

mechanism of enolization of protonated *o*-isobutyrylbenzoic acid is complicated by the fact that it exists predominantly in the lactol form as shown in eq. 13, leading to the possibility of a catalysis of the un-ionized lactol form by water. However, catalysis of the un-ionized form of the substrate by water is excluded by the absence of (more powerful) buffer catalysis.

The catalytic constant k_{OH} for the iodination of *o*-isobutyrylbenzoate ion represents intermolecular hydroxide ion attack on this anion. A comparison of the rate constant of this reaction with the hydroxide ion catalyzed iodination of isobutyrophenone (calculated as discussed previously) shows that the former reaction is about 20 times slower than the latter reaction. The difference can of course be attributed to electrostatic repulsion of the hydroxide ion by the *o*-carboxylate ion in the former reaction.

Several mechanisms can be written for the hydronium ion catalyzed enolization, measured in 1 *M* perchloric

acid. These mechanisms involving the protonated ketone or the protonated lactol cannot be differentiated at the present time.

The demonstration of a powerful intramolecular general basic catalysis of ketone enolization in *o*-isobutyrylbenzoate ion may serve as a model for the enolization of dihydroxyacetone phosphate by a general base of the enzyme aldolase in the enzyme-substrate complex formed between these two substances. Certainly there are more efficient bases on the enzyme than the carboxylate ion investigated here. However, the present experiments do show the possibility that a considerable portion of the rate enhancement in enzymatic enolization processes may involve intramolecular or intracomplex general basic catalysis.

Acknowledgment. The authors are grateful to Dr. Ferenc J. Kézdy for theoretical and experimental assistance.

Stable Carbonium Ions. XVIII.^{1a} Alkynyl Carbonium Ions

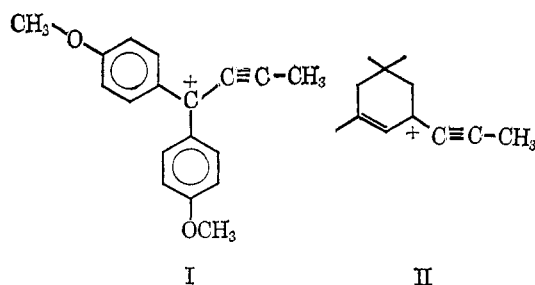
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Contribution from the Eastern Research Laboratory, The Dow Chemical Company, Wayland, Massachusetts. Received August 16, 1965

Using the previously reported method of ionizing alcohols in fluorosulfonic acid-antimony pentafluoride-sulfur dioxide solvent system, seven alkynyl carbonium ions were directly observed by nuclear magnetic resonance spectroscopy. The spectra indicate that allenyl cation forms are strong contributors in alkynyl carbonium ions.

Introduction

The only previous reported observation of alkynyl carbonium ions was that of Richey, Philips, and Rennick who observed ions I and II in concentrated sulfuric acid solution by n.m.r. and ultraviolet spectroscopy.² In their investigations they also reported



recovery of the precursor alcohols by drowning the sulfuric acid solutions with excess sodium hydroxide.

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(2) H. G. Richey, J. C. Philips, and L. E. Rennick, Jr., *J. Am. Chem. Soc.*, **87**, 1381 (1965).

Results and Discussion

Continuing our systematic investigation of different classes of stable carbonium ions³ we wish now to report the direct observation of a series of alkynyl carbonium ions by n.m.r. spectroscopy.⁴

Using the analogy of the alkyl halide-antimony pentafluoride method to generate stable carbonium ions, an attempt was made to generate stable alkynyl carbonium ions from $(\text{CH}_3)_2\text{C}(\text{Cl})\text{C}\equiv\text{CH}$ and $(\text{CH}_3)_2\text{C}(\text{Cl})\text{C}\equiv\text{CCH}_3$.⁵ In neat antimony pentafluoride and also in antimony pentafluoride-sulfur dioxide the spectra obtained were of poor quality and showed extensive by-product formation.

Some time ago Olah, *et al.*, reported⁶ that tertiary alcohols ionize well to the corresponding stable carbonium ions in fluorosulfonic acid-antimony pentafluoride-sulfur dioxide. Using this method, it was found that tertiary alkynyl alcohols ionize to stable alkynyl carbonium ions.

Alkynyl carbonium ions were generated by dissolving the corresponding alkynyl alcohols into liquid SO_2 at $\sim -50^\circ$ and adding this solution to a rapidly stirring solution of $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ at $\sim -70^\circ$.

The n.m.r. spectra of ions III-IX are shown in Figures 1-7, respectively (recorded at $\sim -60^\circ$). The

(3) G. A. Olah, *et al.*, *ibid.*, **84**, 2733 (1962); **85**, 1328 (1963); **86**, 1932, 1265, 1360, 4195, 5679, 5680, 5682 (1964); **87**, 1103, 2997, 2998 (1965).

(4) After our work was completed, we learned of independent work of Professor Richey and his co-workers. We are grateful for preprints of this work.

(5) We are grateful to Professor T. Jacobs, University of California, Los Angeles, for samples of the alkynyl chlorides.

(6) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965).

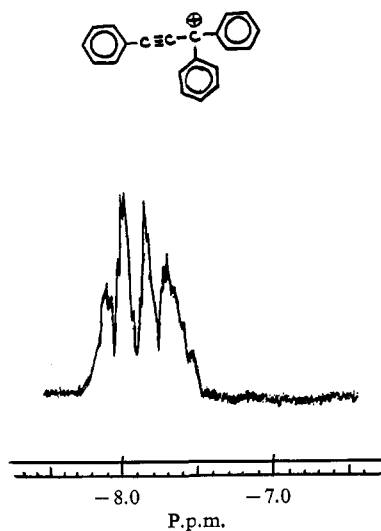


Figure 1.

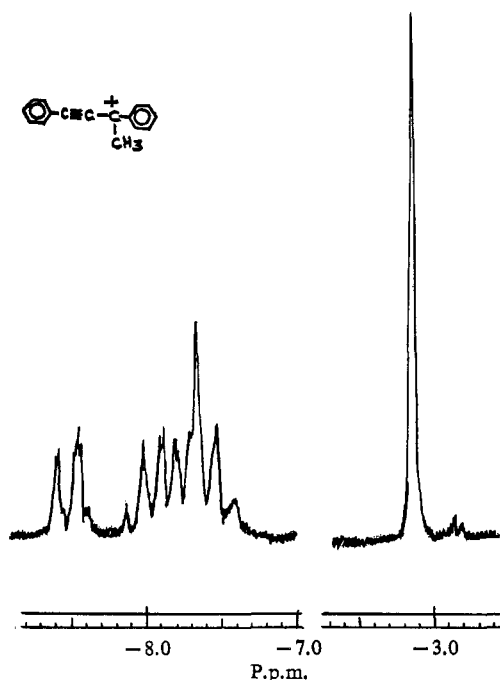


Figure 2.

only spectrum which contains observable impurities besides the carbonium ions is that of ion VI. In this case special conditions had to be used to prepare the ion. A solution of 2-methyl-3-pentyn-2-ol was dissolved into SOClF at -95° and this was injected into a rapidly stirring $\text{SbF}_5\text{-FSO}_3\text{H-SOClF}$ solution at -95° . Even so, a number of small peaks between -2.6 and -1.3 p.p.m. indicate by-product formation. In separate attempts the bands of ion VI remained constant with respect to each other while the by-product bands varied.

Table I tabulates the n.m.r. band positions of the ions. Table II tabulates downfield shifts of the ions relative to the precursor alcohols. It can be readily seen that large downfield shifts occur for the groups attached to the triple bond as well as for groups adjacent to the positive charge. The downfield shift going from the alcohol to the carbonium ion is de-

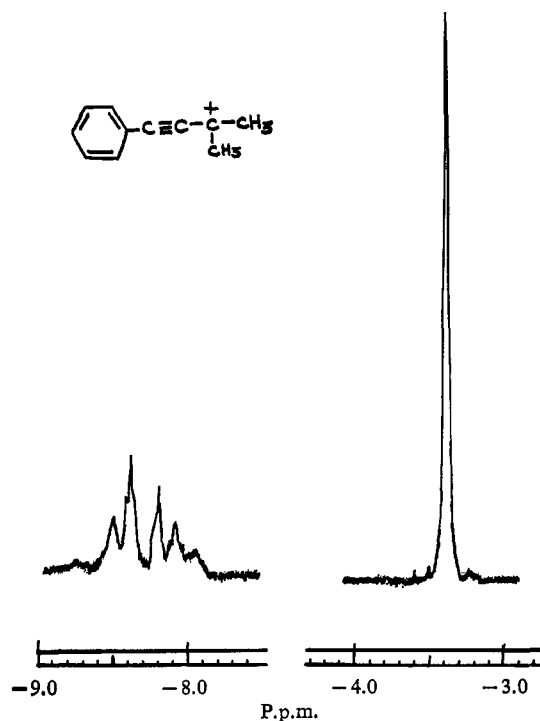


Figure 3

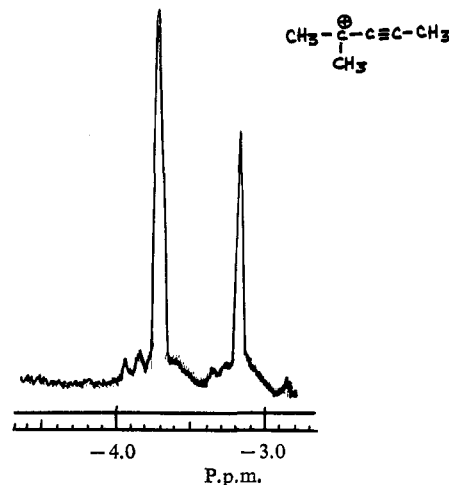


Figure 4

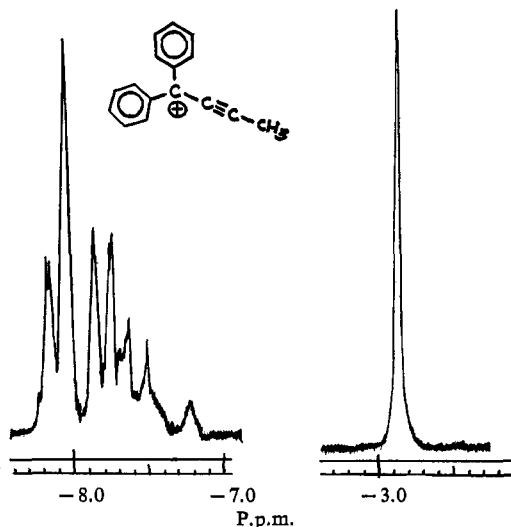


Figure 5.

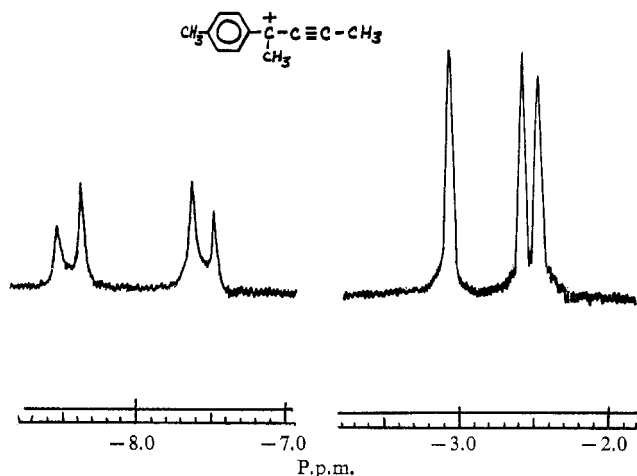
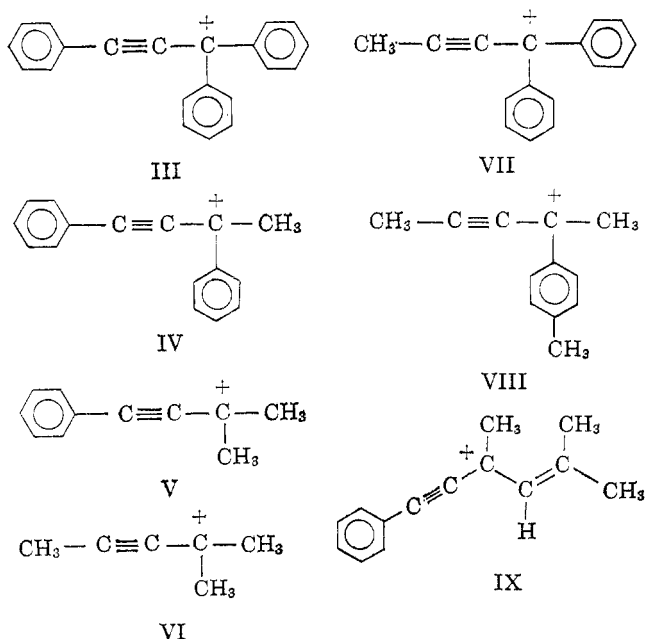


Figure 6.

pendent on the solvent used to examine the alcohol. For instance, SO_2 gives an upfield solvent shift; thus if the change in the chemical shifts ($\Delta\delta$) are calculated based on the alcohol bands observed in SO_2 the $\Delta\delta$ values will be larger. However, the downfield shifts are large going from the alcohol to the ion regardless of which solvent is used to examine the alcohol. These results can be seen in Table II.



Examining Table I the following trends can be noted.

(1) The position in p.p.m. of methyl groups directly attached to the charged carbon steadily moves downfield in the series of ions VIII (−3.05), IX (−3.11), VI (−3.14), V (3.39), and VI (−3.67). This is about the order expected based on the predicted positive charge density at the central carbon. Ion VI has no phenyl or other delocalizing group on the $-\text{C}\equiv\text{C}-\text{C}^+$ system. Thus VI would be expected to have the highest charge density on the $-\text{C}\equiv\text{C}-\text{C}^+$ system. The appearance of the CH_3 groups at −3.67, the lowest field peak in this series, is indicative of this. It is interesting to compare this position with that of the *t*-butyl cation in SbF_5 , (−4.35).⁷ Delocalization of

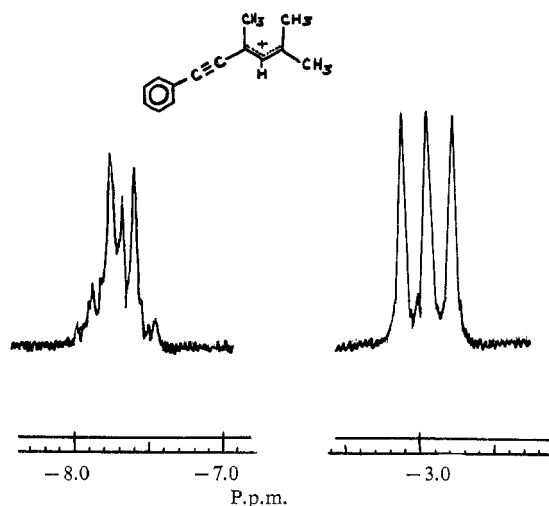


Figure 7.

charge into the phenyl group in ion V would result in a reduced charge density on the $-\text{C}\equiv\text{C}-\text{C}^+$ system, and this accounts for the position of the methyl band at −3.39 which is upfield from the corresponding methyl band in VI. These data indicate that allenyl cation resonance forms play an important part in alkynyl carbonium ions. Allenyl resonance forms contribution was

also found by Richey⁴: $-\text{C}\equiv\text{C}-\text{C}^+ \leftrightarrow -\text{C}^+=\text{C}=\text{C}^-$. In ion VI a phenyl group is now directly attached to the charged carbon, and this delocalizes positive charge thus further reducing the charge density on the $-\text{C}\equiv\text{C}-\text{C}^+$ system. Adding a *p*-methyl to this phenyl group or replacing the phenyl with an isobutenyl group effectively delocalizes positive charge, and the effect of this delocalization is reflected in the listed position of methyl groups adjacent to the positive charge in ions VIII, IX, and IV.

(2) The change in the chemical shift ($\Delta\delta$) in p.p.m. of the methyl groups attached directly to the positively charged carbon when the alcohol is converted to the carbonium ion are −2.27 (ion VI), −1.71 (ion V), and −1.37 (ion IV). This demonstrates that the charge density on the charged carbon decreases as delocalization increases. This trend parallels trend 1.

(3) A methyl group attached to *sp* hybridized carbon experiences a large downfield shift in going from the alcohol to the carbonium ion in each case studied. In ions VI, VII, and VIII the $\Delta\delta$ of the $\text{CH}_3-\text{C}\equiv$ group was greater than −1.2 p.p.m. in each case. The largest shift was found in ion VI where no groups are present to extend the conjugation. This substantial downfield shift is compelling evidence that the allenyl cation resonance structures are strong contributors to the structure of the alkynyl carbonium ions.

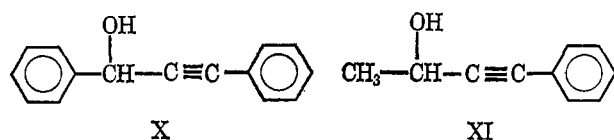
Attempts to ionize alcohols X and XI in fluorosulfonic acid-antimony pentafluoride-sulfur dioxide even at −60° resulted in complex, polymerized reaction mixtures. The failure of X and XI to generate stable carbonium ions is not surprising. Both X and XII are secondary alcohols and would initially generate secondary alkynyl cations in acid. Secondary monophenyl carbonium ions (styryl cation for instance)

(7) G. A. Olah, E. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

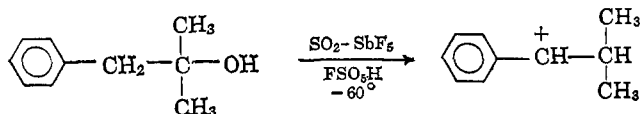
Table I. N.m.r. Band Positions and Assignments of Alkynyl Carbonium Ions (p.p.m. in $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ at -60° Relative to External TMS)

	$^+\text{CCH}_3$	$\text{CH}_3\text{C}\equiv$	$^+\text{C}-\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5-\text{C}\equiv$	$\text{CH}_3-\text{C}_6\text{H}_4-\text{C}^+$	$^+\text{CC}=\text{C}(\text{CH}_3)_2$
			-7.50 to -8.16	-7.50 to -8.16		
	-3.14		-7.40 to -8.60	-7.44 to -8.63		
	-3.39			-7.85 to -8.50		
	-3.67	-3.13				
		-2.88	-7.49 to -8.22			
	-3.05	-2.59	A_2B_2 quartet centered at -8.03		-2.45	
	-3.11			-7.52 to -7.97	-3.00 to -2.82	

have not been observed by direct formation in acidic solutions.^{8,9} The only known example is the phenylisopro-



pyl carbonium ion⁹ and arises from a 1,2-hydride shift in the intermediary formed dimethylbenzyl carbonium ion.



The lack of observation of monomer ions in styrene systems seems to be due to their great propensity to polymerize at the instant of formation. Thus, when a triple bond is introduced to an analogous system (such as X or XI) great reactivity is expected and failure to observe a monomeric carbonium ion is not surprising. Since X does not give a monomeric ion, XI would not be expected to because here a phenyl group has been replaced by a methyl group. This would further decrease the resonance stabilization possibilities.

Experimental Section

Solutions of the alkynyl alcohols in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ were made up in the following way. SO_2 solutions of

(8) Ph.D. Thesis of C. U. Pittman, Jr., Pennsylvania State University, 1964.

(9) G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 3507 (1965).

the alcohols at -70° were added dropwise to $\text{FSO}_3\text{H-SbF}_5$ solutions at $\sim -70^\circ$ with rapid stirring.

N.m.r. spectra were taken on a Varian Associates Model A56-60 n.m.r. spectrometer. The positions are recorded in p.p.m. relative to external TMS. The field was double calibrated using TMS and CCl_3H . Samples were made with excess SbF_5 so that traces of water would present no problem in observing the stable ions. The band positions are the average of three measurements in every case except ion VI.

Preparation of 1,1,3-Triphenyl-2-propyn-1-ol. Phenylethynyllithium was prepared by the dropwise addition of 18 g. of phenylacetylene (K & K Laboratories) to a 1.6 M solution of butyllithium in hexane (Foote Mineral Co.). The solution then was diluted with 50 ml. of anhydrous diethyl ether. Benzophenone (29 g.) in 100 ml. of ether was then added dropwise to the rapidly stirring ethynyllithium solution. A N_2 atmosphere was maintained throughout this preparation. When the addition was completed, the solution was refluxed for 2 hr. and then hydrolyzed with distilled water. The ether layer was separated, water washed three times, and dried over anhydrous MgSO_4 , and the ether was removed by aspiration. The title alcohol was obtained by crystallization and recrystallization from ligroin in 69% yield, m.p. $81\text{--}81.5^\circ$ (lit.¹⁰ 82°). The n.m.r. spectrum of the alcohol in CCl_4 exhibited phenyl hydrogens at -7.1 to -7.55 p.p.m. and the OH hydrogen at -1.97 , with the theoretical 15:1 area. The infrared spectra exhibited no carbonyl band.

(10) K. Hess and W. Wiltzien, *Ber.*, **54**, 2518 (1921).

Table II. N.m.r. Band Positions and Assignments of Alkynyl Alcohols (in CCl₄ or SO₂ as Indicated) and Their Downfield Shift from Alcohol to Carbonium Ion (in SbF₅-FSO₃H-SO₂ at -60°; p.p.m. Relative to TMS)

Compd.	Phenyl H's	OH	$\begin{array}{c} \text{OH} \\ \\ \text{C}-\text{CH}_3 \end{array}$	Vinyl H	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}=\text{C} \\ \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}\equiv \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \Delta \text{CH}_3 \\ \\ -\text{C}\equiv \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \Delta \text{C}- \\ \\ \text{CH}_3 \end{array}$	$\Delta \text{C}\equiv$	ΔC^+
	-7.10 ^a to -7.65	-2.0							-0.47 ^a	-0.47 ^a
	-7.12 ^a to -7.75	-2.89	-1.77						-1.37	-0.46 ^a
in SO ₂ , -60°	-6.85 to -7.50	-3.18	-1.36						-1.78	-0.72 ^a
	-7.08 to -7.29	-2.93	-1.57						-1.82	-1.01
in SO ₂ , -60°	-6.89	-3.00	-0.93						-2.46	-1.28
	-6.9 to -7.54	-3.10							-1.66	-1.22
	A ₂ B ₂ quartet centered at 7.0	-3.38	-1.55						-1.65	-1.23
	-7.10 to -7.40	-3.25	-1.65	-5.42	-1.70 and -1.95 ^b					
		-2.92	-1.40						-1.76	-1.37
									-2.27	

^a The two kinds of phenyl hydrogens cannot be separated. ^b Both bands coupled to the vinyl H with $J = \sim 1$ c.p.s.

Preparation of 2,4-Diphenyl-3-butyn-2-ol. The reaction of phenylacetylene with KOH to form phenylethynyl anion followed by addition of acetophenone failed to give the title alcohol. Thus, butyllithium was used and acetophenone was added to the formed phenylethynyllithium as described above. The crude product was worked up as described above and the crude alcohol was distilled at 161° (2 mm.) followed by further purification by recrystallizing the title alcohol twice from petroleum ether (b.p. 40-60°). A 72% yield was obtained, m.p. 73-75° (lit.¹¹ 77°). The n.m.r. spectrum in CCl₄ exhibited phenyl, OH, and methyl bands at -7.30, -2.52, and -1.77 p.p.m., respectively, with areas in the expected ratio of 10:1:3. The infrared spectrum showed no carbonyl band.

Preparation of 4-Phenyl-2-methyl-3-butyn-2-ol. Phenylacetylene (51 g.) was added to a 200-ml. ether

suspension of powdered KOH (100 g.) at 0°. The addition took 1 hr. and, on completion, 58 g. of acetone was added dropwise with rapid stirring. An additional 30 min. was allowed for completion of the reaction and then a large excess of water was added to the reaction mixture. The ether layer was separated and washed with water two times. The ether layer was then dried over anhydrous MgSO₄ and aspirated. Crude crystals of title alcohol were obtained on cooling the remaining oil in a Dry Ice-acetone bath. The title alcohol was purified by twice recrystallizing it from petroleum ether to give a 63% yield, m.p. 49-51° (lit.¹² m.p. 51°). The n.m.r. spectrum in CCl₄ contained phenyl, OH, and CH₃ bands at -7.28, 2.93, and -1.57 p.p.m., respectively, with the expected area ratio of 5:1:6. The infrared spectrum contained no carbonyl band.

(11) J. U. Nef, *Ann.*, **308**, 281 (1933).

(12) A. I. Zakharova and Z. I. Sergeeva, *Zh. Obshch. Khim.*, **18**, 1322 (1948).

Preparation of 2-Methyl-3-pentyn-2-ol. Propyne gas was bubbled directly into a hexane solution of butyllithium at 0°. Seven grams of propyne was added to the theoretical amount of butyllithium solution under an N₂ atmosphere with rapid stirring. A white solid, 1-propynyllithium,² precipitated and was partially redissolved by the addition of anhydrous ether to the reaction mixture. An additional 20 min. was allowed for the reaction to go to completion. An ether solution of 7 g. of acetone was added dropwise to this mixture with rapid stirring. The reaction mixture was gently refluxed for 0.5 hr. after the addition was completed. The reaction mixture was hydrolyzed with 7 g. of water and the ether layer was separated and dried over anhydrous MgSO₄. The ether layer should not be water washed since the title alcohol is quite water soluble. The ether layer was then aspirated and distilled through an 8-in. Vigreux column, and the fraction boiling at 130–140° was collected and redistilled. The title alcohol was obtained boiling from 132 to 135° (lit.¹³ b.p. 133.5–134.5°). The infrared spectrum gave an OH at 2.95 and a carbonyl band at 5.96 μ which is probably mesityl oxide formed by the condensation of acetone as a side reaction. The n.m.r. spectrum showed the title alcohol to be present in 85% yield. The methyls adjacent to the OH give a band at –1.40 p.p.m. The other methyl group appears at –1.76 and the OH hydrogen at –2.92 p.p.m. The areas were 6:3:1 as expected.

Preparation of 1,1-Diphenyl-2-butyne-1-ol. 1-Propynyllithium was prepared from 7 g. of propyne and butyllithium as described previously. Then 28 g. of benzophenone in 100 ml. of diethyl ether was added dropwise with rapid stirring. The reaction was worked up as has been already described and the crude product was purified by distillation. The title alcohol was obtained in 68% yield, b.p. 130–133° (0.32–0.33 mm.) (lit.¹⁴ 125–126° (0.3 mm.)). The infrared spectrum contained no carbonyl band but a strong OH band at 2.85 and a C \equiv C band at 4.45 μ . The n.m.r. spectrum in CCl₄ was in agreement with structure, and the bands are listed in Table II.

Preparation of 2-p-Tolyl-3-pentyn-2-ol. 1-Propynyllithium was prepared from 7 g. of propyne and butyllithium as described previously. Then 20 g. of *p*-

methylacetophenone was added dropwise in its volume of ether to the reaction mixture with vigorous stirring. The reaction was worked up in the usual way, and the title alcohol was collected in 31% yield at 83–84° (0.7 mm.). The n.m.r. spectrum was in accord with the structure, and the band positions and assignments are listed in Table II. The infrared spectrum gave no carbonyl band.

Preparation of 1-Phenyl-3,5-dimethyl-1-hexyn-4-en-3-ol. Phenylethynyllithium was prepared as previously described and to this was added 20 g. of mesityl oxide in ether solution. The reaction was run and worked up in the usual way and the title alcohol was obtained (in 68% yield) on distillation, b.p. 101–103° (0.7–0.6 mm.). The compound has been reported¹⁵ without a boiling point. The boiling point agreed with that of isomeric 7-phenyl-2,5-dimethyl-6-heptyn-4-en-2-ol (139–142° (2 mm.))¹⁶. The n.m.r. spectrum agreed with structure, and the bands are listed in Table II. The infrared spectrum had an OH band at 2.90 μ and no carbonyl band.

Preparation of 1,3-Diphenyl-2-propyne-1-ol. Phenylethynyllithium was prepared from 30 g. of phenylacetylene and butyllithium as described previously. Then an ether solution of 30 g. of benzaldehyde was added dropwise with rapid stirring. The reaction was completed and worked up in the usual way. The title alcohol was distilled and obtained in 73% yield, b.p. 165–168° (5 mm.). The infrared spectrum was free of carbonyl absorption and contained an OH band at 3540 and 3360 and a C \equiv C band at 2195 cm.^{–1}.

Preparation of 1-Phenyl-1-butyne-3-ol. Phenylethynyllithium was prepared from 20 g. of phenylacetylene and butyllithium as described previously. To this solution an ether solution of 10 g. of acetaldehyde was added dropwise with rapid stirring. The reaction was completed and worked up in the usual manner. The title alcohol was purified by distillation and was collected in 87% yield at 89–92° (3 mm.). The n.m.r. spectrum of the alcohol in CCl₄ agreed with structure, and the band positions and assignments are listed in Table II. The infrared spectrum contained no carbonyl band but contained a hydroxyl band at 2.91 and a C \equiv C band at 4.45 μ .

(15) A. I. Nogaideli and K. Ya. Dzagnidze, *Tr. Tbilissk. Gos. Univ.*, **74**, 153, (1959).

(16) T. A. Favorskaya and L. A. Parlova, *Zh. Obshch. Khim.*, **27**, 52, (1957).

(13) R. Fleck and J. E. Kmiecik, *J. Org. Chem.*, **22**, 90 (1957).

(14) P. Lauger, M. Aost, and R. Charlier, *Helv. Chim. Acta*, **42**, 2379 (1959).