1.07 (2 methyl groups), *ca.* 3.0 (CHCN, m), 3.60 (CH_2OH, broad s).

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.70; H, 10.15; N, 8.44.

Registry No.—**1**, 40962-87-6; **2**, 40962-88-7; **3**, 40962-89-8; **4**, 40962-90-1; **5**, 40962-91-2; **6**, 40962-92-3; **7**, 13854-87-0; **8**, 32231-98-4; **9**, 40962-95-6; **10**, 40962-96-7; **11**, 40962-97-8.

Synthetic Reactions of Propynyllithium and Propynylsodium

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An investigation of the reactions in aprotic solvents of propynyllithium and propynylsodium is reported. Optimum conditions for the formation of 1-(1-propynyl)cyclohexanol, 91% yield, and 2-butynoic acid, 87% yield, are given. A number of other reagents reacted with these two propynyl alkali metal compounds in good to high yield. The coupling of these compounds with alkyl halides was studied in a number of solvents.

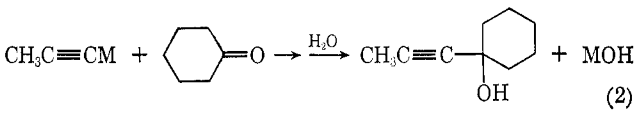
Considerable literature exists describing the optimum conditions for the reaction of alkali metal acetylides ($HC{\equiv}CM$) with organic compounds in aprotic solvents, but there are few such references delineating preferred reaction conditions for propynyl alkali ($CH_3C{\equiv}CM$), and higher alkynyl alkali metal ($RC{\equiv}CM$) compounds in aprotic solvents. The optimum reaction conditions for lithium or sodium acetylide with organic compounds should not necessarily correspond to the higher alkynyl alkali metal compounds because of the greater basicity of the substituted acetylenic anions and potential solubility differences. This paper reports a study of the optimization of reaction conditions for propynyllithium and propynylsodium with cyclohexanone and carbon dioxide in aprotic solvents. A number of other organic compounds also reacted with these two compounds. An optimization study of the reaction of *n*-butyllithium with ketones has recently been published in which the higher reactivity observed of the alkyl anion contrasts with the greatly reduced reactivity of the alkynyl anion in this study.[1]

Propynyllithium and propynylsodium may be prepared from the corresponding metal and propyne in liquid ammonia or other solvents, by the reaction of an organometallic and propyne, and by the reaction of lithium or sodium hydride with dimethyl sulfoxide (DMSO) with subsequent addition of propyne.[2] These references also include examples of specific reactions of propynyl alkali compounds. Propynyllithium and propynylsodium are nonpyrophoric, white to off-white powders rapidly decomposed by air and moisture, and are insoluble in hydrocarbon solvents, diethyl ether, 1,2-dimethoxyethane and tetrahydrofuran (THF).[3,4] These two compounds are soluble in DMSO, but the metalation of the DMSO is a competing reaction (eq 1).[2c,5] In fact, this equilibrium appears to be general and favors the dimsyl anion for all alkynes higher than acetylene itself. *N,N*-Dimethylacetamide was slowly attacked by propynyllithium when it was used as the reaction solvent. Therefore, this study focused on the use of the nonreactive solvents, THF, diethyl ether, and hydrocarbons.

$$CH_3C{\equiv}CM + CH_3SOCH_3 \longrightarrow CH_3SOCH_2M + CH_3C{\equiv}CH \quad (1)$$

Results and Discussion

Optimization of Reaction Conditions for Cyclohexanone.—A commonly used reaction of acetylenic alkali metal compounds is the reaction with ketones to form tertiary alcohols.[6] Cyclohexanone which is sensitive to enolization side reactions was selected as a model ketone to determine the optimum conditions and important factors for the reaction of propynyllithium and propynylsodium with ketones (eq 2).



(2)

M = Li, Na

The results of this study are summarized in Table I. Solvent and temperature were found to be the most critical factors in obtaining a good yield of the tertiary alkynyl alcohol from cyclohexanone. An explanation for the higher yields obtained in THF than in diethyl ether or benzene may be a greater "incipient" solubility of the propynyllithium and/or the lithium salt of the product. The presence of ethylenediamine (EDA) increased the yields greatly in diethyl ether and slightly in THF, probably owing to the increased solubility of the propynyllithium–EDA complex. [The $(CH_3C{\equiv}CLi)_2$–EDA complex has been isolated.][7] The effect of the EDA is almost catalytic considering the first 0.1 mol gives the greatest increase in yield and there is no benefit above 0.5 mol. The dramatic effect of temperature may also be due to a slightly increased "incipient" solubility of the propynyllithium or the salt of the reaction product. Competing side reactions become a problem over 40–45° so that this is the optimum temperature range for cyclohexanone. The addition of lithium bromide to suppress the amount of enolization and increase the solubility of the propynyl-

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[1] J. D. Buhler, *J. Org. Chem.*, **38**, 904 (1973).

[2] (a) D. Tarrant, J. Savoy, and E. S. Iglehart, *J. Org. Chem.*, **29**, 2009 (1964); (b) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951); (c) J. Kriz, M. J. Benes, and J. Peska, *Collect. Czech. Chem. Commun.*, **32**, 398 (1967); (d) O. F. Beumel, Jr., and W. N. Smith, Jr., U. S. Patent 3,410,918 (1968); (e) E. J. Corey and K. A. Kirst, *Tetrahedron Lett.*, 5041 (1968); (f) H. F. Eriff, *et al.*, *J. Organometal. Chem.*, **15**, 247 (1968); (g) B. C. Pant, W. E. Davidsohn, and M. C. Henry, *J. Organometal. Chem.*, **16**, 413 (1969); (h) Hoffman-La Roche and Co., A. G., British Patent 839,105 (1960).

[3] G. M. Whitesides and W. J. Ehman, *J. Amer. Chem. Soc.*, **91**, 3800 (1969).

[4] Solubility in THF with 1 mol of LiBr present is 0.05 *M*.

[5] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **85**, 3054(1963).

[6] (a) O. F. Beumel, Jr., and R. F. Harris, *J. Org. Chem.*, **29**, 1872 (1964); (b) K. R. Martin, C. W. Kamienski, M. H. Dellinger, and R. O. Bach, *J. Org. Chem.*, **33**, 778 (1968).

[7] O. F. Beumel, Jr., unpublished work.

TABLE I

REACTION OF PROPYNYLLITHIUM[a] AND PROPYNYLSODIUM[b] WITH CYCLOHEXANONE[c]

Run[d]	Propynyl M	Solvent	Additive	Reactn temp, °C	Addn time, hr	Yield,[e] %
1	Li	Et_2O		35	0.25	12[f]
2	Li	Et_2O	0.5 equiv EDA	35	1.5	71
3	Li	THF		40	0.25	84
4	Li	THF		25	1.5	74
5	Li	THF	0.1 equiv EDA	25	1.5	83
6	Li	THF	0.5 equiv EDA	25	1.5	86
7	Li	THF	1.0 equiv EDA	25	1.5	73
8	Li	THF	0.5 equiv RDA	40	1.5	83[e]
9	Li	THF	0.5 equiv EDA	40	1.5	81[g]
10	Li	THF		0	1.5	6
11	Li	THF		40	1.5	87[g,h]
12	Li	THF		40	1.5	87[g,i]
13	Li	THF	LiBr satd	40	1.5	89[g]
14	Li	THF		40	1.5	91[g,j]
15	Li	THF		50	1.5	82[g]
16	Li	THF		64	1.5	76
17	Li	Benzene		40	1.5	3
18	Li	DMSO		30	1.25	26
19	Li	DMSO	Propyne satd	30	1.25	51
20	Na	Et_2O		20	1.5	2
21	Na	THF	1.0 equiv EDA	40	1.5	8
22	Na	THF		40	1.25	23
23	Na	DMSO	Propyne satd	30	1.25	68

[a-c] Registry numbers are, respectively, 4529-04-8, 10486-71-2, and 108-94-1. [d] All runs made at 0.8–1.0 *M* and reacted 1 hr after addition of 5% excess propynyl compound. [e] Yield by isolation; ethylenediamine (EDA). [f] Reacted 3 hr. [g] 15% excess propynyllithium used. [h] Run at 0.47 *M*. [i] Run at 1.35 *M*. [j] 90% yield after sublimation.

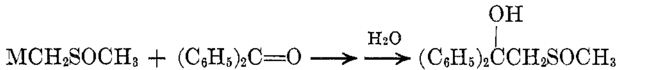
lithium had little effect in the case of cyclohexanone. Slow addition gave only a slight increase in yield. The 91% yield in run 14 represents the maximum yield obtained under any conditions with cyclohexanone.

Solutions of propynyllithium and propynylsodium in DMSO reacted rapidly, but gave only moderate yields, even when run under a propyne atmosphere owing to the equilibrium in eq 1.

Propynylsodium in general did not give good yields with cyclohexanone, but it and its reaction products are generally less soluble than the corresponding lithium compounds in aprotic organic solvents. The higher yield found with DMSO under propyne supports the explanation that a lack of solubility, with increased enolization, accounts for the lower yields of propynylsodium with cyclohexanone in other solvents.

Reactions of Propynyllithium with Other Ketones and Reagents.—The optimum conditions for reaction of propynyllithium with cyclohexanone were used initially with other ketones (THF, and 40–45° for addition and reaction temperature). The results for a number of reactions of propynyllithium are listed in Table II. If the yield was relatively poor, then several other conditions were examined. For more reactive reagents than ketones, such as propionyl chloride, carbon dioxide, and ethyl chloroformate, lower temperatures gave better results with propynyllithium. Less reactive compounds required higher temperatures for reasonable yields such as ethyl sulfate, paraformaldehyde, and ethylene oxide. The yields were generally lower the more rapidly the ketone underwent enolization, and sodium or lithium bromide was added to suppress this. Reactions with esters using 2 equiv of propynyllithium to form the tertiary alcohols gave low yields of unidentified oils.

Reaction of propynyllithium in DMSO with benzophenone at 30° gave a 93% yield of the dimsyl anion–benzophenone adduct providing further evidence of the existance of the dimsyl–alkynyl anion equilibria.[5]



$$\mathrm{MCH_2SOCH_3} + (\mathrm{C_6H_5})_2\mathrm{C{=}O} \longrightarrow \xrightarrow{\mathrm{H_2O}} (\mathrm{C_6H_5})_2\overset{\overset{\displaystyle\mathrm{OH}}{|}}{\mathrm{C}}\mathrm{CH_2SOCH_3} \qquad (3)$$

The reaction of carbon dioxide and propynyllithium was extensively studied. The two sets of conditions listed in Table II represent the best result out of a large number of runs, and a typical lower yield result.

Reactions of Propynylsodium.—Propynylsodium gave either low yields or no isolable product with enolizable ketones, although other reactions did proceed in good yield. The optimum conditions for propynyllithium were not effective for propynylsodium, for example, run 22 in Table I. The reactions of propynylsodium investigated are listed in Table III. The reactions of propionyl chloride and of ethyl chloroformate gave higher yields with propynylsodium than with propynyllithium. The insolubility of the propynylsodium during the reaction, especially considering that toluene was the solvent in one case, minimized side reactions with the reactive soluble product, which is produced directly in these two cases. The explanation for the high yield of tetrolic acid from carbon dioxide and propynylsodium may be that the relative molar volumes of the propynylsodium and sodium tetrolate are about the same permitting the solid–gas reaction to proceed. There may be a greater difference in the lithium case causing a tapering off in the rate of reaction. This reaction was extensively studied under a wide variety of conditions with propynylsodium and the two runs in Table II represent the optimum and a near optimum condition.

Reaction of Organic Halides.—Another frequently used reaction of alkynyl alkali metal compounds is the coupling reaction with an organic halide. A number of attempts to force the coupling reaction (4) to take place with propynyllithium and propynylsodium in THF and other solvents with several reactive halides all essentially failed, with the starting halide isolated unchanged. This reaction apparently cannot proceed unless there is significant solubility of the alkynyl alkali metal compound in the reaction solvent.

$$\mathrm{R'X} + \mathrm{RC{\equiv}CM} \longrightarrow \mathrm{RC{\equiv}CR'} + \mathrm{MX} \qquad (4)$$

In spite of the presence of equilibrium 1 in DMSO, this solvent was tried for the coupling reaction. Only when the solvent was pure DMSO and saturated with propyne were significant yields of the coupled alkyne obtained. These results are listed in Table II. Even an alkyl chloride gave a reasonable yield, but as expected the yield was higher with the corresponding iodide.

Experimental Section

Materials.—Ketones, organic halides, acyl chlorides, and other organic reagents were reagent grade or the best grade available and were obtained from Aldrich Chemical and Eastman Organic Chemicals. EDA was Dow anhydrous commercial grade. DMSO was obtained from Crown Zellerbach. All liquid reagents were distilled before using. Propynyllithium, propynylsodium, and anhydrous LiBr were Foote Mineral Co. products. The hydrocarbon solvents and Et_2O were dried over Na wire before use. THF was purified by drying over KOH

Table II

Reactions of Propynyllithium

Run	Reagent	Registry no.	Addn time, hr	Reactn temp, °C	Reactn time, hr	Product	Registry no.	% yield[a]
1	Acetone	67-64-1	0.3	40	1.0	2-Methyl-3-butyn-2-ol	115-19-5	50
2	Acetophenone	98-86-2	0.7	40	1.5	2-Phenyl-3-pentyn-2-ol	6712-32-9	23
3	Acetophenone[b]		1.5	40	1.5	2-Phenyl-3-pentyn-2-ol		58
4	Benzaldehyde	100-52-7	1.0	40	1.0	1-Phenyl-2-butyn-1-ol	32398-66-6	66
5	Benzophenone	119-61-9	0.5	40	1.0	1,1-Diphenyl-2-butyn-1-ol	836-87-3	91
6	Carbon dioxide	124-38-9	0.5[c]	64	0.5	2-Butynoic acid (tetrolic acid)	590-93-2	78
7	Carbon dioxide[d]		1.5	20		2-Butynoic acid (tetrolic acid)		27
8	Chlorotriphenyltin	639-58-7	1.5	50	0.5	Triphenyl(1-propynyl)tin	1231-17-0	84
9	Cyclopentanone	120-92-3	0.7	64	0.3	1-(1-Propynyl)cyclopentanol	2809-80-5	50
10	Cyclopentanone		0.7	40	0.3	1-(1-Propynyl)cyclopentanol		30
11	Cyclopentanone		0.7	55	0.3	1-(1-Propynyl)cyclopentanol	41174-76-9	43
12	Diisopropyl ketone	565-80-0	0.7	40	0.3	3-Isopropyl-2-methyl-4-hexyn-3-ol		68
13	Diisopropyl ketone		0.7	65	0.3	3-Isopropyl-2-methyl-4-hexyn-3-ol		57
14	Ethyl chloroformate[e]	541-41-3	0.7	35	1.0	Ethyl 2-butynoate	4341-76-8	6
15	Ethyl chloroformate[e]		0.7	30	1.0	Ethyl 2-butynoate		5
16	Ethyl chloroformate[e]		0.3	64	0.5	Ethyl 2-butynoate		Trace
17	Ethyl chloroformate[b]		0.3	30	0.5	Ethyl 2-butynoate		68
18	Ethyl chloroformate[b]		0.3	10	0.5	Ethyl 2-butynoate		71
19	Ethylene oxide[f]	75-21-8	0.5	55	2.0	3-Pentyn-1-ol	10229-10-4	43
20	Ethylene oxide[d]		0.3	55	1.0	3-Pentyn-1-ol		0
21	Ethylene oxide[g]		0.3	50	1.0	3-Pentyn-1-ol		10
22	Ethylene oxide[h]		2.0	60		3-Pentyn-1-ol		30
23	Fluorenone	486-25-9	0.5	40	1.0	9-(1-Propynyl)fluoren-9-ol	16557-07-6	85
24	Methyl ethyl ketone	78-93-3	0.5	40	1.5	3-Methyl-4-hexyn-3-ol	6320-68-9	53
25	Paraformaldehyde[b]	30525-89-4	0.3	60	1.0	2-Butyn-1-ol	764-01-2	55
26	Paraformaldehyde		0.3	60	18.0	2-Butyn-1-ol		0
27	Paraformaldehyde[h]		0.3	60	1.0	2-Butyn-1-ol		53
28	Paraformaldehyde[i]		0.3	60	3.0	2-Butyn-1-ol		0
29	Propionyl chloride[b]	79-03-8	0.3	25	0.8	4-Hexyn-3-one	10575-41-4	54
30	Ethyl sulfate	64-67-5	0.3	64	2.5	2-Pentyne	627-21-4	46
31	1-Chlorobutane[i]	109-69-3	0.5	35	2.0	2-Heptyne	1119-65-9	36
32	1-Chlorobutane[j]		0.5	35	2.0	2-Heptyne		35[l]
33	1-Chlorobutane[k]		1.0	40	2.0	2-Heptyne		13
34	1-Iodobutane[j]	542-69-8	0.5	20	1.5	2-Heptyne		48

[a] Yields are calculated on isolated product; reactions were run at 0.6–1.0 *M* concentrated with 10% excess propynyllithium in THF; addition temperature was the same as the reaction temperature unless otherwise stated. [b] Solution was saturated with NaBr. [c] CO_2 was added at 0° initially. The slurry was then permitted to warm slowly over 1 hr to 64° and held for 0.5 hr under CO_2. [d] 0.5 equiv of EDA present. [e] Solvent: Et_2O. [f] Contained 1.0 equiv of LiBr. [g] Contained 1.2 mol of DMSO; propyne saturated. [h] 0.5 equiv of LiBr present. [i] 0.1 equiv of EDA present. [j] Solvent: DMSO; propyne saturated. [k] Solvent: 50:50 DMSO:THF; propyne saturated. [l] Propynylsodium was used.

Table III

Reactions of Propynylsodium

Run	Reagent	Solvent	Addn time, hr	Reactn temp, °C	Reactn time, hr	Product	% yield[a]
1	Benzophenone	THF	1.1	66	1.3	1,1-Diphenyl-2-butyn-1-ol	64
2	Ethyl chloroformate[b]	THF	0.8	35	18	Ethyl 2-butynoate	77
3	Ethyl chloroformate	Toluene	1.0	75	0.5	Ethyl 2-butynoate	51
4	Ethyl chloroformate	Toluene	0.05	90	2.5	Ethyl 2-butynoate	50
5	Propionyl chloride	Toluene	0.05	30	2.5	Ethyl (1-propynyl) ketone	64
6	Carbon dioxide	Xylene	1.0[c]	65	0.5	2-Butynoic acid (tetrolic acid)	87
7	Carbon dioxide	Xylene	1.5	60		2-Butynoic acid (tetrolic acid)	78
8	Ethyl sulfate	THF	0.15	64	3.0	2-Pentyne	46
9	Ethyl sulfate	Et_2O	0.15	35	3.0	2-Pentyne	0
10	Stannic chloride	THF	0.5	25	18	Tetra(1-propynyl)tin	53[d]

[a] Reactions were run at 0.6–2.0 *M* with yields based on isolation. [b] Contained 0.1 equiv of NaBr. [c] Addition of CO_2 was at 0–5° for 1 hr; then temperature was raised to 65°. [d] Decomposes slowly in air.

overnight, then over $CaCl_2$ overnight, and finally distilled from $LiAlH_4$ under argon. All elemental analyses were performed by Microanalysis, Inc., of Wilmington, Del.

General.—All reaction setups were flushed with argon for 1 hr before use. Glc analyses were performed on a Varian Aerograph 90P3 using a 6 ft × 0.25 in. SE-30 on Chromosorb W column. Ir spectra were run on a Perkin-Elmer Infracord. The same reaction setup and procedure was used for all runs unless otherwise noted.

Gases were added using a gas addition tube fitted to the flask. Liquid reagents were added neat. Paraformaldehyde, fluorenone, and benzophenone were added as saturated solutions in THF. Satisfactory elemental (±0.3% for C and H) were obtained for all compounds. Ir spectra were consistent with all products obtained. The physical constants of the known compounds prepared were in agreement with literature values. Table IV lists the physical properties obtained for the products together with the corresponding literature values.

TABLE IV

PHYSICAL PROPERTIES OF PRODUCTS

Product	Bp, (mm), or mp, °C	Corresponding lit. value
1-(1-Propynyl)cyclohexanol	49.5	49.5[a]
2-Methyl-3-butyn-2-ol	104–106 (760)	104 (760)[b]
2-Phenyl-3-pentyn-2-ol	39 (0.3) 41–42	 42–43[c]
1-Phenyl-2-butyn-1-ol	91–92 (0.3)	88 (0.2)[d]
1,1-Diphenyl-2-butyn-1-ol	153–154 (0.5) 48.5–49.5	165 (1.5)[e]
2-Butynoic acid	75	76[d]
1-(1-Propynyl)cyclopentanol	53 (1.0)	99 (30)[f]
3-Isopropyl-2-methyl-4-hexyn-3-ol	46 (0.4)	99 (45)[g]
Ethyl 2-butynoate	160 (760)	160 (760)[b]
3-Pentyn-1-ol	158–159 (760)	152–153 (760)[h]
9-(1-propynyl)fluoren-9-ol	103–104	107–108[c]
3-Methyl-4-hexyn-3-ol	59 (15)	53.5 (20)[i]
2-Butyn-1-ol	140–141 (760)	143 (760)[b]
4-Hexyn-3-one	46 (12)	35–39 (10)[j]
2-Pentyne	52–56 (760)	56 (760)[b]
2-Heptyne	110–113 (760)	112 (760)[b]
1,1-Diphenyl-2-methylsulfinylethanol	129–135[k]	148[l]
Triphenyl(1-propynyl)tin	111 dec	74–75[m]
Tetra(1-propynyl)tin	159–160	150[m]

[a] R. Mantione, *C. R. Acad. Sci., Paris, Ser. C24*, 1668 (1967). [b] Handbook of Chemistry and Physics, 53rd ed, CRC Publishing Co., Cleveland, 1972. [c] C. Schopf and J. H. Strauss, *Monatsh. Chem.*, **98** (4), 1274 (1967). [d] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951). [e] S. G. Kuznetsov and L. V. Fedorova, *Zh. Obshch. Khim.*, **32,** 3775 (1962); *Chem. Abstr.*, **58,** 11179*c* (1963). [f] B. R. Fleck and J. E. Kmiecik, *J. Org. Chem.*, **22,** 90 (1957). [g] I. A. Favorskaya and Yu. P. Artsybasheva, *Zh. Obshch. Khim.*, **30,** 789; *Chem. Abstr.*, **55,** 350*i* (1960). [h] M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1788 (1957). [i] K. Suga, S. Watanabe, and T. Suzuki, *Can. J. Chem.*, **46,** 3041 (1968). [j] E. S. Turbanova, Yu. I. Porfir'eva, and A. A. Petrov, *Zh. Org. Khim.*, **2** (5), 772 (1966); *Chem. Abstr.*, **65,** 10480*c* (1966). [k] Not recrystallized. [l] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **85,** 3054 (1963). [m] M. L. Quan and P. Cadiot, *Bull. Soc. Chim. Fr.*, **1,** 35 (1965).

The propynylsodium and propynyllithium were bottled in 6-oz bottles with Polyseal caps. These compounds were added to the flasks under argon by weighing the bottle, then transfering the bottle into a closed plastic bag purged with argon and with the cap removed. The closed plastic bag was carefully fitted over one neck of a three-neck flask being purged with argon and the desired amount of propynyl alkali compound carefully poured from the bottle into the flask while grasping it through the bag film. The flask was quickly stoppered, the cap of the bottle put back on, and the bottle weighed. The amount of propynyl alkali compound used was the difference in weight.

Reaction of Cyclohexanone with Propynyllithium (Propynylsodium).—A 500-ml flask, equipped with pressure-equalizing dropping funnel, stirrer, condenser, and thermometer and sealed from the atmosphere by an oil bubbler, was charged with 160 ml of THF and 16 g of propynyllithium (0.35 mol). The slurry was heated to 40° and 33 ml of cyclohexanone (0.32 mol) was added over 1.5 hr. The slurry was stirred an additional hour and then hydrolyzed with excess water. The aqueous solution was extracted with Et_2O three times; the extracts were combined and dried over anhydrous Na_2SO_4. The product oil, after solvent removal using a rotary film evaporator, weighed 42.9 g (93% purity by glc or 91% yield). This oil was sublimed to give 39.5 g of 1-(1-propynyl)cyclohexanol, 90% yield, mp 47°, resublimation mp 49.5°.

Carbonation of Propynyllithium.—A slurry of 20.8 g of propynyllithium (0.45 mol) in 300 ml of THF in a 500-ml flask was stirred and cooled to 0° under argon. At this point, CO_2 was bubbled into the slurry while maintaining 0° with cooling. The rate of addition was observed using an oil bubbler with the system. The solution was no longer exothermic after 0.25 hr. After 0.5-hr total time, the slurry was warmed gradually to 64° over 1.0 hr under CO_2. After 0.5 hr at reflux, the slurry was cooled under CO_2 and then hydrolyzed with an excess of water. The aqueous layer was extracted twice with Et_2O. The aqueous layer was then acidified with aqueous HCl to pH 2 and the organic layer formed separated from the solution. The acidified aqueous layer was then extracted four times with Et_2O. These Et_2O extracts and the organic layer were combined. (Tetrolic acid appears to form a stable monohydrate.) The oil left after removal of the Et_2O with a rotary film evaporator was extracted three times with boiling cyclohexane in the presence of excess anhydrous Na_2SO_4. The hot cyclohexane extracts were decanted. The solvent from the combined cyclohexane extracts was removed on a rotary film evaporator and the solid tetrolic acid obtained weighed 29.8 g or 78% yield, mp 70–72°. (This product was almost quantitatively sublimed, mp 74.5–75.0°.)

Carbonation of Propylsodium.—The same experimental setup as described before was used. CO_2 was added to a slurry of 27.0 g of propynylsodium in 300 ml of xylene at 0–5° for 1.0 hr (exotherm lasts for 0.3 hr). The slurry was warmed to 65° gradually over 1.0 hr and maintained at 65° for 0.5 hr. The slurry was cooled and hydrolyzed at 20° with excess water. The yield was 31.8 g or 87% of tetrolic acid using the previously described workup procedure.

Reaction of 1-Chlorobutane with Propynyllithium.—The same laboratory setup was used as described for the reaction with cyclohexanone. The solution of 17.1 g of propynyllithium (0.37 mol) in 300 ml of DMSO was saturated with propyne at 33°. A propyne atmosphere was maintained while 34.4 g of 1-chlorobutane (0.37 mol) was added over 0.5 hr at 36–40°. The reaction was exothermic. The solution was permitted to cool to room temperature, while stirring over an additional 2-hr period, and then hydrolyzed with a large excess of water. The aqueous DMSO layer was extracted two times with Et_2O. The combined Et_2O extracts were dried over anhydrous Na_2SO_4. A yield of 72.9 g of 2-heptyne, 36%, was obtained on fractional distillation, bp 110–113° (760 mm).