Table II
Slopes of the Zucker–Hammett Plots, *z*, and Bunnett's *w* Parameters

Compound	*z*	*w*
$HC{\equiv}C{-}S{-}C_2H_5$	1.16 ± 0.04	−2.4 ± 0.3
$CH_3C{\equiv}C{-}S{-}C_2H_5$	1.31 ± 0.04	−3.4 ± 0.5
$C_2H_5C{\equiv}C{-}S{-}C_2H_5$	1.16 ± 0.04	−2.4 ± 0.5
$CH_3C{\equiv}C{-}S{-}C(CH_3)_3$	1.03 ± 0.03	−0.2 ± 0.5

also in the acid catalyzed hydration of acetylenic thioethers covalent bonding of water is not of much importance in the transition state of the proton transfer step.

As a matter of completeness, in Table II we have given the slopes w of plots of (log k + H_0) *vs.* log a (H_2O) according to Bunnett.[8] These negative values are in the range believed to be characteristic for reactions in which water is not involved in the rate-determining step.

References and Notes

(1) Supported by the Netherlands Organization for the Advancement of Pure Research (ZWO).

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Cuprous Trimethylsilylacetylide. Preparation and Reaction with Acid Chlorides

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The title compound, cuprous trimethylsilylacetylide (1), is of interest in that (1) trimethylsilyl protected acetylenes can be readily cleaved[1] to regenerate the terminal acetylenic function, (2) cuprous acetylide, itself, does not undergo the reactions of other cuprous acetylides, and (3) it represents the simplest Castro coupling reagent.[2] To the best of our knowledge acetylide 1 has not been prepared.[1,3]

In this paper we wish to report the preparation of 1 and its reaction with acid chlorides. Treatment of trimethylsilylacetylene in tetrahydrofuran (THF) with cuprous *tert*-butoxide[4,5] afforded a solution containing 1. Although an orange-red solid can be isolated from this solution upon dilution with ether, it is unstable and readily decomposes, even at −20°. We have tentatively assigned the structure of 1 to the orange-red solid based upon the infrared (Nujol mull) absorption bands at 1890 ($C{\equiv}C$), 1250 ($SiMe_3$), and 855 cm^{-1} ($SiMe_3$). The insolubility and instability of this precipitated material have precluded further characterization. The THF solutions of 1 are relatively stable at 0° provided they are not allowed to stand for extended periods of time. Thus 1 is best prepared in solution and used immediately without isolation. Furthermore, when preparing 1 it was found essential for cuprous iodide and trimethylsilylacetylene to be in excess of the lithium *tert*-butoxide, as 1 decomposed upon prolonged exposure to basic reagents. We have also prepared 1 from trimethylsilylacetylene by the butyllithium–cuprous iodide method,[6] but this method was not as satisfactory as the cuprous *tert*-butoxide procedure.

So far all attempts to obtain the Castro coupling product from 1 and the very reactive substrate methyl 2-iodobenzoate have been unsuccessful due to the instability of 1 under the reaction conditions. However, treatment of 1 with acid chlorides afforded the trimethylsilylethynyl ketones listed in Table I.

Table I
Trimethylsilylethynyl Ketones

R	Amt, mmol: RCOCl	Amt, mmol: 1[a]	$RCOC{\equiv}CSi(CH_3)_3$, % yield
CH_3	15	12.8	30
CH_3	15	25.6	24
$CH_3(CH_2)_4$	8	12.8	38
$CH_3(CH_2)_4$[b]	8	12.8	62
$(CH_3)_2CH$[b]	8	12.8	48
C_6H_5	15	12.8	66
C_6H_5	15	25.6	66
p-$CH_3C_6H_4$	8	12.8	48
p-ClC_6H_4	8	12.8	61

[a] Prepared *in situ* from $CuOC(CH_3)_3$ and $HC{\equiv}CSi(CH_3)_3$ with the assumption of a quantitative formation of 1. [b] The solution containing 1 was evaporated to dryness under reduced pressure and the residue redissolved in THF before the addition of RCOCl.

The data in Table I show that there is no advantage in using an excess of either 1 or the acid chloride. When aliphatic acid chlorides were used, the *tert*-butyl alcohol generated in the preparation of 1 had to be removed (evaporation under reduced pressure) prior to the acid chloride addition since it competed with 1 for the acid chloride. With aryl acid chlorides the competing side reaction with *tert*-butyl alcohol was negligible.

Trimethylsilylethynyl ketones have previously been prepared by the action of trimethylsilylethynylmagnesium bromide on acid anhydrides[7] and by the aluminum chloride catalyzed reaction of acid chlorides with bis(trimethylsilyl)acetylene.[8]

The present procedure is complementary to the above methods in that it uses acid chlorides instead of the less readily available anhydrides required by the former, and the reaction conditions are essentially neutral as compared to the strongly acidic conditions of the latter.

In summary, cuprous trimethylsilylacetylide proved to be too unstable for Castro coupling; however, it does react readily with acid chlorides to give trimethylsilylethynyl ketones.[9]

Experimental Section[10]

General Procedure. To a magnetically stirred suspension of cuprous iodide in 40 ml of THF at 0° under nitrogen was added 0.9 equiv of lithium *tert*-butoxide. The mixture was stirred for 45 min at 0° and then 1 equiv of trimethylsilylacetylene[11] dissolved in 10 ml of THF was added with the temperature being maintained at 0°. After 30 min, the acid chloride was added and the cooling bath was removed. The reaction mixture was stirred for 20 hr at room temperature and the solvent was then removed on a rotary evaporator. The residue was treated with ether and filtered, and the filtrate was evaporated on a rotary evaporator. The residue was chromatographed on a small column of silica gel eluting with hexane up to 0.5% ether–hexane. The products so collected were then distilled under reduced pressure. In each chromatography run a small forefraction, ranging from 12 to 18%, of bis(trimethylsilyl)-1,4-butadiyne was obtained as a coupling product from 1.

Phenyl trimethylsilylethynyl ketone was isolated as a pale yellow liquid: bp 98–99° (1.0 mm) [lit.[7] bp 103–104° (2.5 mm)]; ir (CCl_4) 2165 (C≡C), 1640 (C═), 1250 ($Si(CH_3)_3$), 865 ($Si(CH_3)_3$), 855 cm^{-1} ($Si(CH_3)_3$); nmr (CCl_4) δ 0.32 (s, 9, $Si(CH_3)_3$), 7.50 (m, 3, Ar H), 8.05 (m, 2, Ar H).

***p*-Chlorophenyl trimethylsilylethynyl ketone** was isolated as a pale yellow liquid: bp 105–106.5° (0.5 mm) [lit.[8b] bp 80–84° (10^{-3} mm)]; ir (CCl_4) 2160 (C≡C), 1645 (C═0), 1250 ($Si(CH_3)_3$), 865 ($Si(CH_3)_3$), 855 cm^{-1} ($Si(CH_3)_3$); nmr (CCl_4) δ 0.32 (s, 9, $Si(CH_3)_3$), 7.15 (d, 2, J = 9 H_z, Ar H), 7.75 (d, 2, J = 9 Hz, Ar H).

***p*-Methylphenyl trimethylsilylethynyl ketone** was isolated as a pale yellow liquid: bp 110–112° (0.75 mm) [lit.[8b] bp 74–78° (10^{-3} mm)]; ir (CCl_4) 2170 (C≡C), 1640 (C═O), 1250 ($Si(CH_3)_3$), 865 ($Si(CH_3)_3$), 855 cm^{-1} ($Si(CH_3)_3$); nmr (CCl_4) δ 0.30 (s, 9, $Si(CH_3)_3$), 2.28 (s, 3, Ar CH_3), 6.92 (d, 2, J = 8 Hz, Ar H), 7.62 (d, 2, J = 8 Hz, ArH).

Methyl trimethylsilylethynyl ketone was isolated as a colorless liquid: bp 62–64° (28 mm) [lit.[7] bp 51.5° (12 mm)]; ir (CCl_4) 2160 (C≡C), 1675 (C═O), 1255 ($Si(CH_3)_3$), 870 ($Si(CH_3)_3$), 855 cm^{-1} ($Si(CH_3)_3$); nmr (CCl_4) δ 0.25 (s, 9, $Si(CH_3)_3$), 2.25 (s, 3, $C(O)CH_3$).

***n*-Pentyl trimethylsilylethynyl ketone**[12] was isolated as a colorless liquid: bp 74–75° (1.0 mm); ir (CCl_4) 2160 (C≡C), 1670 (C═O), 1250 ($Si(CH_3)_3$), 870 ($Si(CH_3)_3$), 855 cm^{-1} ($Si(CH_3)_3$); nmr (CCl_4) δ 0.24 (s, 9, $Si(CH_3)_3$), 0.70–1.90 (cm, 9), 2.38 (t, 2, J = 6 Hz, $C(O)CH_2$).

Isopropyl trimethylsilylethynyl ketone[12] was isolated as a colorless liquid: bp 78.2–81.8° (17 mm); ir (CCl_4) 2160 (C≡C), 1670 (C═O), 1255 ($Si(CH_3)_3$), 865 ($Si(CH_3)_3$), 855 cm^{-1} ($Si(CH_3)_3$); nmr (CCl_4) δ 0.28 (s, 9, $Si(CH_3)_3$), 1.16 (d, 6, J = 7 Hz, $CH(CH_3)_2$), 2.50 (heptet, 1, J = 7 Hz, $CH(CH_3)_2$).

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—1, 53210-13-2; RCOCl (R = CH_3), 75-36-5; RCOCl [R = $CH_3(CH_2)_4$], 142-61-0; RCOCl [R = $(CH_3)_2CH$], 79-30-1; RCOCl (R = C_6H_5), 98-88-4; RCOCl (R = p-$CH_3C_6H_4$), 874-60-2; RCOCl (R = p-ClC_6H_4), 122-01-0; cuprous *tert*-butoxide, 35342-67-7; trimethylsilylacetylacetylene, 1066-54-2; phenyl trimethylsilylethynyl ketone, 13829-77-1; *p*-chlorophenyl trimethylsilylethynyl ketone, 37166-46-4; *p*-methylphenyl trimethylsilylethynyl ketone, 37166-45-3; methyl trimethylsilylethynyl ketone, 5930-98-3; *n*-pentyl trimethylsilylethynyl ketone 53210-14-3; isopropyl trimethylsilylethynyl ketone, 53210-05-2.

References and Notes

(1) D. R. M. Walton, "Protective Groups in Organic Chemistry," J. F. W. McOmie, Ed., Plenum Press, London, 1973, pp 5–8.

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(4) T. Tsuda, T. Hashimoto, and T. Saegusa, *J. Amer. Chem. Soc.*, **94,** 658 (1972).

(5) Cuprous *tert*-butoxide was not isolated as in ref 4 but was prepared *in situ* by the action of lithium *tert*-butoxide on cuprous iodide.

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(9) *Trimethylsilylethynyl ketones are* easily desilylated with an aqueous Borax solution to give ethynyl ketones; see ref 8b for details.

(10) All boiling points are uncorrected. Ir spectra were recorded on a Perkin-ElmerModel 257 spectrophotometer. Nmr spectra were recorded on a Hitachi Perkin-Elmer Model R-20A spectrometer with tetramethylsilane as an internal standard. All column chromatography was performed on Grace Davison 950 silical gel. The acid chlorides used, except for caproyl chloride, were commercial samples that were distilled prior to use. Tetrahydrofuran was distilled from $LiAlH_4$. Cuprous iodide was obtained from Alfa Inorganics and dried in *in vacuo* at 130°. *Lithium tert-butoxide* was prepared by the action of anhydrous *tert*-butyl alcohol on 1 equiv of lithium metal suspended in anhydrous ether followed by the removal of the ether on a rotary evaporator.

(11) N. V. Komarov and O. G. Yarosh, *Zh. Obshch. Khim.*, **37,** 264 (1967), *Chem. Abstr.*, **66,** 95126 (1967).

(12) A satisfactory combustion analysis could not be obtained due to contamination with a small amount of the desilylated ketone whose presence was detected by the appearance of 3300 and 2105 cm^{-1} bands in the ir spectrum. It appears that the trimethylsilyl group is partially removed during attempted purifications.

Alkyllithium Additions to Allylic Alcohols

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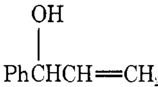
In some previous work, we had established that α-vinylbenzyl alcohol (**1**) can react in a variety of ways when treated with alkyllithium reagents. Treating **1** with n-butyllithium in tetrahydrofuran (THF) gave good yields of propiophenone (**2**), by way of a dianion intermediate (**3**).[2] In contrast to this result, the same starting materials in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA) and with hexane as the solvent gave the alcohol **4** (R = n-Bu) and saturated compound **5** (R = n-Bu) in a 3:1 ratio, and no ketone.[3] The alcohol, which is produced in a highly stereospecific manner, presumably arises by addition of n-butyllithium to the internal end of the double bond giving rise to intermediate **6** (R = n-Bu), which upon hydrolysis affords **4.** The saturated product **5** more than likely arises by way of addition of n-butyllithium to the terminal end of the double bond, giving rise to **7** (R = n-Bu) which eliminates Li_2O to **8** (R = n-Bu) and subsequently undergoes a second addition of n-butyllithium to the conjugated double bond.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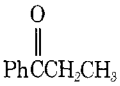
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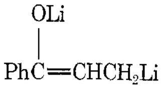
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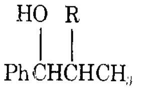
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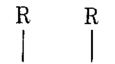
4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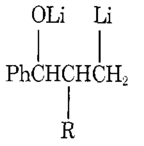
5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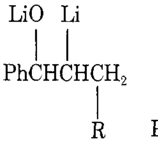
6


$\mathrm{Ph\overset{LiO}{\overset{|}{C}}H\overset{Li}{\overset{|}{C}}H\underset{\underset{R}{|}}{C}H_2}$

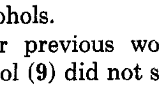
7

$\mathrm{PhCH{=}CHCH_2R}$

8

Treatment of α-vinylbenzyl alcohol (**1**) with *tert*-butyllithium in the presence of TMEDA and hexane gave 23% ketone (**2**), 9% *cis*-**8** (R = t-Bu), 36% *trans*-**8** (R = t-Bu), and 32% **5** (R = t-Bu).[3] Consequently, in the case of *tert*-butyllithium the only addition products that result come from addition to the terminal end of the double bond and not the internal end. These differences led us to investigate the addition of n- and *tert*-butyllithium to two other homologous alcohols.

In our previous work, we reported that 2-phenyl-3-buten-2-ol (**9**) did not show any addition or rearrangement products when treated with excess n-butyllithium. However, it has now been found (after several trials) that overnight refluxing of a solution of **9**, 3 equiv of n-butyllithium, and 1 equiv of TMEDA in the solvent hexane resulted in the production of two new compounds, together with a considerable amount of unreacted starting material remaining.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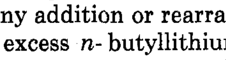
9



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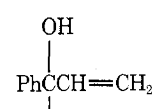

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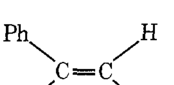

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