Pergamon

Tetrahedron Letters 40 (1999) 5943–5944

TETRAHEDRON
LETTERS

Electrophile Induced Rearrangement of 1-Alkynylaluminium Ate Complexes

Antoine Debuigne, Julien Gérard and Làszlò Hevesi*[#]

Department of Chemistry, Facultés Universitaires Notre-Dame de la Paix
61, rue de Bruxelles, B-5000 NAMUR (Belgium)

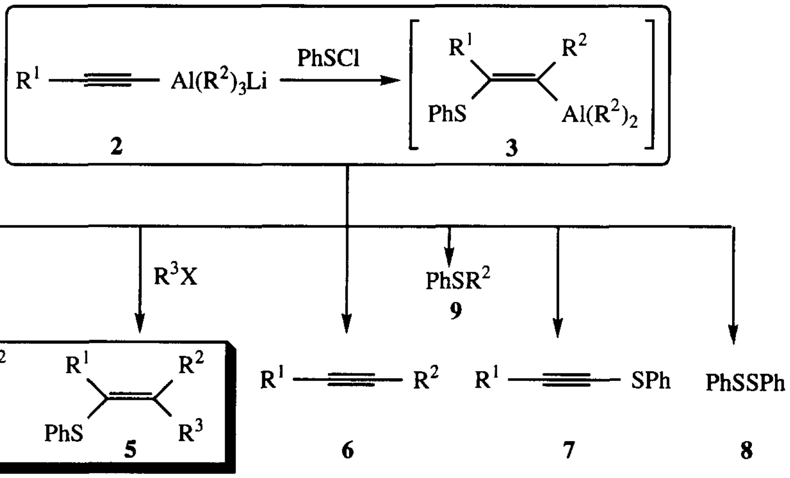
Received 29 April 1999; accepted 15 June 1999

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

PII: S0040-4039(99)01179-X

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.

Financial support from Project INTAS/RFBR 95-126 is gratefully acknowledged.

References and Notes

e-mail: laszlo.hevesi@fundp.ac.be; fax: +32-81-724530

1. Lipshutz, B. H., and Sengupta, S. *Organic Reactions*, **1992**, *41*, 135-631

2. a) Pelter, A., Smith, K., and Brown, H. C. *Borane Reagents*, Academic Press, London, **1988**, b) Wrackmeyer, B. in *Advances in Boron Chemistry*, Ed. Siebert, W., The Royal Society of Chemistry, Cambridge, **1997**, p. 73.

3. a) Hooz, J., and Mortimer, R. *Tetrahedron Lett.*, **1976**, 805; b) Hooz, J., and Mortimer, R. *Can. J. Chem.*, **1978**, *56*, 2786; c) Wang, K. K., Chu, K.-H. *J. Org. Chem.*, **1986**, *51*, 767; d) Wang, K. K., Chu, K.-H., Lin, Y., and Chen, J.-H. *Tetrahedron*, **1989**, *45*, 1118; e) Wang, Z., and Wang, K. K.,*J. Org. Chem.*, **1994**, *59*, 4738.

4. Reetz, M.T. in *Organometallics in Synthesis - A Manual*, Ed. Schlosser, M., John Wiley & Sons Ltd., Chichester (UK), **1994**, 195-282, and references cited.

5. Inoue, R., Shinokubo, H., and Oshima, K. *J. Org. Chem.*, **1998**, *63*, 910 and references cited

6. a) Harada, T., Wada, H., and Oku, A. *J. Org. Chem.*, **1995**, *60*, 5370; b) Harada, T., Otani, T., and Oku, A. *Tetrahedron. Lett.* **1997**, *38*, 2855

7. a) Zweifel, G., and Miller, J. A. *Organic Reactions*, **1984**, *32*, 375-517; b) Yamamoto, H. in *Organometallics in Synthesis - A Manual*, Ed. Schlosser, M., John Wiley & Sons Ltd., Chichester (UK), **1994**, 509-533

8. a) Skrydstrup, T., Bénéchie, M., and Khuong-Huu, F. *Tetrahedron. Lett.*, **1990**, *31*, 7145-48; b) Lipshutz, B. H. and Tirado, R *J. Org. Chem.*, **1994**, *59*, 8307-11

9. Gérard, J., Bietlot, E., and Hevesi, L. *Tetrahedron. Lett.*, **1998**, *39*, 8735

10. The *E* stereochemistry has been assigned by comparison of the ^{1}H 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.