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ON THE STEREOCHEMISTRY OF ALLENE FORMATION FROM MESTRANOL METHANESULFINATE BY *t*-BUTYLSILVER(I).

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Summary: The reaction of [*t*-BuAgBr]MgCl·2LiBr with mestranol methanesulfinate (**1**) in a mixture of THF and HMPT leads to (*S*)-allene **2** via a *syn* 1,3-substitution process. This stereochemistry is identical to that observed for the corresponding cuprate reaction.

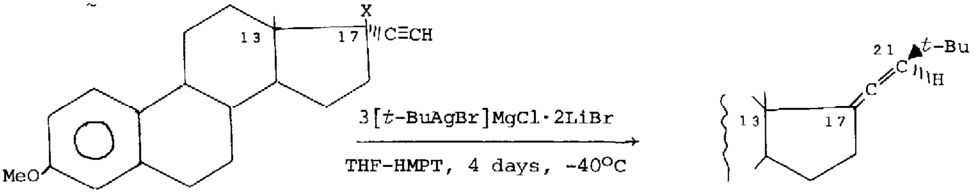
From the literature it is well known that organocuprates are suitable reagents to convert various propargylic esters via a 1,3-substitution into allenes. Much attention has been paid to stereochemical features of this interesting reaction. The available data show that the *syn/anti*-ratio of the reaction depends on several factors such as type of substrate,[1-6] nature of leaving group,[7,8] reaction temperature,[7] and experimental procedure.[7]

Hitherto, the behaviour of organosilver(I) compounds towards propargylic esters have not received attention in the literature. In our opinion this is mainly due to the traditionally assumed high instability of silver(I) compounds.[9] We recently noted, however, that the stability of silver(I) compounds is considerably improved by lithium bromide.[10] We further showed that such stabilized organosilver(I) compounds give 1,4-adducts with conjugated enynes,[10] and that they add *trans* to the C≡C bond of 2-alkynenitriles.[11] In view of the reported *cis* addition of cuprates to 2-alkynenitriles,[12] the stereochemical course of the corresponding argentate reaction is quite remarkable.

In principle, organosilver(I) and organocopper(I) compounds could also exhibit a different stereochemistry in 1,3-substitution reactions. To study this we decided to investigate the stereochemical course of an organosilver(I) induced 1,3-substitution in easily available mestranol methanesulfinate (**1**, see Scheme)[3] and compare the substitution mode with that observed for the corresponding cuprate reaction.

It soon appeared that the conversion of **1** by argentates took place very slowly. For instance, treatment of a solution of **1** (0.01 mol) in a mixture of tetrahydrofuran (THF, 100 ml) and hexamethylphosphoric triamide (HMPT, 15 ml) with 3 mole equiv. of [*t*-BuAgBr]MgCl·2LiBr for 3 hrs at -40°C furnished the desired allene **2** (see Scheme) in about 15% yield. Lengthening of the reaction time to 4 days resulted in a better conversion of 1, *viz.* 75%. Under similar conditions [MeAgBr]MgCl·2LiBr completely failed to react with 1.

Allene 2 could easily be purified by column chromatography (Al_2O_3/H-hexane); after this purification it showed a sharp melting point (62.2-62.5°C). The following characteristic spectroscopic data for 2 were found: $[\alpha]_D^{20}$ (in CH_2Cl_2) -50.8°; ^{1}H-NMR ($CDCl_3$, TMS): signals at δ 0.88 (13-Me), δ 1.05 (21-*t*-Bu), and δ 5.15 (21-H). These values are identical to those reported for allene 2 with the *t*-butyl group in β-position.[13] Consequently, the conversion of 1 by [*t*-BuAgBr]MgCl·2LiBr into 2 follows the *syn* mode:



1 (X=MeS(O)O-)

(*S*)-2 (yield: 75%)

In a recent paper we have already noted that the cuprate [MeCuBr]MgCl exclusively induces a *syn* 1,3-substitution in sulfinate 1.[3] A reaction of 1 with [*t*-BuCuBr]MgCl has not been reported yet. We therefore allowed 1 (0.01 mol) to react with an equivalent amount of [*t*-BuCuBr]MgCl·LiBr in THF (60 ml) for 30 min at -50°C. This short reaction time appeared to be long enough for a nearly quantitative conversion (> 98%) of 1 into its 1,3-substitution product. Analysis of this product showed that it consisted of pure (*S*)-allene 2, *i.e.* the *syn* 1,3-substitution product.

The present study thus shows that, in contrast with the complementary stereochemical behaviour reported for the addition reaction of argentates and cuprates with 2-alkynenitriles, [*t*-BuAgBr]MgCl·2LiBr as well as [*t*-BuCuBr]MgCl·LiBr induce a *syn* 1,3-substitution in ester 1, although with different rates. Further work in this field is in progress.

References

1. P. Rona and P. Crabbé, J. Amer. Chem. Soc. 91, 3289 (1969).
2. L.A. van Dijck, B.J. Lankwerden, J.G.C.M. Vermeer, and A.J.M. Weber, Recl. Trav. Chim. Pays-Bas, 90, 801 (1971).
3. P. Vermeer, H. Westmijze, H. Kleijn, and L.A. van Dijck, *ibid.* 97, 56 (1978).
4. G. Tadema, R.H. Everhardus, H. Westmijze, and P. Vermeer, Tetrahedron Lett. 1978, 3935.
5. J.L. Luche, E. Barreiro, J.M. Dollat, and P. Crabbé, *ibid.* 1975, 4615.
6. H. Westmijze and P. Vermeer, *ibid.* 1979, 4101.
7. W.H. Pirkle and C.W. Boeder, J. Org. Chem. 43, 1950 (1978).
8. L.-I. Olsson and A. Claesson, Act. Chem. Scand. B 33, 679 (1979).
9. C.D.M. Beverwijk, G.J.M. van der Kerk, A.J. Leusink, and J.G. Noltes, Organometal. Chem. Rev. A., 5, 215 (1970).
10. H. Westmijze, H. Kleijn, and P. Vermeer, J. Organometal. Chem. 172, 377 (1979).
11. H. Westmijze, H. Kleijn, and P. Vermeer, Tetrahedron Lett. 1979, 3327.
12. H. Westmijze, H. Kleijn, and P. Vermeer, Synthesis 1978, 454.
13. L.A. van Dijck, B.J. Lankwerden, and J.C.G.M. Vermeer, Recl. Trav. Chim. Pays-Bas 98, 533 (1979).

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