Table I. 2-Pyridyl and Pyrazinylhydrazones[a]

| Hydrazone | Hydrazine | Ketone | Mp, °C | Yield | Cryst. solvent |
|---|---|---|---|---|---|
| I | Pyridyl | Acetylpyrazine | 140 | 52.4 | $CH_3OH$ |
| II | Pyridyl | Benzoylpyrazine | 188 | 29.0 | $CH_3OH$ |
| III | Pyridyl | 3-Acetylpyridazine | 137 | 40.0 | $CH_3OH+(C_2H_5)_2O$ |
| IV | Pyridyl | Di(2-pyridyl)ketone | 140 | 81.2 | $CH_3OH+(C_2H_5)_2O$ |
| V | Pyridyl (2 moles) | Phenylglyoxal | 225 | 66.7 | 2-Methoxyethanol |
| VI | Phenyl | Benzoylpyrazine | 165 | 33.3 | $CH_3OH$ |
| VII | Pyrazinyl | Pyridine-2-carboxaldehyde | 208 | 46.2 | $C_2H_5OH$ |
| VIII | Pyrazinyl | 2-Acetylpyridine | 153 | 37.7 | $CH_3OH$ |
| IX | Pyrazinyl | 2-Benzoylpyridine | 176 | 29.0 | $CH_3OH$ |
| X | Pyrazinyl | Di(2-pyridyl)ketone | 152 | 36.2 | $CH_3OH$ |
| XI | Pyrazinyl | Acetylpyrazine | 209 | 27.4 | $C_2H_5OH$ |
| XII | Pyrazinyl | Benzoylpyrazine | 157 | 17.4 | $C_2H_5OH$ |
| XIII | Pyrazinyl (1 mole) | Phenylglyoxal | 153 | 39.0 | $C_2H_5OH$ |
| XIV | Pyrazinyl (1 mole) | Benzil | 141 | 21.4 | $CH_3OH$ |
| XV | Pyrazinyl (1 mole) | Pyridil | 196 | 64.5 | $C_2H_5OH$ |
| XVI | Pyrazinyl | 3-Acetylpyridazine | 193 | 26.7 | $CH_3OH$ |
| XVII[b] | Pyrazinyl | *N*-2-pyridylthiobenzamide | 180 | 50.0 | $C_2H_5OH$ |
| XVIII[b] | Pyrazinyl | *N*-2-pyridylthiopicolinamide | 150 | 30.0 | $CH_3OH$ |
| XIX | Pyrazinyl | Isatin | 313 | 77.6 | 2-Methoxyethanol |
| XX[c] | Pyrazinyl (1 mole) | XV | 250 | 30.0 | Aq pyridine |
| XXI | Pyrazinyl (2 moles) | Phenylgloxal | 263 | 52.6 | 2-Methoxyethanol |

[a] Elemental analyses in agreement with theoretical values were obtained and submitted for review. [b] Five hours of refluxing. [c] Five hours of heating at 150–160 without solvent.

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# Generation and Reactions of Some Dimethyl Benzylphosphonate Carbanions: Synthesis of trans-Diaryl-Substituted Ethylenes


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**A series of *p*-substituted benzylphosphonate carbanions is generated and reacted with a variety of substituted aromatic aldehydes to afford trans-diaryl-substituted ethylenes. In no case could the cis-isomer be isolated. The influence of substituents and solvent and base variations on the stereochemical nature of the resulting ethylenes is examined. Structural assignments of the products are based on IR and NMR spectral evidence.**


The role of phosphonium ylide chemistry in the synthesis of a variety of olefinic products is widely accepted (*16, 17, 25, 26*). However, there are number of cases in which the olefin synthesis via phosphonium ylide fails because of insufficient reactivity of the latter. Recent research on the newer variation of phosphonium ylide olefination, which involves the reaction of phosphonate carbanions with carbonyl compounds (*3*), has made a significant contribution in the synthesis of sensitive olefins not preparable by ylide olefination reactions (*14, 29, 34*).

Many of the initial reports of olefin synthesis from phosphonate carbanions have shown that stereochemistry of the reaction is stereospecific and favors the formation of only the trans-isomer (*13, 14, 34*). Recently, it has been reported that in some cases this reaction is not stereospecific and a mixture of cis- and trans-isomers can be produced (*3*), the ratio of which appears to be dependent on the nature of grouping substituted on the $\alpha$-carbon of the phosphonate carbanion (*30*), carbonyl compounds (*3, 5, 6, 8*), and solvent used (*10, 24*).

With the intent of examining the stereochemical pathway of the phosphonate carbanion olefination reaction, we have studied the reactions of some phosphonate carbanions (compounds 2a–e) generated from *p*-methylbenzylphosphonate (compound 1a), *p*-chlorobenzylphosphonate (compound 1b), *p*-bromobenzylphosphonate (compound 1c), *p*-iodobenzylphosphonate (compound 1d), and *p*-nitrobenzylphosphonate

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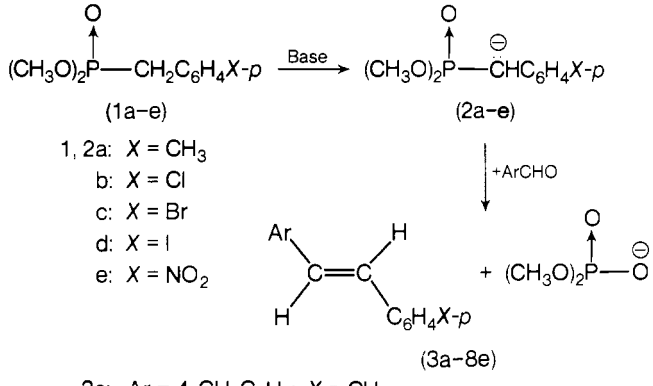
(compound 1e), with a range of substituted aromatic aldehydes, to see the influence of substituents on the stereochemical nature of the resulting diaryl-substituted ethylenes. Attempts have also been made to examine the effect of solvent and base variations.

**Results and Discussion**

Heating a mixture of trimethylphosphite and *p*-substituted benzyl bromides at 150°C gave *p*-substituted benzylphosphonates (compounds 1a–e) in good yields. Treatment of phosphonates (compounds 1a–e) with suitable bases in appropriate solvents effected the proton abstraction generating pale yellow to intense red colors due to formation of phosphonate carbanions (compounds 2a–e). A convenient procedure for reacting the phosphonate carbanions (compounds 2a–e) consists of adding phosphonates (compounds 1a–e) to a slurry of sodium hydride in dimethylformamide at room temperature. An exothermic reaction accompanied by the evolution of hydrogen gas took place. As the carbonyl compound was added, a precipitate of sodium dimethyl phosphate was formed. The resulting diaryl-substituted ethylenes (compounds 3a–7h) (Scheme 1) were isolated by dilution of the reaction mixture with water and extraction with chloroform. Variations made in the experimental conditions involved the use of different bases and solvents ranging from sodium methoxide, sodamide to sodium hydride and from benzene, dimethylformamide (DMF) to tetrahydrofuran (THF).

Scheme 1




3a: Ar = 4-$CH_3C_6H_4$; X = $CH_3$
b: Ar = 4-$OHC_6H_4$; X = $CH_3$
c: Ar = 3-$OHC_6H_4$; X = $CH_3$
d: Ar = 2-$OHC_6H_4$; X = $CH_3$
e: Ar = 4-$ClC_6H_4$; X = $CH_3$
f: Ar = 3,4-$(OCH_2O)C_6H_3$; X = $CH_3$
g: Ar = 4-$NO_2C_6H_4$; X = $CH_3$
h: Ar = 2-OH-1-naphthyl; X = $CH_3$

4a: Ar = $C_6H_5$; X = Cl
b: Ar = 4-$CH_3C_6H_4$; X = Cl
c: Ar = 4-$ClC_6H_4$; X = Cl
d: Ar = 4-$NO_2C_6H_4$; X = Cl
e: Ar = 3,4-$(OCH_2O)C_6H_3$; X = Cl
f: Ar = 3,4-$(CH_3O)_2C_6H_3$; X = Cl
g: Ar = 2-furyl; X = Cl

5a: Ar = $C_6H_5$; X = Br
b: Ar = 4-$CH_3OC_6H_4$; X = Br
c: Ar = 4-$CH_3C_6H_4$; X = Br
d: Ar = 4-$ClC_6H_4$; X = Br
e: Ar = 4-$NO_2C_6H_4$; X = Br

6a: Ar = $C_6H_5$; X = I
b: Ar = 4-$CH_3OC_6H_4$; X = I
c: Ar = 3-$CH_3OC_6H_4$; X = I
d: Ar = 2-$CH_3OC_6H_4$; X = I
e: Ar = 4-$CH_3C_6H_4$; X = I
f: Ar = 3,4-$(CH_3O)_2C_6H_3$; X = I
g: Ar = 3,4-$(OCH_2O)C_6H_3$; X = I
h: Ar = 4-$ClC_6H_4$; X = I
i: Ar = 2,4-$(Cl)_2C_6H_3$; X = I
j: Ar = 3-$NO_2C_6H_4$; X = I

7a: Ar = 4-$CH_3C_6H_4$; X = $NO_2$
b: Ar = 4-$ClC_6H_4$; X = $NO_2$
c: Ar = 4-$NO_2C_6H_4$; X = $NO_2$
d: Ar = 3,4-$(OCH_2O)C_6H_3$; X = $NO_2$
e: Ar = 3,4-$(CH_3O)_2C_6H_3$; X = $NO_2$
f: Ar = 3,4-$(CH_3O)_2$-6-$BrC_6H_2$; X = $NO_2$
g: Ar = 2-furyl; X = $NO_2$
h: Ar = 2-pyridyl; X = $NO_2$

8a: Ar = 4-$CH_3C_6H_4CH{=}CHC_6H_4$—; X = $CH_3$
b: Ar = 4-$ClC_6H_4CH{=}CHC_6H_4$—; X = Cl
c: Ar = 4-$BrC_6H_4CH{=}CHC_6H_4$—; X = Br
d: Ar = 4-$IC_6H_4CH{=}CHC_6H_4$—; X = I
e: Ar = 4-$NO_2C_6H_4CH{=}CHC_6H_4$—; X = $NO_2$

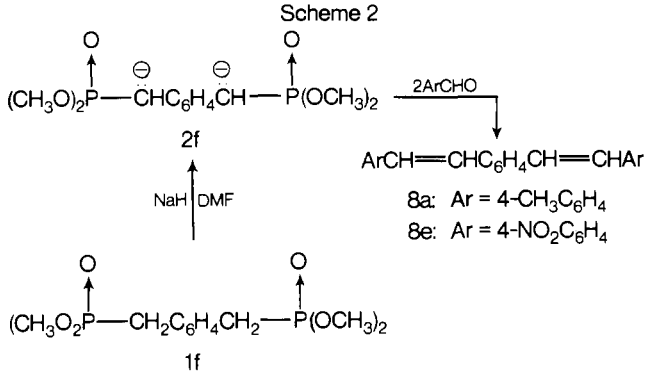
Thus, when a solution of phosphonate (compound 1a) in DMF was reacted with a range of mono- and disubstituted aromatic aldehydes in the presence of sodium hydride, trans-4-methylstilbenes (compounds 3a–h) were produced in good yields. Similarly, the reaction of substituted aromatic aldehydes with *p*-halosubstituted phosphonate carbanions (compounds 2b–d), generated from the interaction of phosphonates (compounds 1b–d) with sodium methoxide in methanol or sodium hydride in THF or sodamide in benzene/THF and carried out at room temperature, gave good yields of trans-*p*-halosubstituted stilbenes (compounds 4a–6j). Likewise, intense red-colored phosphonate carbanion (compound 2e), prepared in situ, reacted smoothly with various mono-, di-, and trisubstituted benzaldehydes at room temperature to afford trans-*p*-nitrostilbenes (compounds 7a–h) in high yields. Interestingly, the synthesis of trans, trans-distyryl benzenes (compounds 8a–e) was also achieved successfully at room temperature, by the above reaction which involved the interaction of carbanions (compounds 2a–e) with terephthaldehyde (Scheme 1).

All of the phosphonate carbanions (compounds 2a–e) in their reaction with substituted aromatic aldehydes favors only trans-olefination. In no case could the cis-isomer be isolated as indicated by thin-layer chromatography (TLC). TLC of the crude product in all cases indicated the formation of only one product, which after careful isolation by preparative TLC or by column chromatography, was shown to be the trans-isomer by IR and NMR spectra and literature data, when available. Different benzyl para-substituents at phosphonate carbanions showed no influence on the stereochemical behavior of the phosphonate carbanion modification of the Wittig reaction. Similarly, the variation of substituents from electron donating to strongly electron withdrawing groups at benzaldehydes failed to bring about any change in cis/trans proportion of the products.

Many attempts similar to those used successfully with the Wittig reaction (*21*) were made to alter the cis/trans ratio of ethylenic products by using sterically and electronically different starting materials but produced no changes in the stereospecific nature of the phosphonate carbanion modification of

the Wittig reaction. 4-Methyl-4′-nitrostilbene, 4-methyl-4′-chlorostilbene, and 4-chloro-4′-nitrostilbene, prepared by two alternative routes by interchanging *p*-substituents at phosphonate carbanions and benzaldehydes, gave only the trans-isomer which is in accord with the observations of Wadsworth et al. (*35*) and in contrast with the behavior of the Wittig reaction with phosphonium ylides (*21*). Similarly, 1,4-bis(4-methylstyryl)benzene (compound 8a) and 1,4-bis(4-nitrostyryl)benzene (compound 8e), prepared by an alternative route (Scheme 2) which involves the reaction of *p*-xylylene-bisphosphonate carbanion (compound 2f) with *p*-methylbenzaldehyde and *p*-nitrobenzaldehyde, respectively, showed no influence on the steric nature of the products and only the trans, trans-isomer could be isolated.

Scheme 2




Other factors such as solvents and bases were also incapable of influencing the stereochemical pathway of the phosphonate carbanion olefination reaction. However, best results in respect to reaction time and yield of the products are obtained when electron withdrawing substituents are present at the phosphonate carbanion portion and at carbonyl compounds and when DMF–sodium hydride is used as the solvent-base pair.

Various trans-diaryl-substituted ethylenes (compounds 3a–8e) (most of them are new) are listed in Table I. The versatibility of the phosphonate carbanion olefination reaction in the stereospecific synthesis of trans-ethylenes is obvious from the inspection of Table I.

The spectra (KBr) (Table II) of trans-diaryl-substituted ethylenes (compounds 3a–8e) showed characteristic absorption bands at 1625–1490 $cm^{-1}$ ($\nu$ C=C) and at 981–925 $cm^{-1}$. The latter absorptions are associated with out-of-plane deformations of hydrogen attached to the trans-olefinic system (*2*). The NMR spectra ($CDCl_3$), in general, exhibited ethylenic protons in the range of $\delta$ 6.82–7.30 and an aromatic multiplet ranging from $\delta$ 7.00–8.58 (Table II).

## Experimental

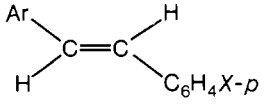
Melting points were determined on a GallenKamp apparatus and are uncorrected. A Perkin-Elmer infracord spectrophotometer was used to determine the IR spectra (KBr). The NMR spectra ($CDCl_3$) were recorded on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Thin-layer chromatography was done using the ascending method. For TLC, glass slides coated with silica-gel "G" (E. Merck) were used. The spots on these slides were detected by iodine. Products were isolated and purified by preparative TLC or column chromatography. Unless otherwise stated, all reactions were run under nitrogen.

*p*-Substituted benzylphosphonates (compounds 1a–e) and *p*-xylylenediphosphonate (compound 1f) were prepared by the Arbuzov reaction with corresponding bromides and trimethylphosphite (*23*).

***Preparation of various trans-diaryl-substituted ethylenes (compounds 3a–8e).*** The following procedures were used which involve the use of different base additives and reaction media.

*Procedure A.* To a stirred suspension of appropriate phosphonate carbanion (compounds 2a–e), prepared from 0.02 mole of phosphonate (compounds 1a–e) and sodium methoxide (0.02 mole) in 100 ml of methanol, were added equimolar amounts of aromatic aldehyde. The mixture was stirred at room temperature for 6 hr, and the resulting reaction mixture was diluted with an equal volume of water. The resulting solid

Table I. Structure and Physical Properties of trans-Diaryl-Substituted Ethylenes (Compounds 3a–8e)




| Compound | Molecular formula | Ar | X | Phosphonate[a] | Procedure used[b] | Base solvent | Mp,[c] °C | Yield, % | Recryst. solvent[d] |
|---|---|---|---|---|---|---|---|---|---|
| 3a | $C_{16}H_{16}$ | 4-$CH_3C_6H_4$ | $CH_3$ | 1a | A | $CH_3ONa$ $CH_3OH$ | 182–84[e] | 65 | EtOH |
| | | | | | C | NaH DMF | 181–82 | 68 | EtOH |
| 3b | $C_{15}H_{14}O$ | 4-$OHC_6H_4$ | $CH_3$ | 1a | C | NaH DMF | 210–12[f] (dec.) | 60 | EtOH–$H_2O$ |
| 3c | $C_{15}H_{14}O$ | 3-$OHC_6H_4$ | $CH_3$ | 1a | C | NaH DMF | 179–80 (dec.) | 50 | EtOH |
| 3d | $C_{15}H_{14}O$ | 2-$OHC_6H_4$ | $CH_3$ | 1a | C | NaH DMF | 300 (dec.) | 52 | $CHCl_3$ MeOH |
| 3e | $C_{15}H_{13}Cl$ | 4-$ClC_6H_4$ | $CH_3$ | 1a | A | $CH_3ONa$ $CH_3OH$ | 206–7[g] | 78 | EtOH |
| | | | | | B | $NaNH_2$ Benzene | 205–6 | 70 | EtOH |
| | | | | | C | NaH DMF | 205–6 | 80 | EtOH |

(Continued on page 128)

**Table I.** Continued

| Compound | Molecular formula | Ar | X | Phosphonate[a] | Procedure used[b] | Base solvent | Mp,[c] °C | Yield, % | Recryst. solvent[d] |
|---|---|---|---|---|---|---|---|---|---|
| 3f | $C_{16}H_{14}O_2$ | 3,4-$(OCH_2O)$—$C_6H_3$ | $CH_3$ | 1a | C | NaH DMF | 249–50 | 65 | EtOH |
| 3g | $C_{15}H_{13}NO_2$ | 4-$NO_2C_6H_4$ | $CH_3$ | 1a | A | $CH_3ONa$ $CH_3OH$ | 146–47[h] | 85 | AcOH |
| | | | | | C | NaH DMF | 147–48 | 90 | AcOH |
| | | | | | D | NaH THF | 147–49 | 90 | AcOH |
| 3h | $C_{16}H_{16}O$ | 2-OH-1-naphthyl | $CH_3$ | 1a | C | NaH DMF | 160–62 | 50 | EtOH |
| 4a | $C_{14}H_{11}Cl$ | $C_6H_5$ | Cl | 1b | A | $CH_3ONa$ $CH_3OH$ | 127–28[i] | 80 | EtOH |
| | | | | | B | $NaNH_2$ $C_6H_6$ | 126–28 | 80 | EtOH |
| | | | | | C | NaH DMF | 127–28 | 82 | EtOH |
| 4b | $C_{15}H_{13}Cl$ | 4-$CH_3C_6H_4$ | Cl | 1b | C | NaH DMF | 205–7[j] | 80 | EtOH–$H_2O$ |
| 4c | $C_{14}H_{10}Cl_2$ | 4-$ClC_6H_4$ | Cl | 1b | A | $CH_3ONa$ $CH_3OH$ | 173–74[k] | 90 | AcOH |
| | | | | | C | NaH DMF | 174–75 | 92 | AcOH |
| 4d | $C_{14}H_{10}NO_2Cl$ | 4-$NO_2C_6H_4$ | Cl | 1b | A | $CH_3ONa$ $CH_3OH$ | 182–83[l] | 92 | AcOH |
| | | | | | C | NaH DMF | 185 | 95 | AcOH |
| | | | | | D | NaH THF | 184–86 | 95 | AcOH |
| 4e | $C_{15}H_{11}O_2Cl$ | 3,4-$(OCH_2O)C_6H_3$ | Cl | 1b | C | NaH DMF | 119–20[m] | 70 | EtOH |
| 4f | $C_{16}H_{15}O_2Cl$ | 3,4-$(CH_3O)_2C_6H_3$ | Cl | 1b | C | NaH DMF | 109–10[n] | 65 | AcOH |
| 4g | $C_{12}H_9OCl$ | 2-Furyl | Cl | 1b | A | $CH_3ONa$ $CH_3OH$ | 97[o] | 60 | EtOH–$H_2O$ |
| | | | | | C | NaH DMF | 96–97 | 63 | EtOH–$H_2O$ |
| 5a | $C_{14}H_{11}Br$ | $C_6H_5$ | Br | 1c | A | $CH_3ONa$ $CH_3OH$ | 133–34[p] | 65 | EtOH |
| | | | | | B | $NaNH_2$ $C_6H_6$ | 132–33 | 62 | EtOH |
| | | | | | C | NaH DMF | 133–35 | 68 | EtOH |
| 5b | $C_{15}H_{13}BrO$ | 4-$OCH_3C_6H_4$ | Br | 1c | C | NaH DMF | 132 | 70 | AcOH |
| 5c | $C_{15}H_{13}Br$ | 4-$CH_3C_6H_4$ | Br | 1c | A | $CH_3ONa$ $CH_3OH$ | 145–47 | 65 | AcOH |
| 5d | $C_{14}H_{10}BrCl$ | 4-$ClC_6H_4$ | Br | 1c | C | NaH DMF | 226–28 | 75 | $CHCl_3$–hexane |
| | | | | | D | NaH THF | 226–28 | 75 | Hexane |
| 5e | $C_{14}H_{10}BrNO_2$ | 4-$NO_2C_6H_4$ | Br | 1c | A | $CH_3ONa$ $CH_3OH$ | 193–94[q] | 85 | AcOH |
| | | | | | C | NaH DMF | 192–94 | 90 | AcOH |
| 6a | $C_{14}H_{11}I$ | $C_6H_5$ | I | 1d | D | NaH THF | 148–50[r] | 70 | $C_6H_6$–hexane |
| 6b | $C_{15}H_{13}IO$ | 4-$OCH_3C_6H_4$ | I | 1d | D | NaH THF | 215–17 | 79 | $CHCl_3$–hexane |
| 6c | $C_{15}H_{13}IO$ | 3-$OCH_3C_6H_4$ | I | 1d | D | NaH THF | 88–89 | 70 | EtOH (90%) |
| 6d | $C_{15}H_{13}IO$ | 2-$OCH_3C_6H_4$ | I | 1d | D | NaH THF | 205–6 | 70 | EtOH (90%) |
| 6e | $C_{15}H_{13}I$ | 4-$CH_3C_6H_4$ | I | 1d | A | $CH_3ONa$ $CH_3OH$ | 211–13 | 72 | Hexane |
| | | | | | C | NaH DMF | 211–13 | 75 | Hexane |

| Compound | Molecular formula | Ar | X | Phosphonate[a] | Procedure used[b] | Base solvent | Mp,[c] °C | Yield, % | Recryst. solvent[d] |
|---|---|---|---|---|---|---|---|---|---|
| 6f | $C_{16}H_{15}IO_2$ | 3,4-$(OCH_3)_2$ $C_6H_3$ | I | 1d | B | $NaNH_2$ $C_6H_6$ | 135–36 | 67 | AcOH |
| | | | | | C | NaH DMF | 135–37 | 67 | AcOH |
| 6g | $C_{15}H_{11}IO_2$ | 3,4-$(OCH_2O)$ $C_6H_3$ | I | 1d | D | NaH THF | 153–55 | 72 | $CHCl_3$–$CH_3OH$ |
| 6h | $C_{14}H_{10}ClI$ | 4-$ClC_6H_4$ | I | 1d | A | $CH_3ONa$ $CH_3OH$ | 199–200 | 80 | $C_6H_6$–hexane |
| 6i | $C_{14}H_9Cl_2I$ | 2,4-$(Cl)_2$ $C_6H_3$ | I | 1d | D | NaH THF | 120–21 | 68 | $CHCl_3$–$C_6H_6$ |
| 6j | $C_{14}H_{10}INO_2$ | 3-$NO_2C_6H_4$ | I | 1d | A | $CH_3ONa$ $CH_3OH$ | 125–26 | 85 | $C_6H_6$–hexane |
| | | | | | C | NaH DMF | 124–26 | 90 | $C_6H_6$–hexane |
| 7a | $C_{15}H_{13}NO_2$ | 4-$CH_3C_6H_4$ | $NO_2$ | 1e | A | $CH_3ONa$ $CH_3OH$ | 148–49[s] | 78 | AcOH |
| | | | | | B | $NaNH_2$ $C_6H_6$ | 148 | 75 | AcOH |
| | | | | | C | NaH DMF | 150 | 80 | AcOH |
| | | | | | D | NaH THF | 148–50 | 80 | AcOH |
| 7b | $C_{14}H_{10}NO_2Cl$ | 4-$ClC_6H_4$ | $NO_2$ | 1e | A | $CH_3ONa$ $CH_3OH$ | 189–90[t] | 85 | AcOH |
| | | | | | C | NaH DMF | 188–90 | 85 | AcOH |
| 7c | $C_{14}H_{10}N_2O_4$ | 4-$NO_2C_6H_4$ | $NO_2$ | 1e | A | $CH_3ONa$ $CH_3OH$ | 288–90[u] | 96 | AcOH |
| | | | | | D | NaH THF | 289–90 | 95 | AcOH |
| 7d | $C_{15}H_{11}NO_4$ | 3,4-$(OCH_2O)$—$C_6H_3$ | $NO_2$ | 1e | C | NaH DMF | 191–95[v] | 75 | $C_6H_6$–hexane |
| 7e | $C_{16}H_{15}NO_4$ | 3,4-$(CH_3O)_2$ $C_6H_3$ | $NO_2$ | 1e | A | $CH_3ONa$ $CH_3OH$ | 133–34[w] | 68 | EtOH–$H_2O$ |
| 7f | $C_{16}H_{14}NO_4Br$ | 3,4-$(CH_3O)_2$— 6-Br-$C_6H_2$ | $NO_2$ | 1e | A | $CH_3ONa$ $CH_3OH$ | 110–15[x] | 73 | AcOH |
| 7g | $C_{12}H_9NO_3$ | 2-Furyl | $NO_2$ | 1e | C | NaH DMF | 128–30[y] | 70 | EtOH |
| 7h | $C_{13}H_{10}N_2O_2$ | 2-Pyridyl | $NO_2$ | 1e | A | $CH_3ONa$ $CH_3OH$ | 130–32[z] | 70 | $C_6H_6$–hexane |
| | | | | | C | NaH DMF | 132–33 | 72 | $C_6H_6$–hexane |
| 8a | $C_{24}H_{22}Cl$ | 4-$CH_3C_6H_4CH$=$CH$— $C_6H_4$— | $CH_3$ | 1a | C | NaH DMF | 198–200* | 58 | Toluene |
| | | | | 1f | C | NaH DMF | 199–200 | 65 | Toluene |
| 8b | $C_{22}H_{16}Cl_2$ | 4-$ClC_6H_4CH$=$CH$— $C_6H_4$— | Cl | 1b | C | NaH DMF | 290–92** | 65 | Xylene |
| 8c | $C_{22}H_{16}Br_2$ | 4-$BrC_6H_4CH$=$CH$— $C_6H_4$— | Br | 1c | C | NaH DMF | 175–77 | 80 | Toluene |
| 8d | $C_{22}H_{16}I_2$ | 4-$IC_6H_4CH$=$CH$— $C_6H_4$— | I | 1d | C | NaH DMF | 253–54 | 85 | Toluene |
| 8e | $C_{22}H_{16}N_2O_4$ | 4-$NO_2C_6H_4CH$=$CH$— $C_6H_4$— | $NO_2$ | 1e | A | $CH_3ONa$ $CH_3OH$ | 286–87† | 90 | Xylene |
| | | | | | C | NaH DMF | 285–89 | 90 | Xylene |
| | | | | 1f | C | NaH DMF | 286–89 | 92 | Xylene |

[a] 1a, O,O-dimethyl *p*-methylbenzylphosphonate; 1b, O,O-dimethyl *p*-chlorobenzylphosphonate; 1c, O,O-dimethyl *p*-bromobenzylphosphonate; 1d, O,O-dimethyl *p*-iodobenzylphosphonate; 1e, O,O-dimethyl *p*-nitrobenzylphosphonate; 1f, tetramethyl *p*-xylylenebisphosphonate. [b] See experimental. [c] Melting points of compounds not marked with references are new. [d] Satisfactory analytical data (±0.4% for C, H) were reported for all compounds listed in the table. [e] Lit. (*33*), mp 181–82°C. [f] Lit. (*32*), mp 208–9°C. [g] Lit. (*22*), mp 203–4°C. [h] Lit. (*31*), mp 147–48°C. [i] Lit. (*15*), mp 128–29°C. [j] Lit. (*22*), mp 203.4°C. [k] Lit. (*33*), mp 174–75°C. [l] Lit. (*9*), mp 186°C. [m] Lit. (*19*), mp 118–20°C. [n] Lit. (*19*), mp 108–10°C. [o] Lit. (*11*), mp 97–98°C. [p] Lit. (*1*), mp 135°C. [q] Lit. (*32*), mp 195–96°C. [r] Lit. (*28*), mp 152°C. [s] Lit. (*27*), mp 150°C. [t] Lit. (*9*), mp 186°C. [u] Lit. (*36*), mp 282°C. [v] Lit. (*7*), mp 194°C. [w] Lit. (*18*), mp 133°C. [x] Lit. (*20*), mp 110–15°C. [y] Lit. (*11*), mp 130–31°C. [z] Lit. (*9*), mp 133–133.5°C. * Lit. (*12*), mp 202°C. ** Lit. (*4*), mp 294–95°C. † Lit. (*4*), mp 286–90°C.

Table II. IR and NMR Data for Diaryl-Substituted Ethylenes[a] (Compounds 3a–8e)

| Compound | IR data (KBr), $Cm^{-1}$; out-of-plane deformations of hydrogen attached to trans-olefinic system | | NMR data ($CDCl_3$) | | |
|---|---|---|---|---|---|
| | $\nu$(C=C) | | $\delta$, ppm | No. of protons | Assignment |
| 3a | 1560 | 980 | ... | ... | ... |
| 3f | 1590 | 958 | ... | ... | ... |
| 3g | 1585 | 960 | 7.52–8.58 m | 8H | Aromatic |
| | | | 7.30 q | 2H | Olefinic |
| | | | 2.38 s | 3H | $CH_3$ |
| 4c | ... | ... | 7.21–7.72 m | 8H | Aromatic |
| | | | 7.10 s | 2H | Olefinic |
| 4e | 1565 | 965 | 7.32–7.90 m | 7H | Aromatic |
| | | | 7.02 q | 2H | Olefinic |
| | | | 6.05 s | 2H | —$OCH_2O$— |
| 4g | 1580 | 965 | 7.66–8.20 m | 7H | Aromatic |
| | | | 7.20 q | 2H | Olefinic |
| 5a | 1600 | 925 | 7.16–7.66 m | 9H | Aromatic |
| | | | 7.08 q | 2H | Olefinic |
| 5c | 1590 | 935 | ... | ... | ... |
| 5d | 1590 | 925 | 7.24–7.80 m | 8H | Aromatic |
| | | | 7.12 s | 2H | Olefinic |
| 6a | 1585 | 975 | ... | ... | ... |
| 6b | ... | ... | 7.25–7.72 m | 8H | Aromatic |
| | | | 6.98 q | 2H | Olefinic |
| | | | 3.82 s | 3H | $OCH_3$ |
| 6c | 1600 | 970 | 7.32–7.86 m | 8H | Aromatic |
| | | | 7.16 q | 2H | Olefinic |
| | | | 3.85 s | 3H | $OCH_3$ |
| 6e | 1625 | 978 | 7.08–7.92 m | 8H | Aromatic |
| | | | 6.89 q | 2H | Olefinic |
| | | | 3.60 s | 3H | $CH_3$ |
| 6g | 1620 | 970 | 7.00–7.68 m | 7H | Aromatic |
| | | | 6.82 q | 2H | Olefinic |
| | | | 5.93 s | 2H | —$OCH_2O$— |
| 6i | 1575 | 968 | 7.37–7.94 m | 7H | Aromatic |
| | | | 7.30 q | 2H | Olefinic |
| 6j | 1600 | 978 | ... | ... | ... |
| 7a | ... | ... | 7.51–8.58 m | 8H | Aromatic |
| | | | 7.30 q | 2H | Olefinic |
| | | | 2.40 s | 3H | $CH_3$ |
| 7b | 1585 | 965 | 7.80–5.50 m | 8H | Aromatic |
| | | | 7.47 q | 2H | Olefinic |
| 7c | 1600 | 970 | 7.67–8.25 m | 8H | Aromatic |
| | | | 7.30 s | 2H | Olefinic |
| 7d | 1590 | 960 | 7.35–7.95 m | 7H | Aromatic |
| | | | 7.26 q | 2H | Olefinic |
| | | | 6.10 s | 2H | —$OCH_2O$— |
| 7e | 1580 | 958 | 7.32–8.40 m | 7H | Aromatic |
| | | | 7.12 q | 2H | Olefinic |
| | | | 4.03 s | 6H | $(OCH_3)_2$ |
| 7f | 1585 | 960 | 7.65–8.47 m | 6H | Aromatic |
| | | | 7.40 q | 2H | Olefinic |
| | | | 4.05 s | 6H | $(OCH_3)_2$ |
| 7g | ... | ... | 7.70–8.20 m | 7H | Aromatic |
| | | | 7.45 q | 2H | Olefinic |
| 8a | ... | ... | 7.00–7.76 m | 12H | Aromatic |
| | | | 6.60 s | 4H | Olefinic |
| | | | 2.80 s | 6H | $CH_3$ |
| 8b | 1600 | 970 | 7.11–7.70 m | 12H | Aromatic |
| | | | 6.62 s | 4H | Olefinic |
| 8d | 1605 | 980 | ... | ... | ... |
| 8e | 1620 | 975 | 7.30–7.80 m | 12H | Aromatic |
| | | | 6.82 s | 4H | Olefinic |

[a] m = multiplet; s = singlet; q = quartet.

was collected, washed with water, dried, and purified by chromatographic separation or recrystallization from the appropriate solvent to yield the trans-diaryl-substituted ethylene.

*Procedure B.* To a stirred suspension of sodamide (0.02 mole) in anhydrous benzene (100 ml) was added dropwise, a solution containing equimolar amounts of appropriate phosphonate (compounds 1a–e) and aromatic aldehyde in benzene. The reaction mixture was stirred at 70° for 4 hr and filtered to remove the residual solid. The filtrate was concentrated on a steam bath under reduced pressure. The resulting oily mass was examined by TLC and then isolated by preparative TLC or column chromatography to afford corresponding trans-diaryl-substituted ethylene.

*Procedure C.* In a 250-ml three-necked flask, equipped with a thermometer pocket, a dropping funnel, and a reflux condenser, was placed a slurry of 50% sodium hydride (0.02 mole) in 50 ml of DMF. The slurry was stirred at 20°, and a solution of appropriate phosphonate (0.02 mole) in DMF (50 ml) was added dropwise. After completion of addition, the mixture was stirred at room temperature until hydrogen gas evolution had ceased. To the light creamy solution of phosphonate carbanion thus formed was added a solution of aromatic aldehyde (0.02 mole) in 20 ml of DMF. After complete addition, the stirring was continued for 7 hr at room temperature and was then taken up cautiously in excess water. The aqueous layer was extracted with two 100-ml portions of ether. The combined extracts were dried and concentrated under reduced pressure and examined over TLC. The resulting mass was then chromatographed to yield trans-diaryl-substituted ethylene.

*Procedure D.* This procedure is the same as mentioned above except that tetrahydrofuran was used as the reaction medium in place of DMF.

***Preparation of trans, trans-1,4-distyryl benzenes (compounds 8a, 8e) by alternative route.*** Tetramethyl *p*-xylylenebisphosphonate (3.22 grams, 0.01 mole) (compound 1f) was added dropwise at room temperature to a 50% slurry of sodium hydride (0.48 grams, 0.01 mole) in 100 ml of DMF. After completion of addition, a dark yellow suspension of bisphosphonate carbanion (compound 2f) was formed. To this was added a solution of substituted benzaldehyde (0.02 mole) in 30 ml of DMF. The reaction was continued at 60° for 6 hr, and the procedure outlined in (C) was followed. The product obtained as a dark yellow solid was purified by crystallization from the appropriate solvent.

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