Proton-decoupled Fourier transform ^{13}C spectra were taken with a Bruker HFX-10 system at 22.62 MHz utilizing C_6F_6 in a 3-mm coaxial capillary as external heteronuclear lock. Chemical shifts were measured from internal Me_4Si for $CHCl_3$ solutions, and from internal CH_3OH for water solutions (δ CH_3OH = 141.2; δ CS_2 = 192.5 ppm). C–P coupling constants are ±1.2 Hz. Proton-decoupled ^{31}P NMR spectra (CW mode) were obtained at 36.43 MHz again with a C_6F_6 lock; offsets relative to prerun 85% H_3PO_4 were used to determine δ values. Ir spectra were obtained with a Perkin-Elmer 621 spectrophotometer, and uv spectra with a Cary 15 spectrophotometer.

1-Methyl-4-phosphorinanone Derivatives. The parent ketone 1 was prepared as described previously.[18] Its conversion to sulfide 2 has also been reported.[2] Phosphine 1 readily gave the salt 4 with CH_3I, which was used directly for the NMR study.

Oxidation of 1 was accomplished by stirring 3.0 g (23.1 mmol) in 50 ml of benzene with 1.98 ml (23.1 mmol) of 30% H_2O_2 in an ice bath for 1 hr. Stripping of solvents left a white solid residue of 3 which was recrystallized from a mixture of methylene chloride and petroleum ether: mp 138–142°; ir ($CHCl_3$) ν 1730 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.70 (d, $^2J_{PH}$ = 13 Hz, PCH_3); NMR (D_2O, 30°) δ 2.12 and 2.25 (1:1, each d, $^2J_{PH}$ = 13.5 Hz, PCH_3 for diol and keto forms, respectively, as seen from temperature effects). The compound is extremely hygroscopic and gave only partly satisfactory analyses.

Anal. Calcd for $C_6H_{11}O_2P$: C, 49.32; H, 7.54; P, 21.21. Found: C, 48.92; H, 7.97; P, 20.87.

Oxide 3, previously characterized as the oxime,[19] underwent exchange in D_2O at 75°. After 24 hr, a sample recovered by $CHCl_3$ extraction was found by mass spectral analysis to contain 50% d_4, 25% d_3, 12% d_2, and 7% d_1 derivative; only 3% remained undeuterated.

1-Ethyl-4-phosphorinanone Derivatives. The parent phosphine 5 has been reported previously.[20] Conversion to sulfide 6 was accomplished by a general procedure.[2] The sulfide after vacuum sublimation had mp 60–61.5°.

Anal. Calcd for $C_7H_{13}OPS$: C, 47.71; H, 7.44; P, 17.58. Found: C, 47.83; H, 7.50; P, 17.48.

Phosphine 5 was also oxidized to form compound 7, which had previously been characterized as the oxime.[19] Quaternization of 5 with CH_3I gave salt 8 for the NMR studies.

Registry No.—**1,** 16327-48-3; **2,** 55298-82-3; **3,** 54662-09-8; **4,** 55298-83-4; **5,** 55298-84-5; **6,** 55298-85-6; **7,** 51805-19-7; **8,** 1194-42-9; **9,** 55298-86-7; **10,** 55298-87-8; **11,** 55298-88-9; **12,** 55298-89-0; **13,** 55298-90-3; **14,** 55298-91-4.

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Preparation of (*E,E*)- and (*Z,Z*)-1,4-Dibromo-1,4-diphenylbutadienes and Conversion to Mono- and Dilithio Derivatives

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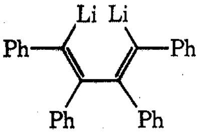
The ready availability of the dilithium reagent 1 by reduction of tolane[1,2] has resulted in its widespread use for the preparation of metallocycles (heterocyclopentadienes).[1a–c,3] The 1,4-diphenyl dilithio compound 2 should be equally and perhaps even more useful than **1.** The published synthesis[4] of the precursor dibromide **4a** is a five-step sequence, however, so that **2** and **4a** have been used infrequently.[5]



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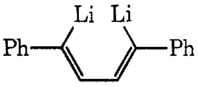

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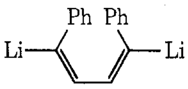
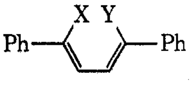


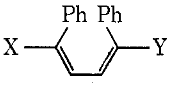
3

We required dibromides **4a** and **5a,** as well as the mono- and dilithium reagents derived from them, in connection with studies on the preparation of chlorolium ions.[6] The most convenient synthesis of **4a** and **5a** would appear to be by bromination–dehydrobromination of the readily available 1,4-diphenylbutadiene.[7] We have developed procedures for the preparation of **4a** and **5a** in pure form by this route. The yields are low, but the procedures are simple, and the products are obtained in pure form by a single crystallization. The principal separation is performed at the tetrabromide stage; the precursor for **5a** is extremely insoluble and is filtered off after the bromine addition. Dehydrohalogenation (KOH–EtOH) of crystals and mother liquor gives the dibromides **5a** and **4a,** respectively.



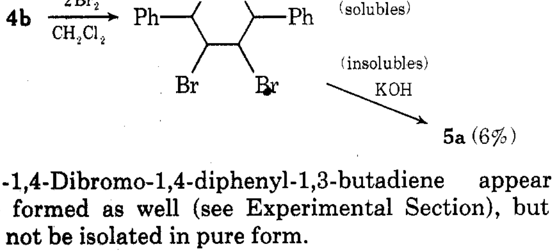
4

	a	**b**	**c**	**d**	**e**	**f**	**g**
X	Br	H	Cl	SCH_3	Br	Br	Br
Y	Br	H	Cl	SCH_3	H	Cl	SCH_3



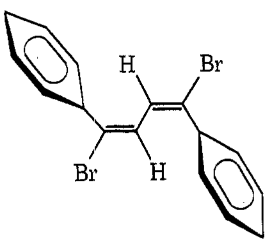
5

	a	**b**	**c**
X	Br	H	Br
Y	Br	H	Li



(*E,Z*)-1,4-Dibromo-1,4-diphenyl-1,3-butadiene appeared to be formed as well (see Experimental Section), but it could not be isolated in pure form.

Stereochemical assignments were made on the basis of several arguments. The chemical shifts of the vinyl protons in **4a** and **5a** are δ 7.30 and 6.63. The pronounced upfield shift in the *E,E* isomer (**5a**) can be in part ascribed to the operation of a phenyl ring current effect. Apparently steric interactions of the ortho protons with the bromine and cis vinyl group result in the phenyl ring being turned out of the diene plane, so that the vinyl hydrogen is located in the shielding region of the phenyl ring current (see conformation **6**). An upfield shift of H_a (δ 6.64) in **7** was attributed to



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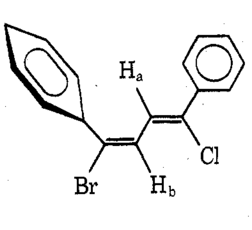


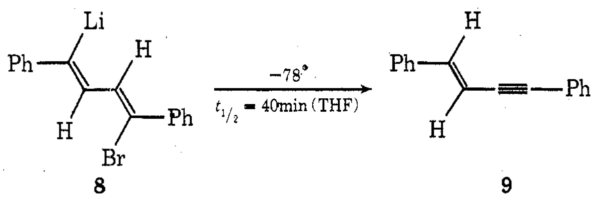
7

the same effect[6] (assignments were unambiguous in 7 since both monodeuterated compounds were also prepared). Proton H_b in 7 appears at δ 7.32, indicating that simply being on an *E* double bond does not result in an upfield shift. Further stereochemical evidence is found in the facile elimination of **4a** to 1,4-diphenylbutadiyne, whereas **5a** is resistant to dehydrohalogenation by KOH in refluxing ethanol.

Compound **4a** was identical in physical and chemical properties with the dibromide prepared by Gilman and coworkers.[4] These workers called this compound the trans,trans isomer, but a figure showed the *E,E* configuration. Their compound undoubtedly has the *Z,Z* structure (**4a**), since the derived dilithium reagent was converted to dimethyl-2,5-diphenylsilole or (*E,E*)-1,4-diphenylbutadiene (**4b**) by reaction with dimethyl dichlorosilane or water. We have confirmed the conversion of **2** to **4b** by protonation and have also shown that protonation of **3** gives (*Z,Z*)-1,4-diphenyl-1,3-butadiene (**5b**). The stereochemistry of the 1,4-diphenyl-1,3-butadienes has been previously assigned.[8] The formation and reactions of vinyllithium reagents, when stereospecific, invariably occur with retention of configuration.[9] Only a small amount of isomerization is observed when the presumably thermodynamically less stable dilithium compound **3** is converted back to dibromide **5a** by reaction with 1,2-dibromoethane.

The dilithio derivative **2** has also been converted to the dichloro (**4c**, reaction with hexachloroethane) and the bismethylthio (**4d**, reaction with dimethyl disulfide) compounds.

Treatment of **4a** with only 1 equiv of *n*-butyllithium gives the monolithio compound **8**, with only a few percent of **2** and **4a** as contaminants. When **8** is prepared in THF, extreme care must be taken to avoid warming the solution above −78° (the *n*-BuLi solution must be cooled to −78° before addition), and the anion must be derivatized promptly to avoid decomposition to **9**. This reaction probably occurs by intramolecular dehydrohalogenation, again consistent with the assigned stereochemistry. In ether solution, however, the anion can be prepared and utilized at 0°, with little formation of **9** even after several hours at this temperature. Huge solvent effects on the rate of reaction of organolithiums on going from THF to ether have been observed previously.[2a,9c,10] We have prepared **4e**, **4f**, and **4g** by protonation, chlorination (C_2Cl_6), and methylsulfenylation (Me_2S_2) of **8**. The NMR spectrum of the monobromo compound **4e** provides further stereochemical evidence. The proton at C-4 is a doublet with *J* = 16 Hz, characteristic of a trans vinyl coupling.



8 9

The monolithio derivative of **5a** (**5c**) can also be prepared by metal–halogen interchange in ether (0°). This anion does not decompose to **9** in THF at −78°, but it appears to react slowly with the butyl bromide present.

Experimental Section

Nuclear magnetic resonance spectra were measured in carbon tetrachloride using a Jeol MH-100 spectrometer. A 5 ft × 0.125 in. column of 3% SE-30 on 100/120 Varaport 30 was used for analytical GLC. Tetrahydrofuran (THF) was freshly distilled from $LiAlH_4$; ether was Mallinckrodt reagent grade. All reactions involving organometallics were carried out in an atmosphere of nitrogen.

In the standard work-up for the organometallic reactions, the reaction mixture was poured into 1:1 ether–pentane and saturated $NaHCO_3$ solution and shaken. The aqueous layer was removed and the organic layer was washed with NaCl solution, dried (Na_2SO_4), and evaporated.

All of the dienes prepared here were configurationally stable when crystalline. Most of the compounds also showed little tendency to isomerize during normal laboratory manipulations, but solutions of the methylthio compounds **4d** and **4g** isomerized over a period of hours during exposure to fluorescent room lights.

(*Z,Z*)-1,4-Dibromo-1,4-diphenyl-1,3-butadiene (4a) and (*E,E*)-1,4-Dibromo-1,4-diphenyl-1,3-butadiene (5a). A solution of 8 ml (0.149 mol) of Br_2 in 25 ml of dichloromethane was added dropwise over about 45 min to a solution of 16 g (0.078 mol) of **4b** in 300 ml of dichloromethane which was stirred magnetically. After the addition stirring was continued for an additional 15 min. The white insoluble tetrabromide which was formed was removed by vacuum filtration. It was transferred to a flask, heated with 50 ml of dichloromethane, filtered and washed thoroughly with dichloromethane, giving 7.47 g. A sample of the tetrabromide was recrystallized by soxhlet extraction with dichloromethane to give material with mp 263° dec.

Anal. Calcd for $C_{16}H_{14}Br_4$: C, 36.54; H, 2.68. Found: C, 36.64; H, 2.78.

The total filtrate was evaporated, 250 ml of absolute ethanol was added, and the mixture was cooled in an ice bath. While the mixture was stirred mechanically 16 g (0.24 mol) of KOH pellets was added in portions at such a rate that the temperature of the reaction mixture was kept below 15°. After 45 min, when all the KOH had dissolved, the ice bath was removed, stirring was continued for 3.5 hr at 25°, $NaHCO_3$ (16 g, 0.19 mol) was added to the slurry, and the ethanol was evaporated. Ether (150 ml), pentane (100 ml), and water (150 ml) were added to the residue. After stirring for 10 min the mixture was filtered, giving a further 1.18 g of insoluble tetrabromide which was washed with ether and water. The organic layer of the filtrate was washed with NaCl solution, dried (Na_2SO_4), and evaporated. The resulting semisolid was crystallized from 20 ml of hexane at 4°, yielding 5.30 g (19%) of **4a**, mp 117–120°, which was 97% pure by analytical GLC. A second crystallization from hexane gave material with mp 122–123° (lit.[4] mp 121–123°); NMR δ 7.2–7.4 (m, including a sharp singlet at 7.30, 8 H), 7.5–7.7 (m, 4 H). The mother liquor from the above crystallization was dissolved in pentane (20 ml) and allowed to crystallize, giving mainly 1,4-diphenylbutadiyne (1.1 g). The filtrate (13.0 g) showed a doublet at δ 6.73 (*J* = 11 Hz), which was assigned to (*E,Z*)-1,4-dibromo-1.4-diphenyl-1,3-butadiene (about 25% of the sample by NMR integration). The chemical shift is as expected on the basis of data for **7**.

The combined insoluble tetrabromide obtained above (8.65 g, 0.016 mol) was refluxed with 4.2 g (0.064 mol) of KOH in 125 ml of absolute ethanol for 4 hr, $NaHCO_3$ (4.2 g, 0.05 mol) was added, and the ethanol was evaporated. Ether (100 ml) and water (100 ml) were added with swirling. Work-up as above followed by crystallization from 10 ml of hexane at 25° (cooling below 25° may result in cocrystallization of 1,4-diphenylbutadiyne) gave 1.56 g (6%) of **5a**, mp 135–138° [NMR δ 6.63 (s, 2 H), 7.2–7.6 (m, 10 H)] which had less than 1% of volatile impurities by analytical GLC and was >90% pure by NMR integration. Further crystallization from ether, hexane, or ethanol gave lower melting material of variable melting point. This erratic behavior could be caused by the change in concentration of an unidentified nonvolatile impurity.

Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32. Found: C, 52.81; H, 3.31.

(*Z,Z*)-1,4-Dichloro-1,4-diphenyl-1,3-butadiene (4c). To a magnetically stirred solution of 3.3 ml of *n*-butyllithium (1.19 *M* in hexane, 4.0 mmol) in 6 ml of THF at −78° was added 0.364 g (1.0 mmol) of **4a**. After stirring for 15 min at −78°, 1.23 g (5.0 mmol) of hexachloroethane (crystallized from hexane) was added, the cooling bath was removed, and after 10 min the reaction mixture was worked up. The resulting solid was crystallized from ethanol, yielding 0.247 g (90%) of **4c**, mp 117–118°, NMR δ 7.1–7.4 (m, including a sharp singlet at 7.27, 8 H), 7.5–7.8 (m, 4 H).

Anal. Calcd for $C_{16}H_{12}Cl_2$: *m/e* 274.03160. Found: *m/e* 274.03202.

(*Z,Z*)-1,4-Bis(methylthio)-1,4-diphenyl-1,3-butadiene (4d). To a magnetically stirred solution of 2.5 ml of *n*-butyllithium (1.19 *M* in hexane, 3.0 mmol) in 6 ml of THF at −78° was added 0.366 g (1.0 mmol) of **4a**. After stirring for 15 min at −78° 0.40 ml (5.0 mmol) of dimethyl disulfide was added, the cooling bath was removed, and after 10 min the reaction mixture was worked up in the usual way including a 5% NaOH wash. The resulting solid was crystallized from ethanol to yield 0.203 g (68%) of **4d**, mp 123–130°. Recrystallization from hexane yielded a sample with mp 131–133°; NMR δ 2.00 (s, 6 H), 7.0–7.4 (m, including a sharp singlet at 7.14, 8 H), 7.4–7.7 (m, 4 H).

Anal. Calcd for $C_{18}H_{18}S_2$: *m/e* 298.08499. Found: *m/e* 298.08474.

(*Z,E*)-1-Bromo-1,4-diphenyl-1,3-butadiene (4e). An ether solution (15 ml) of 0.366 g (1.0 mmol) of **4a** was cooled to 0° with stirring, resulting in a fine suspension, and 0.80 ml of *n*-butyllithium (1.19 *M* in hexane, 1.0 mmol) was added dropwise. After 3 min 0.2 ml of methanol was added to the reaction mixture followed by the usual work-up. GLC analysis showed 95% monolithiation accompanied by 2.6% dilithiation and 2.5% unreacted starting material. Crystallization from pentane yielded 0.246 g (86%) of solid: mp 78–79°; NMR δ 6.84 (d, *J* = 16 Hz, 1 H), 7.02 (d, *J* = 10 Hz, 1 H), 7.1–7.8 (m, 11 H). An analytical sample was collected by preparative GLC on a 0.25 × 8 in. column of 20% SE-30 on 60/80 Chromosorb W, AW-DMCS, mp 79–80°.

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.38; H, 4.59. Found: C, 67.36; H, 4.62.

(*Z,Z*)-1-Bromo-4-chloro-1,4-diphenyl-1,3-butadiene (4f). To 4.5 ml of THF was added 0.02 ml of *n*-butyllithium (1.19 *M* in hexane) followed by 0.185 g (0.50 mmol) of **4a**. After the solid had dissolved, the solution was cooled to −78° and 0.44 ml (0.52 mmol) of *n*-butyllithium which had been cooled to −78° was added. After stirring for 3 min, hexachloroethane (0.149 g, 0.63 mmol) was added, the cooling bath was removed, and after 10 min the reaction was worked up. The solid was crystallized from ethanol, yielding 0.135 g (84%) of **4f**, mp 107–108°, identical with authentic material.[6]

(*Z,Z*)-1-Bromo-4-methylthio-1,4-diphenyl-1,3-butadiene (4g). To 15 ml of ether was added 0.04 ml of *n*-butyllithium (1.19 *M* in hexane) followed by 0.364 g (1.0 mmol) of **4a**. After the solid had dissolved, the solution was cooled to 0° and 0.86 ml (1.0 mmol) of *n*-butyllithium was added dropwise with magnetic stirring. After 3 min dimethyl disulfide (0.11 ml, 1.4 mmol) was added and the reaction mixture was worked up as usual (5% NaOH wash). The product was crystallized from hexane, yielding 0.255 g (77%) of **4g**, mp 80–81°. Another crystallization gave material with mp 83–84°; NMR δ 2.02(s, 3 H), 6.87 (d, *J* = 10 Hz, 1 H), 7.1–7.4 (m, 6 H), 7.4–7.7 (m, 5 H).

Anal. Calcd for $C_{17}H_{15}SBr$: *m/e* 330.00775. Found: *m/e* 330.01078.

(*Z,Z*)-1,4-Diphenyl-1,3-butadiene (5b). An ether solution (15 ml) of 0.364 g (1.0 mmol) of **5a** was cooled to 0° and 2.5 ml of *n*-butyllithium (1.19 *M* in hexane, 3.0 mmol) was added. Methanol (0.2 ml) was added and the reaction mixture was worked up. The product was crystallized from methanol to give 0.134 g (65%) of **5b**, mp 66–68°. A second crystallization from pentane gave material with mp 69–70° (lit.[8] mp 70–70.5°); NMR δ 6.46 (closely spaced AA′BB′, 4 H), 6.9–7.4 (m, 10 H).

Bromination of 3. The dianion **3** was prepared as above and quenched with dibromoethane. NMR showed the product to be **5a**, about 80% pure. GLC analysis indicated that **5a** was 83% pure (retention time 3.6 min at 195°); the impurities, identified by GLC retention times, being 2% of **5b** (0.9 min), 10% of (*E,Z*)-1-bromo-1,4-diphenyl-1,3-butadiene (1.8 min), 0.2% of **4a** (6.6 min), and 5% of a peak tentatively identified as (*E,Z*)-1,4-dibromo-1,4-diphenyl-1,3-butadiene (4.3 min). Thus the formation and reaction of **3** appears to give 94% isomerically pure product with retention of configuration.

Preparation and Decomposition of Monoanion 5c. To a solution of 0.364 g (1.0 mmol) of **4a** in 4.5 ml of THF at −78° was added 0.84 ml of *n*-butyllithium (1.19 *M* in hexane, 1.0 mmol) diluted with 1.5 ml of THF, which had been cooled to −78°. The reaction mixture was stirred at −78° and aliquots were removed and quenched with methanol at −78°. GLC determination of the ratio of **9** to **4e** at four intervals showed **9** increasing with a first-order rate constant of $3.1 \pm 0.1 \times 10^{-4}$ sec^{-1}. The retention times of **9** and **4e** were 1.3 and 3.5 min at 195°. After 3 hr GLC analysis showed 93% **9** and the reaction mixture was worked up. (*E*)-1,4-Diphenyl-3-buten-1-yne (*9*) was identified from its NMR spectrum and GLC retention time: NMR δ 6.30, 6.95 (AB q, *J* = 16.3 Hz, 2 H), 7.1–7.5 (m, 10 H).

Acknowledgment. We thank the Research Corporation and the National Science Foundation for support of this work.

Registry No.—**2**, 55373-67-6; **4a**, 55373-68-7; **4b**, 538-81-8; **4c**, 55373-69-8; **4d**, 55373-70-1; **4e**, 55373-71-2; **4f**, 52516-76-4; **4g**, 55373-72-3; **5a**, 7641-45-4; **5b**, 5807-76-1; **9**, 13343-79-8; bromine, 7726-95-6; 1,2,3,4-tetrabromo-1,4-diphenylbutane, 53446-15-4; hexachloroethane, 67-72-1; dimethyl disulfide, 624-92-0.

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Preparation of Monolithium Acetylide in Tetrahydrofuran. Reaction with Aldehydes and Ketones

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We wish to report a highly convenient and simple method for the preparation of amine-free monolithium acetylide in tetrahydrofuran. This monolithium acetylide reacts with a variety of aldehydes and ketones under exceptionally mild conditions to give high yields of the corresponding ethynyl carbinols.

Monolithium acetylide is a valuable reagent for the preparation of ethynyl carbinols and terminal acetylenes.[1] One disadvantage of this reagent is that it readily disproportionates into dilithium acetylide and acetylene in the absence of a complexing agent.[2] Therefore the reagent is usually prepared in liquid ammonia, which presumably serves

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