ing 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 ± 0.1 × 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).

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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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Table I
Addition of Monolithium Acetylide to Aldehydes and Ketones

RCOR'	Registry no.	% yield[a] of RR'C(OH)—C≡CH	Registry no.	n^{20}D or mp, °C
Acetone	67-64-1	94	115-19-5	
Hexanal	66-25-1	98	818-72-4	1.4420
2-Hexanone	591-78-6	92	17356-17-1	1.4366
Diisobutyl ketone	108-83-8	75, 86[b]	10562-68-2	1.4419
Di-*sec*-butyl ketone	19549-84-9	89	55373-73-4	1.4542
Di-*tert*-butyl ketone	815-24-7	66, 98[b]	33420-19-8	1.4584
Phenylacetone	103-79-7	94	55373-74-5	1.5289
Acetophenone	98-86-2	75	127-66-2	48–50
Benzaldehyde	100-52-7	93	4187-87-5	1.5466
Benzophenone	119-61-9	(85)	3923-52-2	47–48
Cinnamaldehyde	104-55-2	96	14604-31-0	65–66
Mesityl oxide	141-79-7	86 (77)	20109-03-9	1.4625
β-Ionone	14901-07-6	93	17075-53-5	1.5124
Cyclopentanone	120-92-3	94	17356-19-3	1.4725
Cyclohexanone	108-94-1	95	78-27-3	31–33
Cycloheptanone	502-42-1	90 (83)	2809-78-1	1.4896
Cyclooctanone	502-49-8	86	55373-76-7	43–44
Norcamphor	497-38-1	97 (92)[c]	55373-77-8	46–47
Cyclohexanecarboxaldehyde	2043-61-0	98	4187-88-6	1.4830

[a] By VPC based on RCOR'. Isolated yields are in parentheses. [b] 100% excess monolithium acetylide was used. [c] The product was >99% 2-ethynyl-*endo*-2-norbornanol by VPC and ^{13}C NMR examination.

$$2LiC{\equiv}CH \longrightarrow LiC{\equiv}CLi + HC{\equiv}CH$$

as an appropriate complexing agent. An amine, such as ethylenediamine, may similarly be used to stabilize the monolithium acetylide.[3] However, the addition of an amine complexing agent may greatly diminish the reactivity of the monolithium acetylide.

For certain reactions it may be desirable to have the amine-free monolithium acetylide in a solvent, such as tetrahydrofuran. It has been reported that monolithium acetylide may be prepared from acetylene and lithium dispersion in tetrahydrofuran,[4] but Beumel and Harris were unable to reproduce this work.[3] It has also been reported that monolithium acetylide may be prepared from acetylene and lithium napthalide in tetrahydrofuran.[5] However, addition of this lithium acetylide to aldehydes or ketones gives only low yields of ethynyl carbinols. In light of the shortcomings of these preparative methods, we have investigated the preparation of amine-free monolithium acetylide and have developed a convenient procedure based on the reaction of *n*-butyllithium with acetylene.

Addition of *n*-butyllithium to acetylene in tetrahydrofuran at 0° produces a heavy white precipitate. The use of excess acetylene does not suppress the formation of the precipitate. Addition of acetone to this suspension gives only a low yield (32%) of the desired carbinol. If monolithium acetylide is formed under these conditions, it rapidly disproportionates into the more stable dilithium acetylide, which is insoluble.

However, addition of *n*-butyllithium to acetylene at −78° results in a clear solution. Addition of hexanal to this solution, followed by warming to room temperature, produces an essentially quantitative yield of 1-octyn-3-ol.

$$HC{\equiv}CH + n\text{-}C_4H_9Li \xrightarrow[THF]{-78^\circ} LiC{\equiv}CH + C_4H_{10}$$

$$n\text{-}C_5H_{11}CHO + LiC{\equiv}CH \xrightarrow[THF]{-78^\circ} \xrightarrow[H_2O]{25^\circ}$$

$$n\text{-}C_5H_{11}\underset{\displaystyle OH}{\underset{|}{C}}HC{\equiv}CH \quad 98\%$$

The monolithium acetylide is fairly stable when maintained at low temperatures. The solution remains clear for several hours at −78°. Use of such a solution, maintained at −78° for 6 hr, results in a small decrease in the yield of 1-octyn-3-ol to 87%. Warming the solution of monolithium acetylide to 0° results in the irreversible formation of a white solid, presumably dilithium acetylide. Cooling this solution to −78°, followed by addition of hexanal, produces only 39% of the carbinol. Tetrahydrofuran apparently forms a complex which stabilizes the monolithium acetylide at the lower temperatures, but not at the higher temperatures. This unusual stability makes amine-free monolithium acetylide exceptionally suitable for ethynylation reactions.

The monolithium acetylide was added to a number of aldehydes and ketones (Table I). As a standard procedure, the reactants were stirred at −78° for 20 min and then brought to room temperature. In all cases, the reactions appeared to be essentially complete under these conditions. Thus, this monolithium acetylide appears to be far more reactive than lithium acetylide–ethylenediamine. The latter reagent requires longer reaction times and, in some cases, forcing conditions.[6] The milder conditions of the present reagent minimize the occurrence of side reactions, such as diol formation.

Optimum yields are obtained with an approximately 0.5 *M* concentration of monolithium acetylide. At 1.0 *M* the solution becomes slightly cloudy and yields are 10–15% lower.

Most compounds give satisfactory results with a 1:1 ratio of acetylide to carbonyl compounds. As a standard practice, a 10% excess of acetylide is recommended. Certain hindered ketones, such as diisobutyl or di-*tert*-butyl ketone, give somewhat lower yields unless excess monolithium acetylide is used.

This process allows one for the first time to prepare an amine-free tetrahydrofuran solution of monolithium acetylide. The ready availability and high reactivity under exceptionally mild conditions should make it a valuable synthetic reagent.

Experimental Section

Tetrahydrofuran was distilled from lithium aluminum hydride and stored under nitrogen. Acetylene (welding grade) was purified by passage through a −78° trap, then a sulfuric acid trap, and finally through soda lime. The acetylene was transferred to the reaction flask with a gas syringe.[7] *n*-Butyllithium in hexane (Alfa) was standardized by the method of Watson and Eastham.[8]

All ketones were obtained commercially and were used without further purification. All aldehydes were obtained commercially and were distilled under nitrogen prior to use.

All glassware was dried in an oven at 130° for several hours, then assembled hot and flushed with nitrogen while cooling. Liquids were transferred using syringe and double-ended needle techniques.[9,10] Solids were dissolved in tetrahydrofuran and transferred as the solution.

Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 700 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian T-60 and Varian CFT-20 spectrometer, respectively, using tetramethylsilane as an internal standard. High-resolution mass spectra were obtained on a CEC 21-110 instrument. A Hewlett-Packard 5750 gas chromatograph was used for VPC analysis using either a 6 ft × 0.25 in. 10% SE-30 or 10% XE-60 column with Chromosorb W as a stationary phase. Decane (Philips 99%) was used as an internal standard.

General Procedure for Monolithium Acetylide Preparation. 2-Ethynyl-*endo*-2-norbornanol. A dry 500-ml flask equipped with a magnetic stirring bar and septum-capped inlet was connected to a mercury bubbler and flushed with nitrogen. Tetrahydrofuran (200 ml) was placed in the flask and the flask was cooled in a Dry Ice–acetone bath. Acetylene (110 mmol) was added by means of a large gas syringe. *n*-Butyllithium (110 mmol, 49 ml of a 2.24 *M* solution in hexane) was measured into a graduated cylinder[10] by double-ended needle and then transferred dropwise into the reaction flask over a 15-min period. The solution was stirred for 10 min. Norcamphor (100 mmol, 11.1 g) was placed in a graduated cylinder and dissolved in 30 ml of tetrahydrofuran. The solution was added over a 5-min period to the monolithium acetylide. An additional 5 ml of tetrahydrofuran was used to wash the last of the norcamphor into the reaction flask. The solution was stirred for 20 min at −78° and then warmed to room temperature. Water (40 ml) was added followed by anhydrous potassium carbonate until the aqueous phase became pasty. The organic phase was decanted and the aqueous layer was washed with 2 × 30 ml of ether. The combined organic phase was dried (magnesium sulfate) and distilled through a short-path distillation head. There was obtained 12.5 g (92%), bp 84–86° (15 mm). The product solidified upon cooling on Dry Ice: mp 46–47° (lit.[11] mp 45–46°); ^1H NMR ($CDCl_3$) δ 2.47 (s, C≡CH), 2.43–1.2 (complex m, ring H and OH); proton-decoupled ^{13}C NMR δ C_1, 49.6; C_2, 73.1; C_3, 47.6; C_4, 36.8; C_5, 26.7; C_6, 21.0; C_7, 38.7; terminal acetylene, 90.1; internal acetylene, 71.1; exact mass (P − 1) 135.083 (calcd, 135.081).

VPC analyses were obtained from 5-mmol scale reactions. All products were isolated from these reactions by Kugelrohr distillation or preparative VPC. All products exhibited consistent ir, NMR, and mass spectra. Satisfactory exact mass measurements (±0.003 mass units) were obtained for all compounds.

Stability. In a dry 50-ml flask was prepared 5 mmol of monolithium acetylide in 10 ml of tetrahydrofuran. The solution was stirred for 6 hr in a Dry Ice–acetone bath. Then 5 mmol of hexanal was added. After 20 min the flask was warmed to room temperature and 2 ml of water was added. The solution was saturated with potassium carbonate and 5 mmol of decane was added. Analysis by VPC revealed 4.35 mmol (87%) of 1-octyn-3-ol.

In a similar manner, 5 mmol of monolithium acetylide was prepared and after 10 min it was warmed to 0° for 15 min, then cooled to −78°. A white precipitate had formed at 0°. Hexanal was added and the reaction was worked up as above. Analysis revealed 1.95 mmol (39%) of 1-octyn-3-ol.

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Registry No.—Monolithium acetylide, 1111-64-4; acetylene, 74-86-2; *n*-butyllithium, 109-72-8.

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A Facile Synthesis of 1-(Carbethoxyethoxymethyl)camphene

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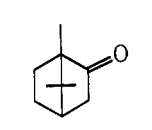
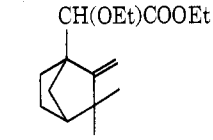
The potential of camphene derivatives possessing a functionalized C-1 side chain as synthetic precursors of natural products and related compounds has been realized in the recent syntheses of isolongifolene[1] and zizaane-type sesquiterpenoids.[2,8] The methods available for their preparation[1-7] were, however, limited to multistep transformations of camphor (1) and often gave the desired products in unsatisfactory yields. In connection with our studies on the regioselectivity of boron trifluoride catalyzed ring enlargement of unsymmetrically substituted cycloalkanones,[8] we have discovered an efficient conversion of *dl*-camphor (1) to the title compound (2) which should prove synthetically useful, particularly in constructing naturally occurring compounds of the zizaane family.[9]



1



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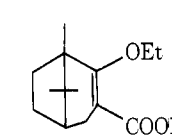

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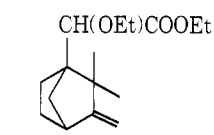

4

Prolonged treatment of *dl*-camphor (1) with an excess of boron trifluoride etherate and ethyl diazoacetate in ether afforded, in addition to a minor amount of 3-carbethoxy-2-ethoxy-1,8,8-trimethylbicyclo[3.2.1]oct-2-ene (3),[8] a mixture of 1-(carbethoxyethoxymethyl)camphene (2) and its positional isomer 4 (2:1) in 63% yield.[10] Subsequent treatment of the mixture with zinc dust and glacial acetic acid at reflux for 24 hr resulted in an essentially quantitative and clean rearrangement of 4 to 2. The structure of 2 was readily assigned on the basis of its spectral data (see Experimental Section) and was further confirmed by its conversion to crystalline iodo lactone 5. The sharp spectral peaks and thin layer chromatographic behavior of 2 and 5 coupled with the sharp melting point of 5 are suggestive of single stereoisomers of both 2 and 5. The data presently available, however, do not permit unambiguous definition of their stereochemistry.