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LETTERS

Electrophile Induced Rearrangement of 1-Alkynylaluminium Ate Complexes

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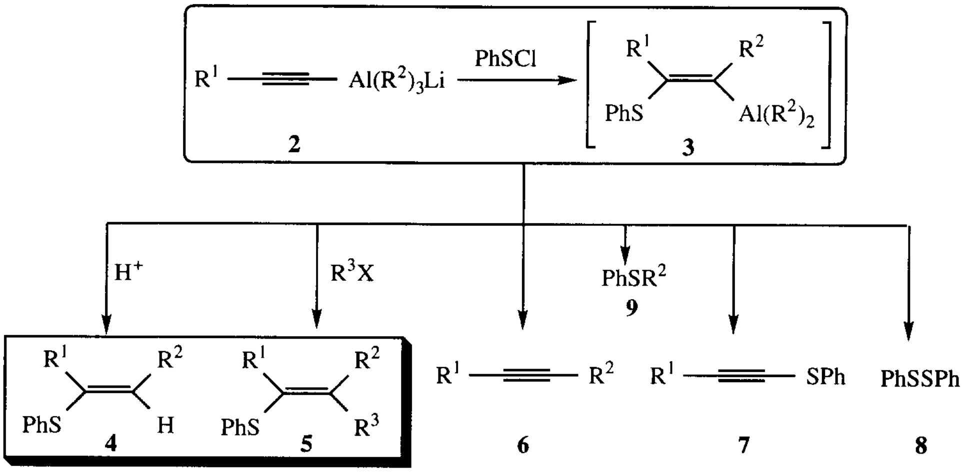
Abstract: The title species have been shown to rearrange under the influence of the electrophile PhSCl to give tetrasubstituted vinylaluminium compounds protonolysis of which led to the corresponding vinyl sulfides in a highly stereoselective manner.

Keywords: alkynylaluminium, ate complex, rearrangement, vinylaluminium, vinylsulfide

Metal ate complexes play an important role in organic synthesis; those of copper[1] and boron[2,3] are probably the best known examples. More recently, ate complexes of other metals (i.e. titanium,[4] manganese,[5] zinc,[6] etc.) have also been reported to undergo interesting transformations. Whereas vinylaluminium ate complexes are also well known,[7] 1-alkynyltrialkylaluminates have been used rarely.[8] Therefore, as a continuation of our work aimed at finding novel methods for the regio- and stereocontrolled synthesis of tri- and/or tetrasubstituted olefins,[9] we started to investigate the possible use of trialkylaluminiums for this purpose. In this letter, we wish to report the first encouraging results we have obtained (Scheme 1, Table 1).

Scheme 1



In close analogy with a number of other alkylmetals, we have found that trialkylaluminiums are able to react with 1-lithio-1-alkynes **1** to form the title ate complexes **2** which react with an electrophile such as PhSCl to undergo the desired rearrangement leading to **3**. This intermediate can be protonolysed to give **4**, or it can be reacted with another electrophile R^3X to give **5** (Scheme 1).

In a typical experiment, 3 mmoles of n-butyllithium (1.6 M in hexanes) were added at -20 °C under argon to a solution of 3 mmoles (289 mg) of 1-heptyne in 12 ml of ether and stirred for 1 h (formation of a white slurry). Then, 3 mmoles of $AlEt_3$ (1M in hexane) were added and the temperature was raised to 0 °C for 45 min. The colorless clear solution so obtained was cooled to -78 °C, 3 mmoles (434 mg) of PhSCl dissolved in 12 ml of ether were added and stirring was continued for 30 min. The temperature was again raised to 0 °C and the reaction mixture was quenched with saturated aqueous NH_4Cl. Standard work-up led to 601 mg of crude product which yielded 316 mg of 4-phenylthio-3-nonene (45%, E/Z = 96/4) after column and thick layer (SiO_2, eluent pentane) chromatographic purification.[10]

Table 1 shows that whilst the title rearrangement appears fairly general (*i.e.* applicable to various trialkylaluminiums), the yields of the vinyl sulfides **4** are not always satisfactory. One reason for this is that their purification can be tedious,[10] but more importantly, besides the desired compound, variable amounts of

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other products **6**-**9** have also been identified in the reaction mixtures. The alkylphenyl sulfides **9** and the 1-phenylthio-1-alkynes **7** most probably arise from the reaction of PhSCl with **2**, and the diphenyldisulfide **8** may originate from PhSCl reacting with PhS-Al$(R^1)_2$, which may have been eliminated from **3** during the warming of the reaction mixture.[11]

Table 1

Entry	R^1	R^2	**4**, Yield[a] (%)	Other Products, Yield[b] (%)
1	n-C_5H_{11}	CH_3	71 (43)	PhSMe(5), PhSSPh(5), n-C_5H_{11}CCSPh(5)
2	n-C_5H_{11}	C_2H_5	75 (45)	PhSEt(5), PhSSPh(10), n-C_5H_{11}CCSPh(5)
3	n-C_5H_{11}	i-Bu	34 (26)	PhSi-Bu(16), PhSSPh(21), n-C_5H_{11}CCSPh(21)
4	n-C_5H_{11}	n-C_8H_{17}	43 (29)	$PhSC_8H_{17}$(21),PhSSPh(8), n-$C_5H_{11}CCC_8H_{17}$(11)
5	n-$C_{10}H_{21}$	C_2H_5	63 (44)	PhSEt(2), PhSSPh(6), n-$C_{10}H_{21}$CCH(22)[c]
6	THPO-C_2H_4	C_2H_5	38 (27)	PhSEt(13), PhSSPh(13), THPO-CH_2CH_2CCH(26)

[a] GC yield (isolated yield); [b] GC yields; [c] Traces of 1-phenylthio-1-dodecyne also observed

We have shown recently[9] that vinyl sulfides of the type **4** can be valuable precursors of trisubstituted olefins. Furthermore, vinyl aluminiums are known to react with electrophiles.[7a] In one case, activation of intermediate **3** ($R^1 = n$-C_5H_{11}, $R^2 = C_2H_5$) with 1 equivalent of n-butyllithium at -40 °C followed by reaction with a threefold excess of allylbromide gave **5** ($R^1 = n$-C_5H_{11}, $R^2 = C_2H_5$, R^3 = allyl) in a reasonable 39% (GC) yield.

Work is being pursued in view of optimizing the novel **2** --> **3** rearrangement as well as expanding its scope.

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10. The *E* stereochemistry has been assigned by comparison of the ^1H NMR spectrum with that of the same compound obtained *via* similar rearrangement of the analogous boron ate complex, see ref. 9. It is worth noting that the *Z* stereoisomer was not present in the crude product mixture; we assume that it originates from the prolonged contact with silica gel during purification.

11. The strongly suspected presence (on the basis of GC/MS scrutiny) of the internal alkynes **6** in most product mixtures is in favor of this interpretation; however, the sometimes uncorrelated relative amounts of **6** and **8** indicate that it isn't entirely satisfactory.