me	69	67:33	11 (R = OMe)			
g 3-NO ₂ -C ₆ H ₄	3-NO ₂ -C ₆ H ₄	95	-----	a Ph	Ph	80	-----
h	-(CH ₂) ₅ -	65	-----	b Ph	4-Me-C ₆ H ₄	83	50:50
i	-(CH ₂) ₆ -	70	-----	c 3-NO ₂ -C ₆ H ₄	3-NO ₂ -C ₆ H ₄	96	-----

^a Yields of E/Z mixtures (based on available X-ray structures as well as ¹H and ¹³C 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 $\text{Ph}(\text{Cl})\text{C}=\text{C}(\text{C}_6\text{H}_4\text{-3-NO}_2)_2$ 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 $(\text{Cl})\text{PhC}=\text{CPh}(\text{Me})$ (**9d**) as a crystalline solid which shows the *upfield* ¹H 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 $(\text{MeO})_2\text{P}(\text{O})\text{CHCl}(\text{Ph})$.^{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

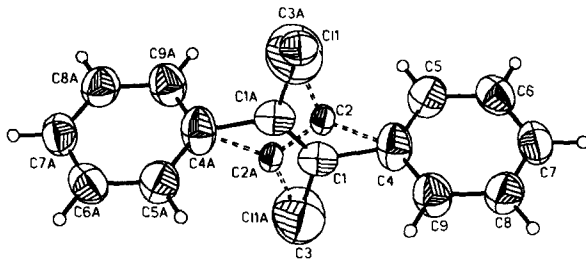


Fig. 1. Molecular structure of the *Z* isomer of **9d**. Selected bond distances: C(1)- C(1A) 1.289(6); C(1)-Cl(1A) 1.686(4); C(1)-C(3) 1.5305 (10); C(2)-Cl(1) 1.7097 (10) Å

Since unambiguous assignment of stereochemistry for the isomers in the above system is difficult, we characterized the isomer of **9b** which has the *downfield* ¹H NMR spectroscopy shift for the $-\text{C}_6\text{H}_4\text{-4-CH}_3$ protons by X-ray crystallography. This isomer has the two phenyl groups positioned *cis* to each other [Fig. 2].

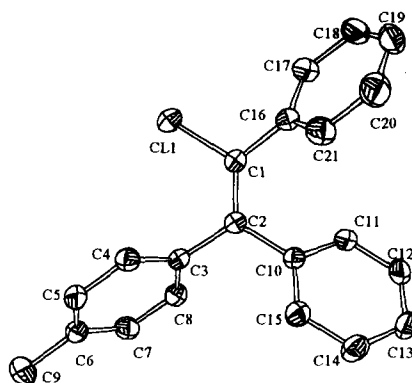
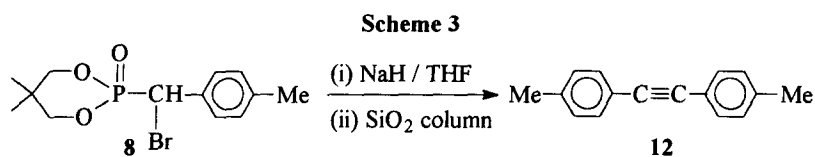


Fig. 2. Molecular structure of the *Z* isomer of **9b** (phenyl groups on the same side). Selected bond distances: C(1)-C(2) 1.340(3); C(1)-Cl(1) 1.752(8); C(1)-C(16) 1.482(3); C(2)-C(3) 1.490(4); C(2)-C(10) 1.489(7) Å.

The *E/Z* ratios for **9e**, **9f** and **10d** are ascertained by comparing their NMR spectra with **9d**; the ^{13}C NMR signal of $=\text{C}-\text{CH}_3$ 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 ^1H NMR spectra with that of **9b**; for **9c** assignment 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 (^1H 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).



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 $\delta(^1\text{H})$ value for $\text{C}_6\text{H}_4-\text{OCH}_3$ or $\text{C}_6\text{H}_4-\text{CH}_3$ protons and the well separated $\delta(^{13}\text{C})$ 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.

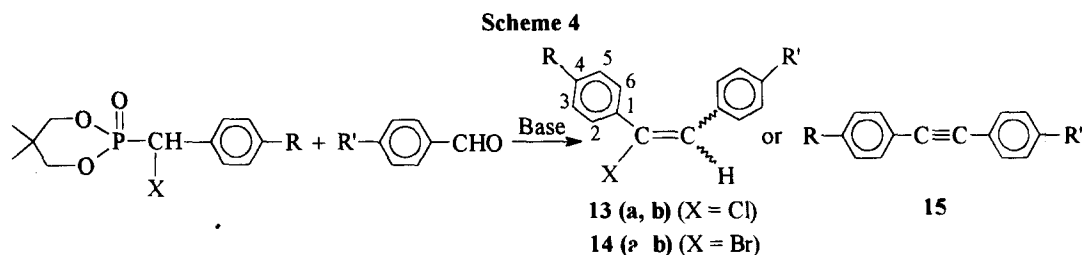


Table 2. Details on the reactions of phosphonates with aldehydes using different bases

Sl. No.	Phosphonate	Aldehyde (R'≡)	Base	Solvent/ Temp/ Time	Product	Yield, % (<i>E/Z</i> 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 ₂ CO ₃ ^c	MeCN/reflux/3 d	13a	83 (55:45)
7	5	H	K ₂ CO ₃ ^c	MeCN/reflux/3 d	13b	88 (60:40)
8	7	4-OMe	K ₂ CO ₃ ^c	MeCN/reflux/5 d	14a	50 (50:50) ^d
9	8	H	K ₂ CO ₃ ^c	MeCN/reflux/5 d	14b	52 (30:70)
10	4	4-OMe	K ₂ CO ₃ ^c	Neat/150°C/1 h	13a	68 (55:45)
11	4	4-OMe	KF or HN(<i>i</i> -Pr) ₂	MeCN/reflux or neat/ 24 h	No reaction	

^a Based on ^1H and ^{13}C NMR spectroscopy.

^b 1.5 mole eq.

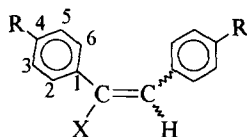
^c 3 mole eq.

^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 K₂CO₃ 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. ¹H and ¹³C NMR spectra were recorded on a Bruker 200 MHz spectrometer in CDCl₃ with chemical shifts (ppm) measured against (CH₃)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=CPh₂ (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 (Na₂SO₄) 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. ¹H NMR: 6.80-7.45 (m). ¹³C 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): ¹H NMR: 2.24, 2.38 (2s, *E* and *Z* isomers respectively; ratio 2:3, 3H, ArCH₃), 6.89-7.39 (m, 14H, ArH). ¹³C 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. ¹H NMR: 2.38 (s, 3H, CH₃), 6.89-7.39 (m, 14H, ArH). ¹³C 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 C₂₁H₁₇Cl: 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. ¹H NMR: 3.75, 3.87 (2s, ratio 1:2, 3H, OCH₃), 6.69-7.77 (m, 14H, ArH). ¹³C 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 C₂₁H₁₇ClO: 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. ¹H NMR: 2.09, 2.40 (2s, ratio 1:8, 3H, CH₃), 7.00-7.60 (m, 10H, ArH). ¹³C 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 C₁₅H₁₃Cl: 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). ¹H NMR: 2.09 (s, 3H, CH₃), 7.20-7.60 (m, 10H, ArH).

9e (mixture, liquid): IR: 1034, 1074, 1111, 1248, 1510, 1607 cm⁻¹. ¹H NMR: 2.07, 2.38 (2s, ratio 1:2, 3H, CH₃), 3.75, 3.87 (2s, ratio 2:1, 3H, OCH₃), 6.70-7.00 (AB qrt, 4H, ArH), 7.10-7.60 (m, 5H, ArH). ¹³C 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 C₁₆H₁₅ClO: C, 74.26; H, 5.85. Found; C, 74.30; H, 5.92.

9f (mixture, liquid): IR: 893, 1020, 1072, 1512, 1599 cm⁻¹. ¹H NMR: 2.10, 2.30 (2s, ratio 1:2, 3H, CH₃), 2.40, 2.44 (2s, ratio 2:1, ArCH₃), 6.90-7.60 (m, 9H, ArH). ¹³C 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 C₁₆H₁₅Cl: 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. ¹H NMR: 7.30-8.40 (m). ¹³C 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. ¹H NMR: 1.57-1.67 (m, 6H, CH₂), 2.17-2.20 (m, 2H, =CCH₂), 2.50-2.60 (m, 2H, =CCH₂), 7.40 (s, 5H, ArH). ¹³C 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 C₁₃H₁₅Cl: C, 75.52; H, 7.32. Found; C, 75.60; H, 7.33.

9i (liquid): IR: 935, 1026, 1070, 1450, 1601 cm⁻¹. ¹H NMR: 1.50-1.70 (m, 8H, CH₂), 2.20-2.30 (m, 2H, =CCH₂), 2.50-2.60 (m, 2H, =CCH₂), 7.40 (s, 5H, ArH). ¹³C 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 C₁₄H₁₇Cl: 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. ¹H NMR: 2.30 (s, 3H, ArCH₃), 6.90-7.40 (m, 14H, ArH). ¹³C 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 C₂₁H₁₇Cl: 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. ¹H NMR: 2.10, 2.15, 2.16, 2.29 (4s of equal intensity, 6H, ArCH₃), 7.30-7.90 (m, 13H, ArH). ¹³C NMR: 21.2, 126.8-142.4 (many lines). Anal. Calcd for C₂₂H₁₉Cl: 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. ¹H NMR: 2.38, 2.39 (2s, ratio 1:1, 3H, ArCH₃), 3.48, 3.60 (2s, 3H, OCH₃), 6.50-7.30 (m, 13H, ArH). ¹³C 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 C₂₂H₁₉ClO: 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} . ^1H NMR: 2.05, 2.27 (2s, ratio 3:2, 3H, CH_3), 2.35–2.40 (2s, ratio 2:3, 3H, ArCH_3), 3.75–3.85 (2s, ratio 2:3, 3H, OCH_3), 6.70–7.40 (m, 8H, ArH). ^{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 $\text{C}_{17}\text{H}_{17}\text{ClO}$: C, 74.84; H, 6.29. Found; C, 74.64; H, 6.40.

10e (liquid): IR: 812, 1022, 1059, 1597, 1668 cm^{-1} . ^1H NMR: 2.23, 2.34 (2s, ratio 1:1, 3H, CH_3), 6.98–8.15 (m, 14H, ArH). ^{13}C NMR: 21.3, 128.0–134.0 (many lines). MS: 332, 334 $[\text{M}]^+$ ($^{35,37}\text{Cl}$), 192. Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{ClO}$: 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} . ^1H NMR: 3.75 (s, 3H, OCH_3), 6.70–7.40 (m, 14H, ArH). ^{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 $\text{C}_{21}\text{H}_{17}\text{ClO}$: 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} . ^1H NMR: 2.25, 2.29 (2s, ratio 1:1, 3H, ArCH_3), 3.77, 3.79 (2s, ratio 1:1, 3H, OCH_3), 6.70–7.38 (m, 13H, ArH). ^{13}C NMR: 21.1, 55.2, 113.3, 126.8–142.4 (many lines), 159.2. Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{ClO}$: 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} . ^1H NMR: 3.79 (s, 3H, OCH_3), 6.74–8.24 (m, 12H, ArH). ^{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 $[\text{M}]^+$ ($^{35,37}\text{Cl}$), 375, 239, 128. Anal. Calcd. for $\text{C}_{21}\text{H}_{13}\text{ClN}_2\text{O}_3$: 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-C₆H₄-C≡C-C₆H₄-4-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 (^1H NMR: 2.26, 2.38, 2.39 (3s, 6H, ArCH_3), 6.90–7.70 (m, 8H, ArH). 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). ^1H NMR: 2.40 (s, 3H, ArCH_3), 7.20 (AB d, 2H, ArH), 7.45 (AB d, 2H, ArH).

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 (Na₂SO₄), solvent removed, and the residue chromatographed over silica gel (3% CH₂Cl₂ in hexane) to afford **13a** (liquid, 0.40 g, 90%). IR: 908, 1033, 1113, 1252, 1510, 1606 cm⁻¹. ¹H NMR: 3.76, 3.86 (2s, ratio 2:3, 3H, OCH₃), 6.70–7.90 (10H, ArH, C=CH). ¹³C 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 C₁₅H₁₃ClO: 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. ¹H NMR: 2.30, 2.36 (2s, ratio 3:2, 3H, CH₃), 6.85–7.85 (m, 10H, ArH, C=CH). ¹³C 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 C₁₅H₁₃Cl: C, 78.70; H, 5.70. Found; C, 78.68; H, 5.71.

13c (liquid): IR: 947, 1032, 1074, 1510, 1597 cm⁻¹. ¹H NMR: 2.30, 2.45 (2s, ratio 2:3, 3H, CH₃), 6.80–7.85 (m, 10H, ArH + C=CH). ¹³C 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 C₁₅H₁₃Cl: 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. ¹H NMR: 2.37, 2.39 (2s, ratio 1:1, 3H, CH₃), 6.80–7.80 (m, 9H, ArH + C=CH). ¹³C 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 C₁₅H₁₂Cl₂: C, 68.46; H, 4.59. Found; C, 68.73; H, 4.80.

13e (liquid): IR: 1030, 1086, 1138, 1250, 1510, 1605 cm⁻¹. ¹H NMR: 3.80, 3.82 (2s, ratio 7:3, 3H, OCH₃), 6.80–7.80 (m, 9H, ArH + C=CH). ¹³C NMR: 55.3, 114.0, 128.6, 128.7, 131.8, 132.6, 133.0. Anal. Calcd. for C₁₅H₁₂Cl₂O: C, 64.50; H, 4.30. Found; C, 64.23; H, 4.37.

13f: Already reported by us¹ (IR: 1116, 1172, 1284, 1508, 1610 cm⁻¹).

13g (liquid): IR: 927, 1030, 1111, 1257, 1510, 1601 cm⁻¹. ¹H NMR: 3.80, 3.85 (2s, 1:1, 3H, CH₃), 6.85–7.85 (m, 10H, ArH + C=CH). ¹³C 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 C₁₅H₁₃ClO: C, 73.60; H, 5.36. Found; C, 73.51; H, 5.30.

14a (liquid): IR: 966, 1030, 1109, 1249, 1510, 1605 cm⁻¹. ¹H NMR: 3.75, 3.85 (2s, ratio 2:3, 3H, OCH₃), 6.65–7.80 (m, 10H, ArH + C=CH). ¹³C 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 C₁₅H₁₃BrO: C, 62.30; H, 4.50. Found; C, 62.60; H, 4.40.

14b (liquid): IR: 814, 903, 1014, 1095, 1510, 1606 cm⁻¹. ¹H NMR: 2.35, 2.40 (2s, ratio 3:7, 3H, Ar-CH₃), 7.00–7.80 (m, 10H, ArH + C=CH). ¹³C 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 C₁₅H₁₃Br: C, 65.90; H, 4.79. Found; C, 66.31; H, 4.95.

14c (liquid): IR: 903, 1009, 1086, 1487, 1608 cm⁻¹. ¹H NMR: 2.35, 2.40, (2s with ratio 2:3, 3H, Ar-CH₃), 6.90-7.70 (m, 9H, ArH + C=CH). ¹³C 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-Br]⁺, 192 [M-Br-Cl]. Anal. Calcd. for C₁₅H₁₂BrCl: 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. ¹H NMR: 2.40, 2.42 (2s, ratio 1:1, 3H, Ar-CH₃), 3.77, 3.87 (2s, 3H, OCH₃), 6.69-7.80 (m, 9H, ArH + CH=CBr). ¹³C NMR: 21.2, 21.4 (2C-CH₃), 55.2, 55.3 (2s, OCH₃), 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 (ArC + CH=CBr).

MS: 302, 304 [M]⁺ (^{79,81}Br), 223, 179, 178, 165, 115. Anal. Calcd. for C₁₆H₁₅BrO: 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)). ¹H NMR: 3.80 (s, 3H, CH₃), 6.80-7.60 (m, ArH). ¹³C 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 C₁₅H₁₂O: 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: C₂₁H₁₇Cl. Formula wt. 304.80. Monoclinic; P2₁/c. *a* = 8.9609 (12), *b* = 9.14 (4), *c* = 20.174 (5) Å. β = 90.771 (17)°. *V* = 1653 (7) Å³. *Z* = 4. Density (calc.) 1.225 Mgm⁻³. MoKα (λ = 0.71073 Å) μ = 0.225 mm⁻¹. θ range: 2.0-25°. Data/ restraints/ parameters 2899/0/200. Goof 1.043. R1 (I > 2σ (I)) = 0.0383; wR2 = 0.1012.¹² Largest diff. peak and hole 0.270 and -0.281 eÅ⁻³.

9d: Empirical formula: C₁₅H₁₃Cl. Formula wt. 228.72. Monoclinic; P2₁/c. *a* = 5.8100 (5), *b* = 17.2620 (10), *c* = 20.174 (5) Å. β = 119.439 (5)°. *V* = 601.87 (8) Å³. *Z* = 2. Density (calc.) = 1.262 Mgm⁻³. MoKα (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 > 2σ (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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