Copper(I)-Promoted Thiophenoxide Ionization in Solution. A Simple Synthesis of Vinyl Phenyl Sulfides

Summary: The concept of carbonium ion generation by the action of cuprous ion on thioacetals and thioketals is applied to the preparation of vinyl sulfides and a furan.

Sir: A common method of initiating carbonium ion reactions in nonprotic solvents is the removal of a halide ion from a suitable alkyl halide by a soluble Lewis acid such as an antimony pentahalide,[1] an aluminum trihalide,[1] or silver nitrate.[2] A soluble Lewis acid for the removal of the thiophenoxide ion from alkyl thiophenoxides would have considerable potential use in such reactions because of the ready availability of compounds bearing the thiophenoxide group; this availability arises partly from the facile high-yield conversion of aldehydes and ketones into thioacetals and thioketals by the action of thiophenol and acid (eq 1)[3] and partly from the ability of the thiophenoxide group to stabilize a negative charge thus permitting the construction of a compound containing the SPh group from precursors containing fewer carbon atoms (e.g., eq 2).[4]

$$RCOR' + 2C_6H_5SH \xrightarrow{H^+} RC(SPh)_2R' + H_2O \qquad (1)$$

$$(PhS)_2C(R)Li + R'X \longrightarrow (PhS)_2C(R)R' + LiX \qquad (2)$$

Table I

Elimination of Thiophenol from Thioacetals and Thioketals Induced by Cuprous Triflate in Benzene-THF at 25°[a]

$$R(R')CHC(SPh)_2R'' + C^+ \xrightarrow[THF]{C_6H_6} RR'C{=}C(SPh)_2R'' + CuSPh + H^+ \qquad (3)$$

R	R'	R''	Time[b]	Cu^+/substrate	% yield[c]
Me	H	H	3 hr	4	91[d]
Ph	H	H	8 hr	6.1	90[e]
Ph	H	H	72 hr	1.2	93[f]
Me	Me	H	1.5 hr	3	85
H	H	Ph	<5 min	2[g]	85[h]
H	$-CH_2CH_2CH_2CH_2-$		10 min	2	92
$-CH_2CH_2CH_2CH_2CH_2-$		H	1 hr	2	92
Me	Me	Me	<5 min	2.4	94[i]

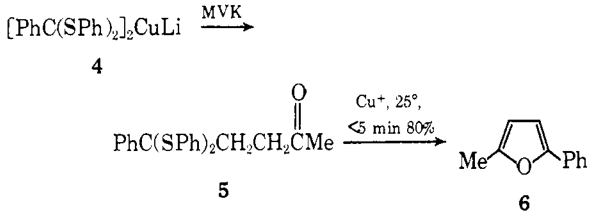
[a] Syntheses were conducted on ca. a 2-mmol scale except for the last entry in which 10.4 mmol of thioketal was employed. [b] For disappearance of substrate (TLC). [c] Isolated yields. [d] Over 90% trans by GLC; when the synthesis was performed at reflux (1 hr), the product was all trans. [e] One half trans. [f] Two thirds trans. [g] Diisopropylethylamine present. [h] Product was contaminated with 6% acetophenone. [i] Product was 2-thiophenoxy-3-methyl-2-butene as indicated by refractive index, TLC, GLC, and NMR; no trace of the positional isomer could be detected.

We now report that cuprous ion, supplied as the benzene complex of cuprous trifluoromethanesulfonate[5] (triflate), a substance which is soluble in a number of organic solvents, is a strong Lewis acid toward thiophenoxide. One application of this finding is a simple, general, high-yield synthesis of vinyl phenyl sulfides (1) by the elimination of thiophenol from thioacetals and thioketals (1.9 mmol) induced by the benzene complex of copper(I) triflate (3.8 mmol, containing 7.6 mg-atoms of Cu^+) in benzene (30 ml)/THF (10 ml) under N_2 (eq 3). For most simple substances (prepared by eq 1 or 2), the reaction occurs at room temperature (Table I).[6] In most cases by-products are not formed and the product is readily isolated by adding water, filtering, and extracting with ether. Insoluble cuprous iodide is ineffective. Previously reported procedures for effecting such an elimination involve pyrolysis in the presence of strong acid[3a,7] or conversion to the sulfoxide and pyrolytic elimination of benzenesulfenic acid.[8] The strong acidity, which develops during the reaction, can be avoided in the case of acid-sensitive products by the presence of 2,6-lutidine or diisopropylethylamine which are readily removable from the product by acid extraction or silica chromatography. An attractive feature of this procedure is its apparently irreversible nature; in most cases the cuprous thiophenoxide precipitates from solution. Two closely related applications are the syntheses of (1) 1-thiophenoxy-1,3-butadiene (**2**,[9] two geometric isomers) by performing the elimination (46°, 24 hr) on the product of the reaction of the lithium salt of dithiophenoxymethane[4] with allyl bromide and (2) ketene diphenyl thioacetal (**3**)[10] by elimination (25°, 5 min) from the product of methylation of the lithium salt of trithiophenoxymethane,[11] both in the presence of lutidine.[12]

$CH_2{=}CHCH{=}CHSPh$ **2** $\qquad$ $CH_2{=}C(SPh)_2$ **3**

Vinyl sulfides and ketene dithioacetals are valuable reactants in a number of synthetic procedures.[9,13] No single method previously available[13a,14–16] would be applicable to the preparation of all of the vinyl sulfides reported here and, in many individual cases, this appears to be the preferred procedure because of its high yield and simplicity.

The reactivity order (Table I) is clearly that expected for rate-determining cation formation.[17] This is also indicated by the smooth production of 2-phenyl-5-methylfuran (**6**) from the adduct (**5**) of methyl vinyl ketone and the cuprate (**4**)[18] derived from the thioacetal of benzaldehyde (eq 4); in this case, the cation is apparently trapped by the carbonyl group before undergoing proton loss.



(4)

Another application is the alkylidenation of a suitable alkyl halide (eq 5).[19] The utility of such a sequence for the general synthesis of conjugated olefins is being explored as well as the generality of the furan synthesis and a number of other synthetic uses of this cation-forming reaction.

$$PhCH_2Br + PhCH(Li)SPh \longrightarrow$$
$$PhCH(CH_2Ph)SPh \xrightarrow[>95\%]{Cu^+,\ 39\ hr,\ 58°} PhCH{=}CHPh(\sim 99\%\ trans) \qquad (5)$$

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A Remarkable Rearrangement and Elimination Reaction in the Solvolysis of Tertiary α-Chloroboronates under Mild Conditions

Summary: Tertiary α-chloroboronic esters, readily available from the base-induced reaction of borinic esters with dichloromethyl methyl ether, undergo a remarkable rearrangement (with hydride or methide shifts) and elimination during solvolysis in aqueous solvents to produce the corresponding olefins in high yield.

Sir: Solvolysis of tertiary α-chloroboronates in 50% aqueous ethanol proceeds via hydride or methide shifts with the concurrent loss of the elements of chlorodimethoxyborane to form the corresponding olefin (eq 1). The reaction occurs essentially instantaneously at room temperature in the presence of aqueous silver nitrate, providing an exceptionally mild route to internal olefins in high yield (eq 2).

Table I
Products Obtained in the Alkaline Hydrogen Peroxide Oxidation of α-Chloroboronic Esters, RR′CClB(OCH$_3$)$_2$

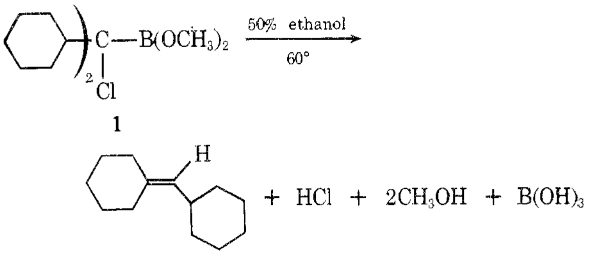
R	R′	Ketone,^{a} %	Olefin,^{a,c} %
Isobutyl	Isobutyl	86^b (56)^c	~10
Cyclopentyl	Cyclopentyl	86^b (59)^c	~10
exo-Norbornyl	*exo*-Norbornyl	62	29
Cyclohexyl	Cyclohexyl	95	0
3-Methyl-2-butyl	3-Methyl-2-butyl	54^b	30
2,3-Dimethyl-2-butyl	Cyclopentyl	43^d	35
2,3-Dimethyl-2-butyl	Cyclohexyl	31^d	29

^{a} By GLC on a 6 ft × 0.25 in. 10% SE-30. ^{b} 1 equiv of DCME and 2 equiv of base were used. ^{c} 1 equiv of DCME and 1 equiv of base were used. ^{d} 2 equiv of DCME and 2 equiv of base were used.

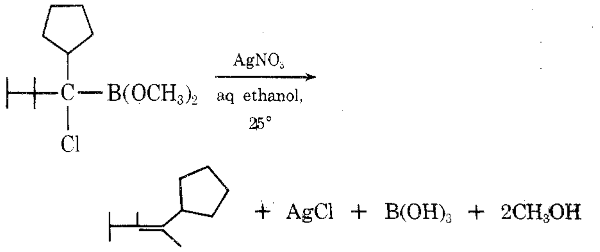
Table II
Olefin Formation by the Reaction of α-Chloroboronic Esters, RR′CClB(OCH$_3$)$_2$, with Silver Nitrate in 50% Ethanol at 25°

R	R′	Olefin^a	Yield,^{b} %
Cyclohexyl	Cyclohexyl	Cyclohexylidenecyclohexane	83
exo-Norbornyl	*exo*-Norbornyl	2-Norbornylidene-*exo*-norbornane	81
2,3-Dimethyl-2-butyl	Cyclopentyl	2-Cyclopentyl-3,4-dimethyl-2-pentene^c	82

^{a} By GLC on a 10% SE-30 column. ^{b} No other organic products were detected. ^{c} The stereochemistry of the methyl groups was not determined.



(1)



(2)

In the course of the alkaline hydrogen peroxide oxidation of α-chloroboronic esters to ketones,[1] we observed formation of internal olefins in significant amounts accompanying the formation of the desired ketones. The amount of the olefin increased for the more hindered cases (Table I). In exploring the factors responsible for olefin formation, the reaction was carried out omitting hydrogen peroxide.