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PHENYLTHIOCOPPER TRIMETHYLPHOSPHITE COMPLEX. A REAGENT FOR THE PREPARATION OF THIOALLENES.

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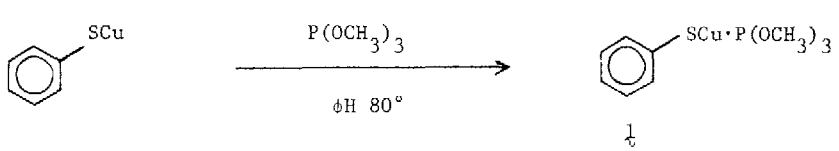
Summary. The title complex reacts with propargyl halides and, in situ generated, propargyl mesylates to produce thioallenes in good yields, via an allylic inversion.

Thioallenes are potentially versatile synthons. They can be readily elaborated by metallation, followed by reaction with a wide variety of electrophiles,[1,2] or they can be rearranged to conjugated dienes.[3,4] Several thioallenes have been prepared by base catalysed isomerisation of readily available propargyl thioethers,[2,5] by alkylation of simple thioallenes or thioacetylenes,[1,2] or (with an allylic inversion) by O-sulfenylation of propargyl alcohols, with a concomitant 2,3-sigmatropic rearrangement, followed by deoxygenation.[1,6] Allylic inversion has also been reported[7] for the action of sodium thiophenoxide on 3-chloro-3-methylbut-1-yne, which forms a thioallene ($\underset{\sim}{3}$ R = R^1 = CH_3) directly. However Julia[8] believes that the latter reaction requires conditions favourable towards the formation of an allenidene carbene, and our attempts to produce either propargyl[5] or allenyl[7] thioethers, under literature conditions, from sodium thiophenoxide and secondary or tertiary propargyl halides led, only to mixtures of widely varying composition of both allenyl and propargyl displacement products.

Dialkyl cuprates react with propargyl electrophiles to produce only the "inverted" allenyl isomers,[9] and propargyl alcohols give allenyl halides in Cu^I catalysed displacement reactions.[10] We reasoned that a suitable phenylthiocopper species might well react with propargyl halides to produce the "inverted" thioallene in a single step.

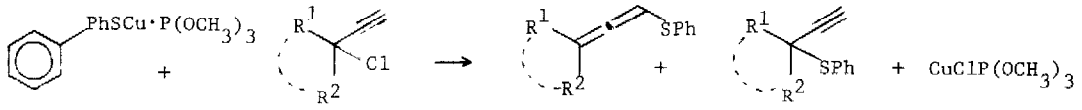
Phenylthiocopper is a polymeric solid completely insoluble in most solvents, but it can be depolymerised by alkyl lithium reagents forming soluble cuprate complexes.[11] Since cuprous halides can be solublized by phosphite ligands,[12] we decided to attempt to depolymerise phenylthiocopper by formation of its trimethylphosphite complex, and to study the synthetic utility of this complex.



$\underset{\sim}{1}$

Phenylthiocopper, slurried in refluxing benzene, was solublized by addition of 1·2 equivalents of trimethylphosphite. Celite filtration, removal of the solvent under reduced pressure, and recrystallisation from ether-hexane gave 1 in 80-90% yields, as an offwhite crystalline solid. Without precautions the complex is unstable, readily losing trimethyl phosphite, but it can be stored for several months at -20°. Complex 1 is soluble in a wide variety of organic solvents including C_6H_6, CH_2Cl_2, $CHCl_3$, THF, DMF and DMSO.

Complex 1 reacted with alkyl, allyl and benzyl halides, in benzene or chloroform to produce the corresponding thioethers in good yields and high purity (see table). With both crotyl and but-1-en-2-yl chlorides, strong preference for terminal (crotyl) substitution is seen.



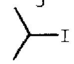
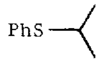
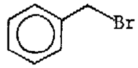
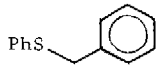
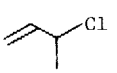
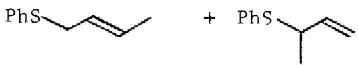
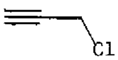
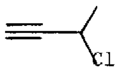
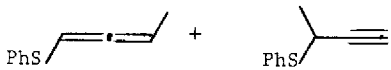
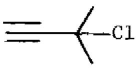
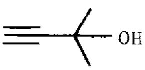
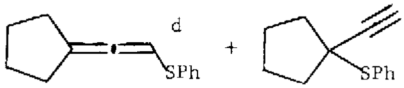
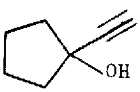
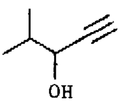
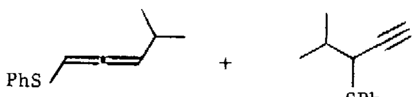
1 2 3 4 5

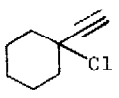
The desired thioallene (3, $R^1 = R^2 = H$) was the major reaction product when 1 reacted with propargyl chloride in THF, and a cleaner, faster reaction was obtained when two equivalents of LiBr were added.[13]

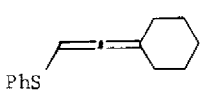
A detailed study was made of the reaction of 1 with 3-chloro-3-methylbut-1-yne (2, $R^1 = R^2 = CH_3$). The course of the reaction was found to be very solvent dependent with allene (3, $R^1 = R^2 = CH_3$) to acetylene (4, $R^1 = R^2 = CH_3$) varying between 1:1 and 5:1 (see table). However when TMEDA was used as solvent, the ratio of allene:acetylene increased to consistently greater than 10:1. Elevated temperatures and reaction times in excess of those needed for complete reaction led to an allene:acetylene ratio of more than 50:1. It appears that the cuprous chloride trimethylphosphite complex 5, formed in the reaction mixture, catalyses[14] the thermodynamically favourable conversion of acetylene (4, $R^1 = R^2 = CH_3$) to allene (3, $R^1 = R^2 = CH_3$), as a mixture of these two compounds equilibrates entirely to the allene when treated with preformed complex 5. Neither the primary (4, $R^1 = R^2 = H$) nor the secondary (4, $R^1 = H, R^2 = CH_3$) propargyl thioethers were isomerized under the same conditions, despite the fact that the reactions of 3-chlorobut-1-yne and 1 show the same type of time and temperature dependency. Using TMEDA as solvent, terminal thioallenes can be prepared in ~80% yields and with good to excellent isomeric purity (see table). However when non terminal acetylenes were used as substrates only direct S_N2 reactions were observed.

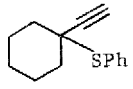
Generally propargyl alcohols are more readily available than the corresponding halides, either commercially or through synthesis.[15] Therefore we decided to investigate the preparation of thioallenes via the mesylates. A one pot synthesis is desirable, not only for simplicity, but also because of the tendency of some neat mesylates to decompose with a spontaneous mild detonation.[16] The mesylates were generated at -5° in CH_2Cl_2 by the method of Crossland and Servis,[17] and 1 in CH_2Cl_2 was added at the same temperature. The reaction mixtures

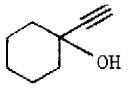
TABLE THIOETHER PREPARATIONS

Substrate	Solvent	Temp.	Time	Products			Yield[a]
CH_3I	$CHCl_3$	20	22h	$PhSCH_3$			66%
	C_6H_6	80	24h				64%
	C_6H_6	80	6h				92%
	$CHCl_3$	20	22h				96%
 [b]	$CHCl_3$	20	24h				(10 : 1) 90%
 [c]	THF	20	24h	as above			(10 : 1) --
	THF/LiBr	20	2h				87%
							
	TMEDA	0→20	24h	5	:	1	--
	TMEDA	80	2min	10	:	1	76%
	TMEDA	80	1h	37	:	1	69%
							
	CH_3CN	20	2h	1	:	1	80%
	THF	20	20h	5	:	1	80%
	TMEDA	0→20	16h	12	:	1	88%
	TMEDA	50	1h	16	·	1	79%
	TMEDA	50	16h	> 100	:	1	74%
	CH_2Cl_2	-5→20	16h	36	:	1	57%
				 [d]			
	TMEDA	30	24h	> 100	:	1	84%
	CH_2Cl_2	-5→20	16h	22	:	1	33%
	CH_2Cl_2	-5→20	16h	 17	:	1	69%



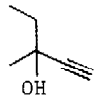


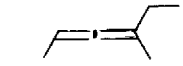


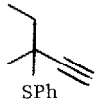


TMEDA 30 24h > 100 : 1 78%

CH_2Cl_2 -5 → 20 16h 30 : 1 63%







CH_2Cl_2 -5 → 20 16h 33 : 1 56%

a) All yields are isolated yields. b) A 4:1 mixture of this and the allylic isomer (below). c) A 2:1 mixture of this and the allylic isomers (above). d) Isolated mainly as a thermally rearranged 1,3 diene.[3]

were stirred overnight at 20°. Yields obtained were moderate to good (generally 50-70%) with usefully high allene:acetylene ratios (> 15:1) Studies of the mechanism of this reaction, and of the utilization of the thioallenes are underway.

A typical procedure is as follows. 3-chloro-3-methyl-but-1-yne (1.02 g, 10 mmol) was added in one portion to a solution of 1 (2.97 g, 10 mmol) in TMEDA (10 ml) stirred under N_2 at 50°. After 12 h the reaction mixture was poured into stirred, ice-cold, dilute HCl (1N, 75 mol) and ether (75 ml). After several minutes the mixture was vacuum filtered, the organic phase of the filtrate was decanted and washed with water (2 x 50 ml) saturated brine (50 ml) and dried (K_2CO_3/celite). The solvent was removed under reduced pressure and the residue was distilled using a Kugelrohr apparatus at 80°/0.2 mm. 3-Methyl-1-phenylthiobuta-1,2-diene (1.30 g, 74%) was obtained as a sweet smelling colourless oil (pure by nmr and gc).

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