Reactions of Vinylphosphonates. 2.[1] Synthesis of Functionalized Dienes, Trienes, and Their Analogues. Synthetic Applications to Regioselectively Functionalized Benzene Derivatives

Toru Minami,* Katsuhide Nishimura, and Ichiro Hirao

Department of Industrial Chemistry, Kyushu Institute of Technology, Sensuicho, Tobata, Kitakyushu 804, Japan

Hiroyuki Suganuma and Toshio Agawa

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan

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The phosphoryl-stabilized carbanions prepared from vinylphosphonates **1a**,**b** and various carbanions **2a**–**c** react with aldehydes **3** to give olefins having various functional groups. The dienes **5c**–**g** produced by the reaction using α,β-unsaturated aldehydes and a methyl (methylsulfinyl)methyl sulfide carbanion (**2b**) easily undergo thermolysis to afford reactive intermediate 1-methylthio 1,3,5-trienes, which are converted into the 1,4-disubstituted benzenes **7a**–**e** in 27–56% overall isolated yields via the electrocyclic reaction into cyclohexadienes and subsequent elimination of methanethiol. Thermolysis of the reaction product using ethyl α-(diethylphosphono)acrylate (**1a**), **2b**, and 1,4-bis(2-formylethenyl)benzene (**3g**) produces 4,4″-bis(ethoxycarbonyl)-1,1′:4′,1″-terphenyl (**7f**) in 16% yield. The reaction using an ethyl (methylthio)acetate carbanion (**2c**) instead of **2b** gives thermally stable dienes **5i**–**l** in 38–52% yields. Oxidation of the dienes **5i**,**k**,**l**, followed by thermolysis, leads to the 1,2,4-trisubstituted (**8a**,**b**) and 1,2-disubstituted benzenes (**9**). Similar treatment of the product **5m** derived from **1a**, **2c**, and 3-phenylpropargylaldehyde (**3f**) produces a mixture of 2,4-bis(ethoxycarbonyl)biphenyl (**8a**) and ethyl 4-(ethoxycarbonyl)-7-phenylhepta-2,4-dien-6-ynoate (**11**) in 23% and 32% yields.

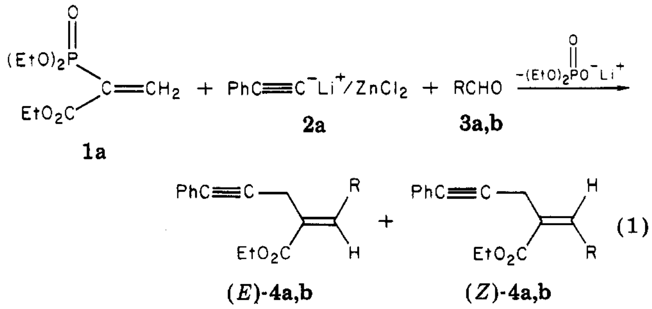
As triphenylvinylphosphonium bromide is a versatile reagent for the synthesis of a variety of carbocyclic[2] and heterocyclic compounds,[3] considerable attention has been recently given to the study of the synthetic utilization of its analogues, vinylphosphonates.[1,4] In the previous paper[1] we reported a new synthesis of vinylphosphonates bearing electronegative substituents such as ethoxycarbonyl and cyano groups and their use in syntheses of functionalized heterocyclic compounds and olefins. In connection with our continuing interest in the synthetic application of the vinylphosphonates, we have now developed a new synthesis of unsaturated systems such as trienes, dienynes, etc. bearing functionality which permitted production of regioselectively substituted aromatic compounds via an electrocyclic reaction.

Results and Discussion

Table I. Synthesis of 1,4-Disubstituted Benzenes 7 from 1, 2b, and 3

7	R′	X	bp, °C (mm), or mp, °C	isolated yield, %
7a	Ph	CO_2Et	145–149 (0.5) [lit.[8] mp 49–53]	50
7b	Me	CO_2Et	79–80 (4) [lit.[9] 235.5 (760)]	38
7c	*n*-Pr	CO_2Et	100–110 (2)	42
7d	Ph	SO_2Me	139–140	56
7e	*n*-Pr	SO_2Me	99–101 (1)	27

The Horner–Emmons reaction of the stabilized phosphonate carbanion, generated from ethyl α-(diethylphosphono)acrylate (**1a**) and a phenylethynyl carbanion (**2a**) in the presence of zinc chloride, with aldehydes **3** led smoothly to functionalized enyne derivatives **4a**,b (eq 1) in good yields, in analogy with cases using other various nucleophiles.[1]



3a, **4a**, R = Ph; **3b**, **4b**, R = Et

The reaction of **1a** and a methyl (methylsulfinyl)methyl sulfide carbanion (**2b**) with aldehydes **3a**,**b** similarly gave functionalized olefins **5a**,**b** (eq 2), which were easily thermolyzed under distillation conditions to 1-(methylthio)-3-(ethoxycarbonyl)-1,3-butadienes **6a**,**b**. Similar treatment of α,β-unsaturated aldehydes such as cinnamaldehyde (**3c**), 2-butenal (**3d**), and 2-hexenal (**3e**) led to the expected dienes **5c**–**g**. Interestingly, thermolysis of the dienes **5c**–**g** in refluxing xylene for 6 h afforded the 1,4-

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(1) For the preceding paper in this series, see: Minami, T.; Suganuma, H.; Agawa T. *Chem. Lett.* **1978**, 285.

(2) (a) Schweizer, E. E., O'Neill, G. J. *J. Org. Chem.* **1965**, *30*, 2082. (b) Kawamoto, I.; Murmatsu, S.; Yura, Y. *Tetrahedron Lett.* **1974**, 4223 and references cited therein.

(3) (a) Schweizer, E. E.; Light, K. K. *J. Org. Chem.* **1966**, *31*, 870. (b) Schweizer, E. E.; Liehr, J.; Monako, D. J. *Ibid.* **1968**, *33*, 2416 and references cited therein. (c) For recent reviews, see: Zbiral, E. *Synthesis* **1974**, 775. Becker, K. B. *Tetrahedron* **1980**, *36*, 1717.

(4) (a) Kleschick, W. A.; Heathcock, C. H. *J. Org. Chem.* **1978**, *43*, 1256. (b) Semmelhack, M. F.; Tomesch, J. C.; Czarny, M.; Boettger, S. *Ibid.* **1978**, *43*, 1259. (c) Semmelhack, M. F.; Yamashita, A.; Tomesch, J. C.; Hirotsu, K. *J. Am. Chem. Soc.* **1978**, *100*, 5565. (d) Ide, J.; Endo, R.; Muramatsu, S. *Chem. Lett.* **1978**, 401. (e) McIntosh, J. M.; Sieler, R. A. *Can. J. Chem.* **1978**, *56*, 226. (f) McIntosh, J. M.; Sieler, R. A. *J. Org. Chem.* **1978**, *43*, 4431. (g) Schmitthenner, H. F.; Weinreb, S. M. *Ibid.* **1980**, *45*, 3372. (h) Venugopalan, B.; Hamlet, A. B.; Durst, T. *Tetrahedron Lett.* **1981**, 191. (i) Mikolajczyk, M.; Grzejszczak, S.; Korbacz, K. *Ibid.* **1981**, 3097. (j) Darling, S. D.; Subramanian, N. *Ibid.* **1975**, 3279. (k) Hellmuth, E. W.; Kaczynski, J. A.; Low, J.; McCoy, L. L. *J. Org. Chem.* **1974**, *39*, 3125. (l) Gareev, R. D.; Loginova, G. M.; Pudovik, A. N. *Zh. Obshch. Khim.* **1979**, *49*, 493; *Chem. Abstr.* **1979**, *91*, 4894. (m) Gareev, R. D.; Pudovik, A. N. *Ibid.* **1979**, *49*, 728; *Chem. Abstr.* **1979**, *91*, 56196.

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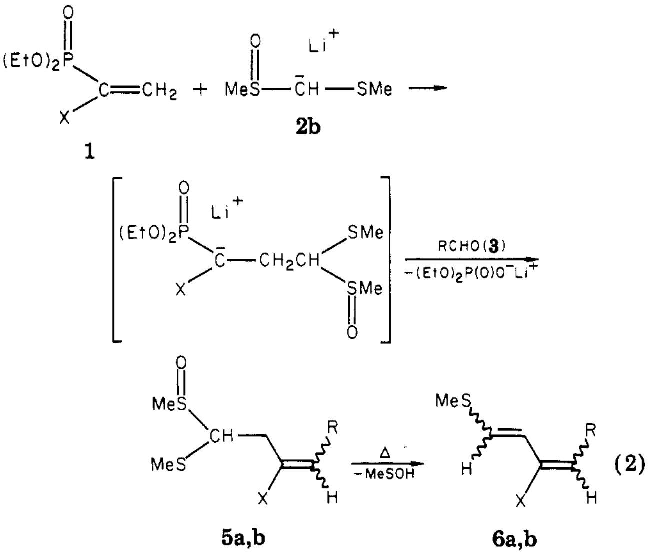
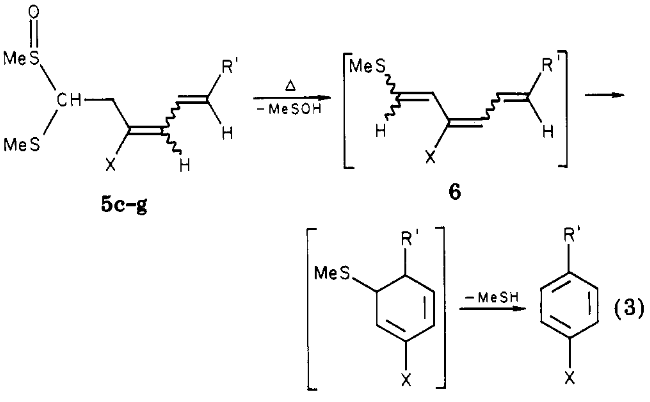


1 + 2b

5a,b → 6a,b

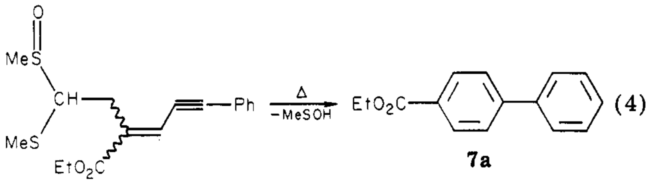
5a, 6a: R = Ph, X = CO_2Et. 5b, 6b: R = Et, X = CO_2Et

disubstituted benzene derivatives **7a–e** (eq 3) in 27–56% overall yields (pure, Table I). As shown in eq 3, the formation of **7** could be explained by an electrocyclic ring closure of the intermediate trienes **6**, which are produced by thermolysis of **5**, to yield the unstable cyclohexadienes, followed by facile elimination of methanethiol. Also, thermolysis of the enyne **5h** prepared by a similar reaction with 3-phenylpropargylaldehyde (**3f**) produced ethyl 4-phenylbenzoate in 43% yield, which was identical with product **7a** obtained in the above reaction. Although the formation of **7a** from **5h** (eq 4) probably involves, electrocyclic ring closure of the intermediate dienyne, elimination of the methylthio moiety, and reduction, no evidence to explain where the reduction process has occurred was obtained. A difunctional α,β-unsaturated aldehyde, 1,4-bis(2-formylethenyl)benzene (**3g**), on similar treatment with **1a** and **2b**, provided the expected 4,4″-bis(ethoxycarbonyl)-1,1′:4′,1″-terphenyl (**7f**, eq 5) albeit in low yield (16% yield).



5c–g → 6 → 7a–e

5c, 7a: X = CO_2Et, R′ = Ph
5d, 7b: X = CO_2Et, R′ = Me
5e, 7c: X = CO_2Et, R′ = n-Pr
5f, 7d: X = SO_2Me, R′ = Ph
5g, 7e: X = SO_2Me, R′ = n-Pr

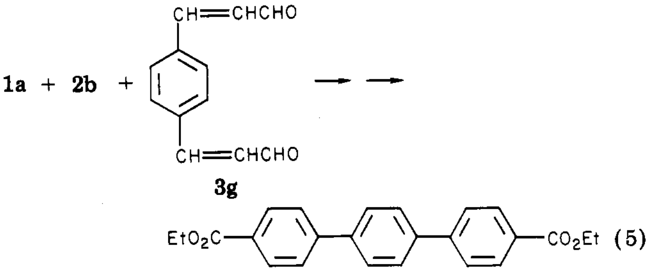


5h → 7a

Table II. Synthesis of Functionalized Dienes 5 from 1, 2c, and 3

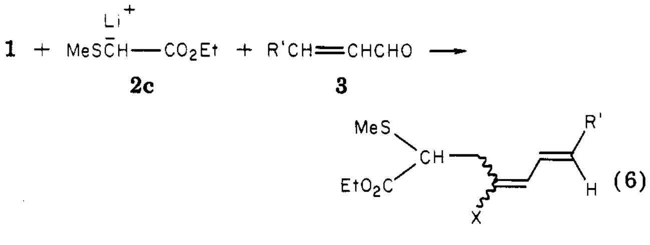
5	R′	X	bp, °C (mm)	isolated yield, %
5i	Ph	CO_2Et	102–105 (1)	43
5j	n-Pr	CO_2Et	153 (2)	52
5k	Ph	SO_2Me	180–215 (1)[a]	38
5l	n-Pr	SO_2Me	160 (2)	39

[a] Isolation of 5k in a pure form was unsuccessful due to decomposition under distillation.

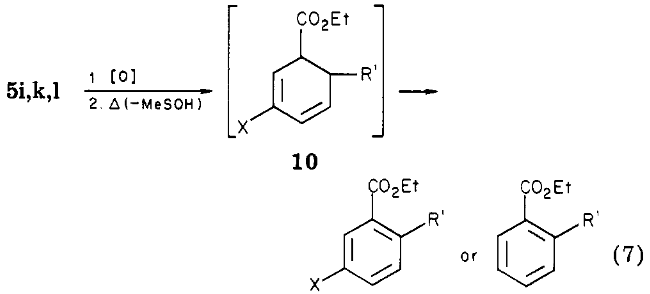


1a + 2b + 3g → 7f

Ethyl (methylthio)acetate carbanion **2c** reacted with α,β-unsaturated aldehydes **3** to give thermally stable dienes **5i–l** (eq 6) in 38–52% isolated yields (Table II). Oxidation of dienes **5i,l** with sodium metaperiodate and subsequent thermolysis led to the 1,2,4-trisubstituted benzene derivatives **8a,b** (eq 7). Similar treatment of **5k** led unexpectedly to ethyl 2-phenylbenzoate (**9**, 80% yield). In all cases, the failure to isolate the expected cyclohexadiene derivatives **10** could be due to the ease of either oxidation of **10** to **8** under the reaction conditions or the elimination of methanesulfinic acid from **10** to **9**. The difference in reactivity between **5k** and **5l** shows that the phenyl substituent favors elimination of methanesulfinic acid from **10** over the alkyl substituent. Thus, the reaction products



1 + 2c + 3 → 5i–l

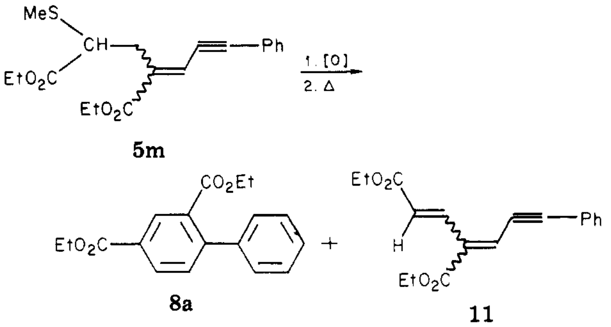


5i,k,l → 10 → 8a,b or 9

5i, 8a: R′ = Ph, X = CO_2Et
5j: R′ = n-Pr, X = CO_2Et
5k,9: R′ = Ph, X = SO_2Me
5l,8b: R′ = n-Pr, X = SO_2Me

are dependent upon the substituent R′ when the second substituent X is the methanesulfonyl group.

On the other hand, thermolysis of the product **5m** (eq 8) provided a mixture of 2,4-diethoxycarbonyldiphenyl (**8a**, 23%) and ethyl 4-(ethoxycarbonyl)-7-phenylhept-2,4-dien-6-ynoate (**11**, 32%). The formation of **8a** can be accounted for by electrocyclic ring closure of **11**, which may be isolated because it is less prone to thermolysis.



5m **8a** **11**

(8)

Thus, vinylphosphonates are versatile reagents for the synthesis of functionalized dienes, trienes, and their analogues, which are converted to the regioselective polyfunctionalized benzene derivatives.

Experimental Section

General Methods. ^{1}H NMR spectra were obtained with a JEOL JNM-FX-60 or JNM-PMX-60 spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded with a JASCO IR-1 or a Shimazu IR-27c instrument. Mass spectra were taken with a Hitachi RMU-6E spectrometer. Melting points were measured in open capillary tubes and are uncorrected.

Materials. Ethyl α-(diethylphosphono)acrylate [**1a**, bp 90–95 °C (0.5 mm)] was prepared according to the established procedures.[1] Diethyl (α-methanesulfonylvinyl)phosphonate[5] [**1b**, bp 138–140 °C (0.5 mm)] was synthesized in ca. 50% yield by dehydration of 2-(diethylphosphono)-2-methanesulfonylethanol, which was prepared from the reaction of (diethylphosphono)methyl methyl sulfone with formaldehyde in the presence of small amounts of pyrrolidine in refluxing benzene containing catalytic amounts of *p*-toluenesulfonic acid.[6] 1,4-Bis(2-formylethenyl)benzene [**3g**; Kugelrohr, bp 130 °C (1 mm)] was prepared in 14% yield together with 4-(2-formylethenyl)benzaldehyde (33% yield) from the reaction of *p*-phthalaldehyde with formylmethylenetriphenylphosphorane[7] in benzene at 80 °C for 24 h.

(1*E*)- and (1*Z*)-2-(Ethoxycarbonyl)-1,5-diphenyl-1-penten-4-yne (4a). To a cooled solution of (phenylethynyl)lithium (8 mmol), prepared from phenylacetylene (0.82 g, 8 mmol) and *n*-butyllithium (8 mmol), in 30 mL of dry THF at −70 °C was added zinc chloride (1.10 g, 8 mmol). After the solution was stirred for 2 h, **1a** (1.90 g, 8 mmol) was added to the solution, and the mixture was stirred for 1.5 h and allowed to warm to room temperature. To this was then added benzaldehyde (0.85 g, 8 mmol), and the reaction mixture was stirred at the reflux temperature for 5 h. After evaporation of the solvent, the residue was extracted with ether and dried over sodium sulfate. Removal of the ether and distillation of the residue gave 1.70 g (73%) of a 3:1 mixture of (1*E*)- and (1*Z*)-**4a**: bp 153–155 °C (1 mm); IR (neat) 1710, 1635 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.37 (t, 3 H, Me), 3.64 (s, 2 H, CH$_2$), 4.37 (q, 2 H, OCH$_2$), 7.20–7.80 (m, 5.25 H, phenyl and (*Z*)-vinyl H), 7.84 (s, 0.75 H, (*E*)-vinyl H); mass spectrum, *m*/*e* 290 (M$^+$).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.49; H, 6.16.

(4*E*)- and (4*Z*)-1-Phenyl-4-(ethoxycarbonyl)-4-hepten-1-yne (4b). The reaction was carried out as described above by using propionaldehyde (0.464 g, 8 mmol) to give 1.31 g (71%) of a 5:4 mixture of (4*E*)- and (4*Z*)-**4b**: bp 124–127 °C (1 mm); IR (neat) 1715, 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.06–1.44 (m, 6 H, Me), 2.20–2.80 (m, 2 H, CH$_2$), 3.46 (s, 2 H, ≡CCH$_2$), 4.34 (q, 2 H, OCH$_2$), 6.44 (t, $^4/_9$ H, (*Z*)-vinyl H), 6.90 (t, $^5/_9$H, (*E*)-vinyl H), 7.20–7.66 (m, 5 H, phenyl H); mass spectrum, *m*/*e* 247 (M$^+$).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.05; H, 7.63.

1-(Methylthio)-3-(ethoxycarbonyl)-4-phenyl-1,3-butadiene (6a). To a solution of a methyl (methylsulfinyl)methyl sulfide carbanion **2b** (15 mmol), generated from methyl (methylsulfinyl)methyl sulfide (1.86 g, 15 mmol) and *n*-butyllithium (16 mmol) at −70 °C, in THF (50 mL) was added **1a** (3.60 g, 15 mmol). After the solution was stirred for 1 h at this temperature, benzaldehyde (1.60 g, 15 mmol) was added to the solution. The mixture was stirred for 0.5 h at room temperature and for 2 h at the reflux temperature. A standard workup gave 3.80 g of an oil, which was chromatographed on silica gel to afford the olefin **5a**, 2.90 g (62% yield). Distillation of **5a** gave 2.09 g (56% over-all yield) of **6a**: bp 129–131 °C (1 mm); IR (neat) 1710, 1605 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.36 (t, 3 H, Me), 2.28 (s, 3 H, SMe), 4.32 (q, 2 H, OCH$_2$), 6.20–7.56 (m, 8 H, phenyl and vinyl H); mass spectrum, *m*/*e* 248 (M$^+$).

Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.73; H, 6.50. Found: C, 67.52; H, 6.61.

1-(Methylthio)-3-(ethoxycarbonyl)-1,3-hexadiene (6b). The reaction was similarly carried out by using propionaldehyde (0.69 g, 15 mmol) to afford **5b** in 2.21 g (56%) yield. Distillation of **5b** produced 1.50 g (50% overall yield) of **6b**: bp 108–110 °C (5 mm); IR (neat) 1710, 1615 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.90–1.50 (m, 6 H, Me), 2.10–2.52 (m, 5 H, SMe and CH$_2$), 4.06–4.53 (m, 2 H, OCH$_2$), 5.71–7.05 (m, 3 H, vinyl H); mass spectrum, *m*/*e* 200 (M$^+$).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.98; H, 8.05. Found: C, 60.39; H, 8.26.

General Procedure for the Synthesis of 1,4-Disubstituted Benzenes 7a–e. To the phosphonate carbanions prepared by the procedure and on the scale as described above were added α,β-unsaturated aldehydes **3c–e**, and the reaction mixtures were refluxed for 3 h. After a standard workup, the resulting oils were dissolved in xylene (50 mL), and the solutions were refluxed for 6 h. After removal of the solvent, the remaining oils were distilled to give pure samples **7a–e**. The boiling or melting points and the yields of the products are summarized in Table I.

Ethyl 4-phenylbenzoate (7a): IR (neat) 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.40 (t, 3 H, Me), 4.44 (q, 2 H, OCH$_2$), 7.92–8.90 (m, 9 H, phenyl H); mass spectrum, *m*/*e* 226 (M$^+$).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.41; H, 6.30.

Ethyl 4-methylbenzoate (7b): IR (neat) 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.39 (t, 3 H, Me), 2.31 (s, 3 H, Me), 4.40 (q, 2 H, OCH$_2$), 7.25 and 8.00 (d, *J* = 8.0 Hz, 4 H, phenyl H).

Ethyl 4-*n*-propylbenzoate (7c): IR (neat) 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.93 (t, 3 H, CH$_2$CH$_3$), 1.38 (t, 3 H, OCH$_2$CH$_3$), 1.15–2.00 (m, 2 H, CH$_2$CH$_2$CH$_3$), 2.65 (t, 2 H, CH$_2$CH$_2$CH$_3$), 4.35 (q, 2 H, OCH$_2$), 7.22 and 7.94 (d, *J* = 8.2 Hz, 4 H, aromatic H); mass spectrum, *m*/*e* 192 (M$^+$).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.49; H, 8.33.

4-(Methylsulfonyl)biphenyl (7d): IR (KBr) 1300, 1150 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.09 (s, 3 H, Me), 7.25–8.09 (m, 9 H, aromatic H); mass spectrum, *m*/*e* 232 (M$^+$).

Anal. Calcd for $C_{13}H_{12}O_2S$: C, 67.23; H, 5.21. Found: C, 67.70; H, 5.28.

1-*n*-Propyl-4-(methylsulfonyl)benzene (7e): IR (neat) 1300, 1150 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.97 (t, 3 H, Me), 1.21–2.02 (m, 2 H, CH$_2$CH$_2$CH$_3$), 2.75 (t, 2 H, CH$_2$CH$_2$CH$_3$), 3.09 (s, 3 H, SO$_2$Me), 7.48 and 7.99 (d, *J* = 8.0 Hz, 4 H, aromatic H); mass spectrum *m*/*e* 198 (M$^+$).

Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.58; H, 7.17. Found: C, 60.70; H, 7.42.

Synthesis of 7a from 1a, 2b, and Propargylaldehyde (3f). The reaction of the phosphonate carbanion (10 mmol) prepared from **1a** and **2b** with **3f** (1.30 g, 10 mmol) provided **5h**. Thermolysis of the crude **5h** gave 0.97 g (43% yield) of **7a**, whose

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[5] It has been recently reported by Mikolajczyk and co-workers[4l] that **1b** was independently prepared by a similar method.

[6] Pudovik, A. N.; Yastrebova, G. E.; Nikitina, V. I. *Zh. Obshch. Khim.* **1966**, *36*, 1232; *Chem. Abstr.* **1966**, *65*, 15418.

[7] Trippet, S.; Walker, D. M. *J. Chem. Soc.* **1961**, 1266.

[8] Fieser, L. F. *J. Am. Chem. Soc.* **1948**, *70*, 3186.

[9] Perkin, W. H. *J. Chem. Soc.* **1896**, 69, 1177.

structure was proved to be that of ethyl 4-phenylbenzoate by comparison of its IR and NMR spectrum with those of the product **7a** obtained above.

Synthesis of 4,4″-Bis(ethoxycarbonyl)-1,1′:4′,1″-terphenyl (7f). Similar treatment of the reaction product of **3g** (0.93 g, 5 mmol) with the phosphonate carbanion (5 mmol) produced 0.30 g (16% yield) of **7f**: >mp 300 °C (from ethanol); IR (KBr) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (t, J = 7.0 Hz, 6 H, Me), 4.41 (q, J = 7.0 Hz, 4 H, CH_2), 7.72 (s, 4 H, aromatic H), 7.69 and 8.13 (d, J = 9.0 Hz, 8 H, aromatic H); mass spectrum, *m/e* 374 (M^+).

Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92. Found: C, 76.63; H, 5.85.

General Procedure for the Synthesis of Dienes 5i–m from 1, an Ethyl (Methylthio)acetate Carbanion (2c), and α,β-Unsaturated Aldehydes 3c,e,f. To a solution of an in situ generated ethyl (methylthio)acetate carbanion (**2c**) from ethyl (methylthio)acetate (1.34 g, 10 mmol) and lithium diisopropylamide (10 mmol) in 40 mL of THF at −78 °C was added **1** (10 mmol). After the solution was allowed to warm to room temperature, an aldehyde was added to it. The reaction mixture was stirred at this temperature for 0.5 h and at reflux temperature for 3 h. After the usual workup, distillation of the residue gave the product **5**. The yields and boiling points of **5i–l** are summarized in Table II.

Ethyl 2-(methylthio)-4-(ethoxycarbonyl)-7-phenyl-4,6-heptadienoate (5i): IR (neat) 1730, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16–1.46 (m, 6 H, Me), 2.19 (s, 3 H, SMe), 2.92–3.12 (m, 2 H, CH_2), 3.33–3.70 (m, 1 H, CH), 3.96–4.44 (m, 4 H, OCH_2), 6.57–7.71 (m, 8 H, vinyl and phenyl H); mass spectrum, *m/e* 348 (M^+).

Anal. Calcd for $C_{19}H_{24}O_4S$: C, 65.49; H, 6.94. Found: C, 64.94; H, 6.66.

Ethyl 2-(methylthio)-4-(ethoxycarbonyl)-4,6-decadienoate (5j): IR (neat) 1720, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H, Me), 1.04–1.77 (m, 8 H, 2 OCH_2CH_3 and $CH_2CH_2CH_3$), 1.86–2.37 (m, 2 H, $CH_2CH_2CH_3$), 2.13 (s, 3 H, SMe), 2.60–3.04 (m, 2 H, $>CHCH_2$), 3.50 (t, 1 H, $>CHCH_2$), 3.80–4.40 (m, 4 H, 2 OCH_2CH_3), 5.80–6.68 (m, 2 H, $CH{=}CH$), 7.10–7.54 (m, 1 H, $>C{=}CH$); mass spectrum, *m/e* 314 (M^+).

Anal. Calcd for $C_{16}H_{26}O_4S$: C, 61.12; H, 8.34. Found: C, 60.99; H, 8.56.

Ethyl 2-(Methylthio)-4-(methylsulfonyl)-7-phenyl-4,6-heptadienoate (5k). Since this compound could not be isolated in a pure form due to decomposition on distilling, the structure of **5k** was confirmed by conversion into **9** as described below.

Ethyl 2-(Methylthio)-4-(methylsulfonyl)-4,6-decadienoate (5l): IR (neat) 1720, 1300, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, 3 H, $CH_2CH_2CH_3$), 1.27 (t, 3 H, OCH_2CH_3), 1.35–1.75 (m, 2 H, $CH_2CH_2CH_3$), 1.93–2.45 (m, 2 H, $CH_2CH_2CH_3$), 2.19 (s, 3 H, SMe), 2.55–3.20 (m, 2 H, $>CHCH_2$), 2.93 (s, 3 H, SO_2Me), 3.75 (t, J = 7.0 Hz, 1 H, $>CHCH_2$), 4.17 (q, 2 H, OCH_2CH_3), 6.15–7.55 (m, 3 H, vinyl H); mass spectrum, *m/e* 320 (M^+).

Anal. Calcd for $C_{14}H_{24}O_4S_2$: C, 52.47; H, 7.55. Found: C, 52.36; H, 7.70.

Ethyl 2-(methylthio)-4-(ethoxycarbonyl)-7-phenylhept-4-en-6-ynoate (5m): 1.73 g (50% yield); bp 100 °C (2 mm); IR (neat) 2150, 1720, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 and 1.32 (t, 6 H, Me), 2.17 (s, 3 H, SMe), 3.11 (d, 2 H, $>CHCH_2$), 3.70 (t, 1 H, $>CHCH_2$), 4.19 and 4.25 (q, 4 H, OCH_2), 6.98 (s, 1 H, vinyl H), 7.05–7.70 (m, 5 H, aromatic H); mass spectrum, *m/e* 346 (M^+).

Anal. Calcd for $C_{19}H_{22}O_4S$: C, 65.87; H, 6.40. Found: C, 66.05; H, 6.53.

General Procedure for the Synthesis of 1,2,4-Trisubstituted Benzenes 8 and a 1,2-Disubstituted Benzene Derivative 9. To a solution of dienes **5** (3 mmol) in ethanol (30 mL) was added an aqueous solution of sodium metaperiodate (0.71 g, 3.3 mmol), and the solution was stirred for 24 h at ambient temperature. After a standard workup, the remaining oil was thermolyzed in a similar manner to give the product.

2,4-Bis(ethoxycarbonyl)biphenyl (8a). From 5i. Treatment of the diene **5i** as described above gave 0.593 g (66% yield) of **8a**: bp 150 °C (1 mm); IR (neat) 1720, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, J = 7.0 Hz, 3 H, Me), 1.42 (t, J = 7.0 Hz, 3 H, Me), 4.11 (q, J = 7.0 Hz, 2 H, CH_2), 4.42 (q, J = 7.0 Hz, 2 H, CH_2), 7.10–7.60 (m, 6 H, aromatic H), 8.17 (dd, J = 1.8, 8.0 Hz, 1 H, an aromatic H), 8.45 (d, J = 1.8 Hz, an aromatic H); mass spectrum, *m/e* 298 (M^+).

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.07; H, 6.09.

From 5m. Similar treatment of **5m** (0.96 g, 2.77 mmol) gave a mixture of **8a** (0.187 g, 23%) and **ethyl 4-(ethoxycarbonyl)-7-phenylhepta-2,4-dien-6-ynoate (11)**, 0.263 (32%). The compound **11** had the following: bp 170 °C (2 mm); IR (neat) 2150, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15–1.55 (m, 6 H, Me), 4.10–4.62 (m, 4 H, CH_2), 7.07–8.67 (m, 8 H, aromatic and vinyl H); mass spectrum, *m/e* 298 (M^+).

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.17; H, 6.04.

Ethyl 2-Propyl-5-(methylsulfonyl)benzoate (8b). Similar treatment of **5l** gave 0.575 g (71%) of **8b** contaminated by small amounts of impurities: bp 170 °C (1 mm); IR (neat) 1710, 1310, 1160 cm^{-1}; mass spectrum, *m/e* 270 (M^+). For confirmation of the structure of **8b**, it was hydrolyzed to afford **2-propyl-5-(methylsulfonyl)benzoic acid**: 0.19 g (26% yield); mp 132–133 °C (benzene–hexane); IR (KBr) 1675, 1310, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (t, 3 H, Me), 1.03–1.95 (m, 2 H, $CH_2CH_2CH_3$), 3.09 (t, 2 H, $CH_2CH_2CH_3$), 3.09 (s, 3 H, SO_2Me), 7.51 (d, J = 8.0 Hz, 1 H, phenyl H), 8.04 (dd, J = 8.0, 2.0 Hz, 1 H, phenyl H), 8.35 (br, 1 H, COOH), 8.60 (d, J = 2.0 Hz, 1 H, phenyl H); mass spectrum, *m/e* 242 (M^+).

Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.02; H, 5.70.

Ethyl 2-Phenylbenzoate (9). Similar treatment of **5k** gave 0.54 g (80%) of **9**: bp 120 °C (1 mm) [lit.[10] bp 166 °C (10 mm)]; IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (t, 3 H, Me), 4.40 (q, 2 H, OCH_2), 7.00–7.92 (m, 9 H, aromatic H); mass spectrum, *m/e* 226 (M^+).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.22; H, 6.42.

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Registry No. 1a, 20345-61-3; **1b**, 80436-51-7; **2a**, 4440-01-1; **2b**, 73657-94-0; **2c**, 81423-63-4; **3a**, 100-52-7; **3b**, 123-38-6; **3c**, 104-55-2; **3d**, 4170-30-3; **3e**, 505-57-7; **3f**, 2579-22-8; **3g**, 3049-37-4; (*E*)-**4a**, 81423-64-5; (*Z*)-**4a**, 81423-65-6; (*E*)-**4b**, 81423-66-7; (*Z*)-**4b**, 81423-67-8; **5a**, 81423-68-9; **5b**, 81423-69-0; **5c**, 81423-70-3; **5d**, 81423-71-4; **5e**, 81423-72-5; **5f**, 81423-73-6; **5g**, 81423-74-7; **5h**, 81423-75-8; **5i**, 81423-76-9; **5j**, 81423-77-0; **5k**, 81423-78-1; **5l**, 81423-79-2; **5m**, 81423-80-5; **6a**, 81423-81-6; **6b**, 81423-82-7; **7a**, 6301-56-0; **7b**, 94-08-6; **7c**, 81423-83-8; **7d**, 6462-34-6; **7e**, 81423-84-9; **7f**, 37527-56-3; **8a**, 81423-85-0; **8b**, 81423-86-1; **9**, 19926-49-9; 11, 81423-87-2; 2-(diethylphosphono)-2-methanesulfonylethanol, 81434-74-4; 4-(2-formylethenyl)benzaldehyde, 77972-48-6; *p*-phthalaldehyde, 623-27-8; formylmethylenetriphenylphosphorane, 2136-75-6; 2-propyl-5-(methylsulfonyl)benzoic acid, 81423-88-3.

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[10] Tommilia, E.; Brehmer, L.; Elo, H. *Ann. Acad. Sci. Fenn., Ser. A2* **1945**, *No. 16*, 14; *Chem. Abstr.* **1947**, *41*, 903*e*.