and 2-propylcyclohexanone (7) which were identified by the agreement of their GLC retention times, IR, and/or ^1H NMR spectra with those of the authentic samples. 2-Allylhexanal (1): IR (liquid film, cm^{-1}) 1730, 1640; ^1H NMR ($CDCl_3$) δ 0.94 (t, 3 H), 1.2–1.8 (m, 6 H), 2.1–2.6 (m, 3 H), 5.0–6.0 (m, 3 H), 9.65 (s, 1 H); mass spectrum (M^+ at m/e) 140. 3-Isopropyl-5-hexen-2-one (2): IR (liquid film, cm^{-1}) 1710, 1642; ^1H NMR ($CDCl_3$) δ 0.91 (d, 6 H), 1.6–2.0 (m, 1 H), 2.13 (s, 3 H), 2.2–2.5 (m, 3 H), 4.8–6.1 (m, 3 H); mass spectrum (M^+ at m/e) 140. 2-(Cyanomethyl)-cyclohexanone (8): IR (liquid film, cm^{-1}) 2245, 1710; ^1H NMR ($CDCl_3$) δ 1.4–2.1 (m, 6 H), 2.2–2.5 (m, 2 H), 2.64 (d, 2 H), 2.8–3.1 (m, 1 H); mass spectrum (M^+ at m/e) 137. 2-Acetonylcyclohexanone (10): IR (liquid film, cm^{-1}) 1710; ^1H NMR ($CDCl_3$) δ 1.2–2.0 (m, 6 H), 2.1–2.5 (m, 2 H), 2.22 (s, 3 H), 2.6–3.3 (m, 3 H); mass spectrum (M^+ at m/e) 154. 2-[(Ethoxycarbonyl)methyl]-cyclohexanone (11): IR (liquid film, cm^{-1}) 1740, 1715; ^1H NMR ($CDCl_3$) δ 1.27 (t, 3 H), 1.4–3.0 (11 H), 4.12 (quart, 2 H); mass spectrum (M^+ at m/e) 184. (*E*)-2,3-Dimethylcyclohexanone (12): IR (liquid film, cm^{-1}) 1710; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 5 Hz, 3 H), 1.09 (d, J = 5 Hz, 3 H), 1.4–2.5 (m, 8 H); mass spectrum (M^+ at m/e) 126. (*Z*)-2,3-Dimethylcyclohexanone (12): IR (liquid film, cm^{-1}) 1710; ^1H NMR ($CDCl_3$) δ 0.85 (d, J = 9 Hz, 3 H), 0.98 (d, J = 9 Hz, 3 H), 1.5–2.6 (m, 8 H); mass spectrum (M^+ at m/e) 126. Methyl 2-ethyl-4-pentenoate (15): IR (liquid film, cm^{-1}) 1740, 1640; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.3–1.8 (m, 2 H), 2.1–2.5 (m, 3 H), 3.69 (s, 3 H), 4.8–6.1 (m, 3 H); mass spectrum (M^+ at m/e) 142. 2-Allyl-4-hepten-2-one (16): IR (liquid film, cm^{-1}) 1720, 1640, 970; ^1H NMR ($CDCl_3$) δ 1.98 (t, 3 H), 2.12 (s, 3 H), 1.6–2.5 (m, 4 H), 3.12 (quart, 1 H), 4.8–6.0 (m, 5 H); ^{13}C NMR ($CDCl_3$) 13.55, 25.65, 28.62, 35.40, 56.86, 116.50, 126.35, 135.76, 136.49, 209.26; mass spectrum (M^+ at m/e) 152.

General Procedure of the Reaction of Aluminum Enolate with Trimethylsilyl Chloride. To a stirred suspension of CuI (190 mg, 0.100 mmol) in 5 mL of THF was added at −10 °C an ether solution of methyllithium (0.100 mmol). HMPA (0.52 mL, 3.0 mmol) and a hexane solution of DIBAH (2.20 mmol) were added successively to the reaction mixture at −50 °C. After being stirred for 0.5 h, an α,β-unsaturated carbonyl compound (2.00 mmol) was added. The mixture was stirred at −50 °C for an approporiate reaction time (0.5–3 h). Trimethylsilyl chloride (0.28 mL, 2.2 mmol) was added, and the mixture was allowed to react at room temperature. After the appropriate time, triethylamine (0.29 mL, 2.2 mmol) was added to prevent the hydrolysis of the product of silyl enol ether during the workup. GLC analysis (a silicone DC 550 column) of the mixture using a hydrocarbon GLC internal standard gave a GLC yield. After evaporation of the greater part of THF, silica gel was added to remove inorganic and polar organic materials. The organic residue was chromatographed on silica gel (elution with hexane or pentane) to afford the silyl enol ether product.

According to this procedure, silyl enol ethers 18–24 (Table II) were isolated and identified as follows, respectively. 18: IR (liquid film, cm^{-1}) 1660, 1595; ^1H NMR ($CDCl_3$) δ 0.17 (s, 9 H), 3.24 (d, J = 7.0 Hz, 2 H), 5.24 (d of t, J = 12.2 and 7.0 Hz, 1 H), 6.33 (d, J = 12.2 Hz, 1 H), 7.23 (s, 5 H); mass spectrum (M^+ at m/e) 206. 19: IR (liquid film, cm^{-1}) 1655; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.93 (d, 3 H), 1.1–2.2 (m, 5 H), 1.57 (s, 3 H), 1.66 (s, 3 H), 4.7–5.3 (m, 2 H), 6.15 (d, J = 12.2 Hz, 1 H); mass spectrum (M^+ at m/e) 226. 20: IR (liquid film, cm^{-1}) 1645; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.90 (d, 3 H), 2.0–2.3 (m, 5 H), 4.50 (s, 1 H); mass spectrum (M^+ at m/e) 170. 21: IR (liquid film, cm^{-1}) 1660; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9 H), 0.90 (d, 3 H), 1.5–2.6 (m, 7 H), 4.74 (d, 1 H); mass spectrum (M^+ at m/e) 184. 22: IR (liquid film, cm^{-1}) 1690, 1640; ^1H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 1.52 (s, 3 H), 1.69 (s, 3 H), 1.7–2.4 (m, 7 H), 4.68 (s, 2 H); mass spectrum (M^+ at m/e) 224. 23: IR (liquid film, cm^{-1}) 1680; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 0.88 (d, 6 H), 1.71 (s, 3 H), 4.28 (d, 1 H); ^{13}C NMR ($CDCl_3$) 0.61, 22.69, 23.27, 24.80, 116.99, 144.64 ppm; mass spectrum (M^+ at m/e) 172. Minor signals that may be assigned to the *E* isomer appear at δ 2.18 (br d) and 4.62 (br d) (^1H NMR) and at 22.4, 23.8, and 25.7 ppm (^{13}C NMR). The approximate ratio of the *Z* isomer to the *E* isomer was 9, which was determined by ^1H NMR. (*Z*)-24: IR (liquid film, cm^{-1}) 1670, 1610; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 9 H), 1.84 (d, J = 1 Hz, 2 H), 3.35 (d, J = 7 Hz, 2 H), 4.66 (t of quart, J = 7 and 1 Hz, 1 H), 7.14–7.42 (m, 5 H); mass spectrum (M^+ at m/e) 220. The ^1H NMR spectra of (*Z*)-24 was admixed with the signals of the *E* isomer: 3.32 (d, J = 8 Hz, 2 H) and 4.88 (t of quart, J = 8 and 1 Hz, 1 H). The ratio of the *Z* isomer to the *E* isomer was 2.6, which was determined by ^1H NMR of the olefinic protons.

1,4-Dehydrobromination of 1-Bromo-1,2,3-butatrienes: An Efficient Synthesis of 1,4-Disubstituted 1,3-Diynes

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Conjugated diynes are versatile synthetic intermediates[1] and are present in a number of natural products.[2] Here we report an efficient one-pot synthesis of phenyl-substituted conjugated diynes (Scheme I). The key to this approach is the Wittig synthesis of bromo[3]cumulenes **2** (buta-1,2,3-trienes). When treated with an alkoxide base in a protic solvent, these intermediates undergo a novel 1,4-elimination of HBr to form the product diyne **3**.

Phosphacumulene ylides (Scheme I) are established precursors in the preparation of aryl[3] and halogen[4]-substituted [3]cumulenes. Though they are generally unstable, the halo[3]cumulenes can be handled without much difficulty. However, only a few examples have been reported.[5] Our diyne preparation represents the first synthetic utilization of these cumulenes.

The phosphonium salt **1a** was prepared as shown in Scheme II by the bromination of 3-phenylpropynol to yield a 75:25 mixture of isomers **4a** and **4b**. A single recrystallization produced the *E* isomer, **4a**. Treatment of **4a** with triphenylphosphine at room temperature resulted in an 88% yield of **1a**. In the interest of simplicity and economy, the mixture of **4a** and **4b** was converted into isomeric **1b** (E/Z = 3) which in turn could be used with

(1) Some of the more recent examples on diacetylene synthesis: Stang, P. J.; Dixit, V. *Synthesis* **1985**, 962. Negishi, E.; Okukado, N.; Lovich, S. F.; Luo, F.-T. *J. Org. Chem.* **1984**, *49*, 2629. Rossi, R.; Carpita, A.; Bigelli, C. *Tetrahedron Lett.* **1985**, *26*, 523. Sinclair, J. A.; Brown, H. C. *J. Org. Chem.* **1976**, *41*, 1079. Holmes, A. B.; Jones, G. E. *Tetrahedron Lett.* **1980**, *21*, 3111. Also see: Hunstman, W. D.; In *Chemistry of the Carbon–Carbon Triple Bond* Patai, S., Ed.; Wiley: New York, 1978; Chapter 13.

(2) Parker, W. L.; Rathnun, M. L; Seiner, V.; Trejo, W. H.; Principe, P. A.; Sykes, R. B. *J. Antibiot.* **1984**, *37*, 431 and references therein. Szendrei, K.; Reisch, J.; Varga, E. *J. Phytochem.* **1984**, *23*, 901 and references therein. Garrod, B.; Lewis, B. G.; Coxon, D. T. *Physiol. Plant Pathol.* **1978**, *13*, 241. Jones, E. R. H.; Thaller, V. In *Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; pp 621–633. Holmes, A. B.; Jennings-White, C. L. D.; Kendric, D. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1594.

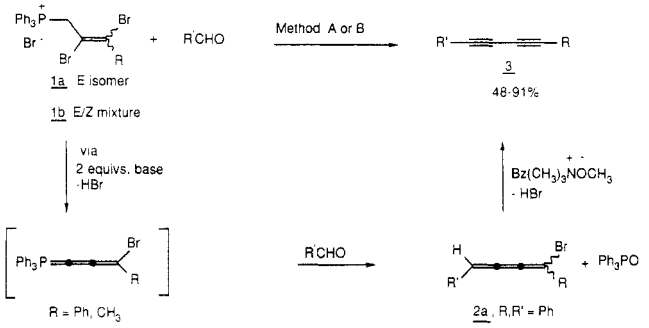
(3) Bestmann, H. J.; Schmid, G. *Tetrahedron Lett.* **1975**, 4025. Bestmann, H. J.; Saalfrank, R. W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 367. Bestmann, H. J.; Saalfrank, R. W.; Snyder, J. P. *Chem. Ber.* **1973**, *106*, 2601. Ratts, K. W.; Partos, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 6112.

(4) Arnold, R. D.; Baldwin, J. E.; Ziegler, C. B., Jr. *J. Chem. Soc., Chem. Commun.* **1984**, 152.

(5) These compounds are air-sensitive and best handled in dilute, argon-degassed CCl_4 solutions. A few examples of known bromo[3]cumulene preparations are the following: Schluback, H. H.; Trautschold, W. *Justus Liebigs Ann. Chem.* **1955**, *594*, 67. Fischer, H.; *Tetrahedron Lett.* **1969**, 435. Other than ref 4, the only example of chloro[3] cumulenes is the parent chlorobutatriene: Vistin, R.; Borg, A.; Lindblom, L. *Acta. Chem. Scand.* **1968**, *22*, 685.

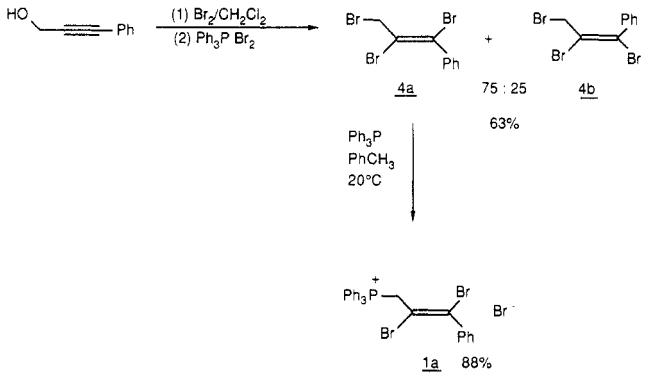
0022-3263/87/1952-0443$01.50/0

Scheme I[a]



[a] (A) $Bz(CH_3)_3N^+O^-CH_3/CH_3OH$, −60 to 0 °C; (B) (i) $LiN(SiMe_3)_2$/THF, −60 °C; (ii) R'CHO, −60 to −20 °C; (iii) $Bz(CH_3)_3N^+O^-CH_3/CH_3OH$, −20 to 0 °C.

Scheme II



little reduction in product diyne yield.[6]

In a typical reaction (see Experimental Section, method A) excess benzyltrimethylammonium methoxide[7] was slowly added to a methanolic solution of the salt (either **1a** or **1b**) and the aldehyde at −60 °C. Product diynes **3** are obtained simply on warming the reaction mixture to 0–20 °C followed by standard workup and purification. Diynes synthesized by this method are shown in Table I with a wide range of aldehydes being converted into phenyl-substituted diynes. These product diynes are presumably formed via the reaction sequence shown in Scheme I. The intermediate bromo[3]cumulene **2** can be isolated by a slight modification of the experimental procedure (method B). The choice of lithium bis(trimethylsilyl)amide in THF used here (R = Ph) facilitates the isolation of 1-bromo-1,4-diphenylbutatriene (**2a**) which was the only product seen (2:1 isomeric ratio, assumed *E*/*Z*).[8] Its identity was confirmed spectroscopically. Treatment of **2a** with excess benzyltrimethylammonium methoxide in methanol at −30 °C resulted in an extremely facile 1,4-dehydrobromination of both *E* and *Z* components to give diphenylbutadiyne (47%). These conditions are markedly simpler than those required in the eliminative route to the simpler parent acetylenic compounds which usually require more forcing conditions.[9]

This diyne synthesis also works well when other appropriately substituted phosphonium salts are used as starting materials. For example, (*trans*-2,3-dibromo-2-buten-1-yl)triphenylphosphonium bromide, prepared from 2-butyn-1-ol, reacted with benzaldehyde to yield a 64% yield of 1-phenyl-1,3-pentadiyne[10] (method A).

Experimental Section

Melting points were determined in open capillary tubes on a Mel-Temp appartus and are uncorrected. The following were used for spectral characterizations: Ultraviolet spectra, Varian Cary 219 spectrophotometer, mass spectra, Varian CH-7 spectrometer, IR spectra, FT Nicolet 7199 spectometer. ^1H (80 MHz) and ^{13}C (75 MHz) NMR spectra were recorded either on a Varian FT80 or a Nicolet NT-300 WB spectrometer. Analtech silica gel GF plates (250 mm) were used for thin layer chromatography. Silica gel (300–400 mesh), Merck Kieselgel 60, or Florisil (200–300 mesh) (Fluka) were employed for flash column chromatography. Solvents used were from freshly opened bottles of spectroscopy grade quality with no special drying procedures observed.

Synthesis of (*trans*-2,3-Dibromo-3-phenyl-2-propen-1-yl)triphenylphosphonium Bromide (1a) via 4a. A solution of 3-phenylpropyn-1-ol (26.4 g, 0.2 mol) in CH_2Cl_2 (100 mL) was slowly treated with bromine (32.9 g, 0.21 mole with stirring at 0 °C, the addition rate not exceeding the rate at which the bromine color was discharged. Removal of the CH_2Cl_2 in vacuo gave a quantitive yield of 2,3-dibromo-3-phenylpropen-1-ol: 58.0 g, (*E*/*Z* = 80:20); bp 128 °C (0.4 mm); ^1H NMR ($CDCl_3$) mixture δ 2.3 (s, 1, OH), 4.25, 4.7 (s, 2, CH_2), 7.4 (s, 5, Ar); IR ($CHCl_3$) ν_{max} cm^{-1} 3360 (OH), 3040, 2940, 2900; MS (CI), *m*/*e* (relative intensity) 294, 292, 290 (10, 23, 12), 277, 275, 273, (50, 100, 52), 213, 211, (21, 25). Anal. Calcd for $C_9H_8Br_2O$: C, 37.02; H, 2.76; Br, 54.74. Found: C, 36.75; H, 2.81; Br, 55.01.

A CH_2Cl_2 solution of triphenylphosphonium dibromide was prepared [(37.8 g, 0.237 mol) from Br_2 addition to 62.0 g (0.237 mol) of triphenylphosphine in CH_2Cl_2 (300 mL) at 0 °C]. To this was added 55.5 g (0.19 mol) of 2,3-dibromo-3-phenylpropen-1-ol in CH_2Cl_2 (50 mL). The reaction was warmed to 20 °C (2 h) and then quenched (H_2O). The product was isolated after an aqueous workup (hexane), drying with $MgSO_4$, then filtration and removal of the solvent in vacuo to give a solid (44.0 g, 63%). 1,2,3-Tribromo-3-phenylprop-2-ene (**4a** and **4b**) (75:25 *E*/*Z* isomers): ^1H NMR ($CDCl_3$) mixture δ 4.15, 4.55 (s, 2, CH_2), 7.3 (s, 5, Ar). The *E* isomer **4a** was isolated pure from methanol recrystallization: (mp 61 °C; ^1H NMR ($CDCl_3$) δ 4.6 (s, 2, CH_2), 7.4 (s, 5, Ar); IR ($CHCl_3$) ν_{max} cm^{-1} 3050, 3020, 1650, 1470, 1450; ^{13}C NMR ($CDCl_3$) δ 38.2, 76.6, 77.0, 117.3, 122.2, 128.2, 128.7, 129.2, 139.5; MS (CI), molecular ion not seen. Anal. Calcd for $C_9H_7Br_3$: C, 30.46; H, 1.99; Br, 67.55. Found: C, 30.20; H, 1.69; Br, 67.68.

Triphenylphosphine (19.7 g, 0.075 mol) and **4a** (23.7 g, 0.06 mol) were stirred in toluene (150 mL) at 20 °C for 36 h in a capped flask. The product salt was collected, washed with toluene and ether, and then dried in vacuo (80–90 °C/0.2 mm) to give 36.4 g (88%) of **1a**: mp 180–191 °C dec (cold Et_2O/EtOH); ^1H NMR ($CDCl_3$) δ toluene impurity, 5.8 (d, 2, CH_2, *J* = 15 Hz), 7.1–8.1 (m, 15, Ar); ^{31}P NMR ($CDCl_3$) δ +27.0; IR (KBr) H_2O impurity ν_{max} cm^{-1} 3050, 3010, 2820, 1620, 1580, 1480, 1440, 1100; MS (FAB), 535 (M^+), 455, 377, 262. Anal. Calcd for $C_{27}H_{22}Br_3P$: C, 52.55; H, 3.59; Br, 38.83; P, 5.02. Found: C, 52.52; H, 3.51; Br, 38.65; P, 4.94.

Similarly, mixtures of **4a** and **4b** were converted to **1b**. For instance, a 1:1 mixture of **2a** and **2b** yielded 22 g (91%) of **1b**: ^1H NMR ($CDCl_3$) δ toluene and H_2O impurity, δ 5.4, 5.8 (2 doublets, 2, CH_2, *J* = 15 Hz), 6.6–8.1 (m, 15, Ar); ^{31}P NMR ($CDCl_3$) δ +26.5 and +27.1.

(6) Reactions involving *E*/*Z* mixtures of **1b** produced similar yields of product diynes. For example, the yield of diphenylbutadiyne isolated from the reaction using **1a** was similar to that realized when **1b** (1:1 *E*/*Z*, 79%) was used under identical reaction conditions.

(7) A base study was performed whereby 3, 7, 10, and 13 equiv of base (relative to **1a**) were used in four reactions with benzaldehyde by using method A. The isolated yields of diphenylbutadiyne were 69%, 91%, 74%, and 78% respectively. Thus, 7 equiv of base were used in all the experiments.

(8) The intermediate cumulene **2a** can also be isolated by using 2 equiv of benzyltrimethylammonium methoxide in methanol at low temperature followed by an aqueous workup. However, the method described for **3** is more convenient and produces cleaner product mixtures. See the Experimental Section for the optimum synthetic procedure for **2a** as well as its spectroscopic data.

(9) Vinyl halides of mixed stereochemistry usually are not dehydrohalogenated with oxygen bases under such mild conditions as are reported here. See, for example: Ben-Efraim, D. A. In *Chemistry of the Carbon–Carbon Triple Bond* Patai, S., Ed.; Wiley: New York, 1978; pp 760–766.

(10) The physical properties matched those found in the literature: Taniguchi, H.; Mathai, I. M.; Miller, S. I. *Org. Synth.* **1970**, *50*, 97.

Table I. 1,4-Disubstituted 1,3-Diynes

no.	aldehyde used	product diyne	isol yield, %	mp/bp (°C) solvent (lit. value)	spectroscopic data: (C≡C) cm^{-1} ($CHCl_3$)	spectroscopic data: ^1H NMR ($CDCl_3$) δ	spectroscopic data: ^{13}C NMR ($CDCl_3$) δ	mol form	MS data m/e (rel int)	analytical data, calcd/found: C	H	N	S
3a	C_6H_5CHO	$C_6H_5C{\equiv}C\text{-}C{\equiv}CC_6H_5$	91	88, CH_3OH/H_2O (88)[a]	3040, 2140, 1590, 1480	7.4 (m)	74.2, 81.8, 121.9 128.6 (2), 129.4, 132.6 (2)	$C_{16}H_{10}$	202 (100)	95.02 95.07	4.98 5.05		
3b	4-ClC_6H_4-CHO	4-$ClC_6H_4C{\equiv}C\text{-}C{\equiv}CC_6H_5$[b]	77	131, CH_3OH/H_2O	3140, 3120, 2160, 1600, 1495, 1420	7.45 (m)		$C_{16}H_9Cl$	238, 236 (37 100), 200 (37)	81.19 81.44	3.83 3.78	14.98 15.03	
3c	4-CH_3O-C_6H_4C-HO	4-$CH_3OC_6H_4\text{-}C{\equiv}C\text{-}C{\equiv}CC_6H_5$[c]	43	85[h]	3060, 3000, 2940, 2840, 2220, 2140, 1600, 1520, 1490	3.8 (s, 3, OCH_3), 6.85 (d, 2, Ar, J = 8 Hz), 7.45 (m, 7, Ar)		$C_{17}H_{12}O$	232 (100), 217 (53), 189 (50)	87.53 87.72	5.62 5.27		
3d	1-$C_{10}H_7$-CHO	1-$C_{10}H_7C{\equiv}C\text{-}C{\equiv}CC_6H_5$[d]	60	78[h]	3060, 2220, 2140, 1590, 1500, 1440	6.8–7.65 (m)		$C_{20}H_{12}$	252 (100), 126 (17)	95.21 95.15	4.79 4.87		
3e	2-C_4H_3S-CHO	2-$C_4H_3SC{\equiv}C\text{-}C{\equiv}CC_6H_5$[e]	63	50[h]	3150, 3140, 3120, 2200, 2170, 1600, 1490, 1420	7.0 (m, 3 H) 7.3 (m, 7 H)	73.7, 74.5, 77.9, 83.6, 121.5, 121.9, 127.1, 128.4 (2), 128.6, 129.2, 132 (2), 134.2	$C_{14}H_8S$	208 (100), 163 (34)	80.73 80.59	3.87 4.10		15.39 15.01
3f	3-C_4H_3S-CHO	3-$C_4H_3SC{\equiv}C\text{-}C{\equiv}CC_6H_5$	60	86–87, (MeOH/H_2O)	3160, 2210, 2180, 1600, 1490, 1425	7.0 (m)		$C_{14}H_8S$	208 (100), 163 (20)	80.73 80.56	3.87 3.86		15.39 15.39
3g	3-C_5H_4N-CHO	3-$C_5H_4NC{\equiv}C\text{-}C{\equiv}CC_6H_5$	77	108–109, (MeOH/H_2O) (108–109)[f]	3080, 3060, 3020, 3000, 2210, 2140, 1560, 1480	7.5 (m, 7), 8.6 (dd, 1, J = 4 Hz), 8.8 (d, 1, J = 1 Hz)	73.3, 77.3, 77.9, 82.7, 119.3, 121.3, 123.0, 128.5 (2), 129.5, 132.5 (2), 139.3, 149.1, 153.0	$C_{15}H_9N$	203 (100), 176 (12), 150 (27)	88.65 88.63	4.46 4.44	6.89 6.70	
3h	t-CH_3-CH=C-H-CHO	t-$CH_3CH{=}C\text{-}HC{\equiv}C\text{-}C{\equiv}CC_6H_5$[g]	72	*i*	3060, 3030, 3000, 2920, 2240, 2210, 2140	1.85 (dd, 3 CH_3, J = 8 Hz, 2 Hz), 5.6 (dq, 1, J = 16.7 Hz), 6.4 (dq, 1, J = 16.7 Hz), 7.4 (m, 5, Ar)		$C_{13}H_{10}$	166 (78), 165 (100), 138 (31)				
3i	$CH_3(CH_2)_5$-CHO	$CH_3(CH_2)_5\text{-}C{\equiv}C\text{-}C{\equiv}CC_6H_5$[j]	48	*i*	3060, 3040, 2960, 2920, 2850, 2240, 1490, 1460	0.9 (t, 3, CH_3), 1.3 (m, 9, CH_2 + H_2O impurity), 2.35 (t, 2 H, CH_2), 7.4 (m, 5, Ar)		$C_{16}H_{18}$	210 (73), 195 (15), 181 (83), 167 (70), 149 (100)				

[a] Hay, A. *J. Org. Chem.* **1962**, *27*, 3320. [b] Safe, S. *Org. Mass Spectrom.* **1973**, *7*, 1329. [c] Reaction was warmed to 40° for two hours after addition of base. [d] Reaction was warmed to 20° for two hours after addition of base. [e] Rossi, R.; Carpita, A.; Bigelli, C. *Tetrahedron Lett* **1985**, *26*, 523. [f] Zimmer, H.; Hickey, K. R.; Schumacher, R. J. *Chimia* **1974**, *28*, 656. [g] Fairbrother, J. R. F.; Jones, E. R. H.; Thaller, V. *J. Chem. Soc. C* **1967**, 1035. [h] Melting points are of chromatographed products, no recrystallization done. [i] Unstable liquid. [j] Sinclair, J. A.; Brown, H. C. *J. Org. Chem.* **1976**, *41*, 1079.

Synthesis of 1,4-Diphenylbutadiyne (3). Method A. Benzyltrimethylammonium methoxide (20 mmol, as a 40% w/w MeOH solution) was slowly added to the phosphonium salt (1.85 g, 3 mmol) and benzaldehyde (450 mg, 4 mmol) in methanol (5 mL) with stirring under argon at -60 °C. The solution was gradually (1 h) warmed to 20 °C and then stirred for 2 h more. The product was isolated after an aqueous workup (Et_2O) and flash silica gel column chromatography (hexane) as 550 mg (91%) of colorless solid. All entries of Table I were prepared by this method.

Synthesis of *E*/*Z* Mixtures of 1-Bromo-1,4-diphenylbutatriene (2a). Method B. Lithium bis(trimethylsilyl)amide (6 mmol as a 1 M THF solution) was added dropwise to a THF suspension (10 mL) of the phosphonium salt **1a** (1.85 g, 3 mmol) at -70 °C under argon. The deep red solution was stirred for 15 min followed by the single-portion addition of benzaldehyde (448 mg, 4 mmol). The reaction was warmed to -25 °C (30 min) and then diluted with Et_2O (50 mL) and filtered through a plug of Florisil. The filtrate was adsorbed onto 20 g of Florisil by removing the solvent at 0-20 °C in vacuo. The product was isolated via flash column chromatography on Florisil (hexane). The product **2a**, a yellow oil, rapidly decomposed in the presence of air at room temperature and was best stored in argon degassed CCl_4 solutions at -20 °C or below: ^1H NMR ($CDCl_3$) *E*/*Z* mixtures δ 6.65, 6.83 (2 s, 1, vinyl, ratio 2:1), 7.2-7.6 (m, 9, Ar), 7.75 (m, 1, Ar); ^{13}C NMR ($CDCl_3/CCl_4$) isomers δ 101.0, 101.4, 109.4, 109.6 (CPh), 127.7, 127.85, 128.1, 128.2, 128.3, 128.4, 128.5, 128.8, 128.9, 129.1, 132.4, 135.8, 136.2, 136.4 (Ar), 152.5, 152.7, 154.6, 154.7 (cumulene carbons); IR (CCl_4) ν_{max} cm^{-1} 3040, 3010, 2010, 1600, 1480, 1435; MS (EI), *m*/*e* (relative intensity) 284, 282 (M^+, 4, 4), 202 (M^+ - HBr, 60), 105 (88), 82 (100).

The yellow oil **2a** was diluted with THF (10 mL) under argon at -30 °C. To this was slowly added (7 mmol, as a 40% w/w MeOH solution) benzyltrimethylammonium methoxide. The resultant solution was warmed to 0 °C (1.5 h) and then quenched (H_2O). The product diphenylbutadiyne, 275 mg (47%), was isolated as in method A.

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Registry No. **1a**, 105836-22-4; (*Z*)-**1b**, 105836-23-5; (*E*)-**2a**, 105836-26-8; (*Z*)-**2a**, 105836-27-9; **3a**, 886-66-8; **3b**, 51624-43-2; **3c**, 23429-36-9; **3d**, 105836-24-6; **3e**, 77093-14-2; **3f**, 105836-25-7; **3g**, 54334-99-5; **3h**, 13641-39-9; **3i**, 58672-84-7; **4a**, 105836-20-2; **4b**, 105836-21-3; PhCHO, 100-52-7; 4-ClC_6H_4CHO, 104-88-1; 4-$MeOC_6H_4CHO$, 123-11-5; (*E*)-$CH_3CH{=}CHCHO$, 123-73-9; $CH_3(CH_2)_5CHO$, 111-71-7; 3-phenyl-2-propyn-1-ol, 1504-58-1; *trans*-2,3-dibromo-3-phenyl-2-propen-1-ol, 105836-18-8; *cis*-2,3-dibromo-3-phenyl-2-propen-1-ol, 105836-19-9; benzyltrimethylammonium methoxide, 122-08-7; 1-naphthylenecarboxaldehyde, 66-77-3; 2-thiophenecarboxaldehyde, 98-03-3; 3-thiophenecarboxaldehyde, 498-62-4; 3-pyridinecarboxaldehyde, 500-22-1; lithium bis(trimethylsilyl)amide, 4039-32-1.

Reaction of 5-Substituted 2-Methoxy 1,4-Quinones with Boron Tribromide

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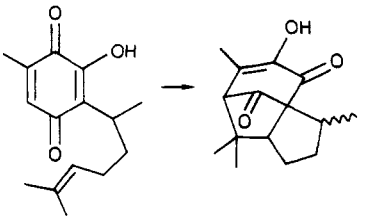
During a study designed to examine the perezone to pipitzol cyclization,[2] (eq 1), we prepared several 2-methoxybenzoquinones containing olefins. Attempted cleavage of the methyl ether moiety with boron tribromide (BBr_3) afforded unprecedented products, the nature of which we report here (Table I).



(1)

A methylene chloride solution of quinone **1**, **3**, **6**, or **9** was treated with BBr_3 at -78 °C for 4 h. The crude products were acetylated to facilitate purification. From literature reports with naphthoquinones,[3] we anticipated little difficulty with this reaction and therefore initially examined quinones **6** and **9**. We were surprised to isolate cyclic ethers **7a** and **7b** in 41% and 46% yields, respectively. Ether **7a** was accompanied by diacetate **8** in 36% yield. Quinone **1** gave a complex mixture containing diacetate **2** in 22% yield. Under these same reaction conditions, about half of quinone **3** was reduced and all of the olefin was brominated, resulting in products **4** and **5**.

The structures have been characterized by routine spectral techniques. The identification of all of the products except **7a** and **7b** requires no comment. Compounds **7a** and **7b** exhibited the expected mass spectral fragment losses of CH_2Br and $CHBrCH_3$, respectively. The carbon and proton magnetic resonance data are consistent with the assigned structures.

Previous reports about BBr_3 or quinone reactions do not suggest a mechanism. After completion of this work, BBr_3 has been shown to reduce sulfoxides to mercaptans[4] and borobrominate alkynes.[5] Neither of these reaction pathways can be invoked in this study. Moore[6] observed that HBr in acetic acid and some quinones yield hydroquinones and molecular bromine.

Moore's[6] report provides a basis for a mechanistic rationalization of our observations (Scheme I). The formation of ether **7** requires quinone reduction and the presence of a bromonium ion. We suggest that BBr_3 coordinates with the quinone carbonyl and that this complex loses bromide ion. Bromide can transfer an electron to the complex, generating a quinone radical and a bromide radical. A second bromide anion can combine with this radical pair to form molecular bromine and a hydroquinone anion complexed to BBr_2. Molecular bromine reacts with the olefinic side chain to provide the observed products.

Three experiments are forthcoming from this mechanism: First, the involvement of bromide anion suggests that added bromide might improve yields or increase reaction rates. Added LiBr did not affect the product mixture from **6**. Second, the analogy with Moore's report[6] implies that HBr/HOAc should give similar results. Quinones **3** and **6** gave the same product mixtures with

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