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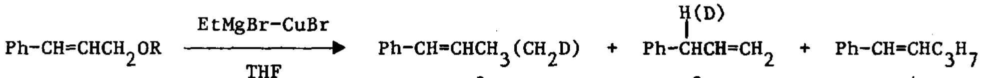
REDUCTIONS OF ALLYLIC COMPOUNDS WITH ORGANOCUPRATES

Alf Claesson* and Christer Sahlberg

Department of Organic Pharmaceutical Chemistry, Biomedical Center, University
of Uppsala, Box 574, S-751 23 Uppsala, Sweden

In a number of cases reductions of acetylenic derivatives with various organocuprates and similar reagents have been described. Thus, propargylic acetates,[1] tosylates,[2] chlorides,[3a] oxiranes[3b] and methyl ethers[4] have been found to yield allenes in which hydrogen instead of an alkyl group has been introduced. In a few cases it has been shown that the hydrogen originates from water as an organometallic intermediate is hydrolysed.[1,2,4] Except for being theoretically interesting this reduction is of preparative interest.[1,4]

Interestingly, no similar reduction of an allylic derivative with an organocuprate seems to have been described. In order to increase the understanding of factors which affect the apparent competition between substitution and reduction in reactions of organocuprates with unsaturated substrates we have tried to effect such a reduction in an allylic system. Indeed, we have found that the cinnamyl methyl ether 1a is almost completely reduced at -25 °C by an excess of organocuprate formed by mixing ethylmagnesium bromide with 0.1 or 0.25 equiv of copper(I)bromide in THF. Upon quenching the yellow reaction mixture with H_2O after 0.5 h the reduction products, 2 and 3, and the substitution product 4 can be indicated in the relative yields shown in the Table. The relative amounts of 2 and 3 varied from sample to sample; compound 2 predominated over 3 in most cases. It was shown by deuterolysis of one reaction mixture that compounds 2 and 3 are derived from an organometallic intermediate; 1.0 mole of deuterium was incorporated per mole of 2 or 3. Using magnesium containing < 5 ppm of other metals and purified CuBr (as the dimethyl sulphide complex) did not change the product ratio.[5] The acetate 1b reacts strikingly different from the corresponding methyl ether in that only minor amounts of reduction products are formed (Table). The total yield of substitution-reduction products was also lower due to cleavage of the ester function.



$$\text{Ph-CH=CHCH}_2\text{OR} \xrightarrow[\text{THF}]{\text{EtMgBr-CuBr}} \text{Ph-CH=CHCH}_3(\text{CH}_2\text{D}) + \text{Ph-}\overset{\text{H(D)}}{\text{C}}\text{HCH=CH}_2 + \text{Ph-CH=CHC}_3\text{H}_7$$

2 3 4

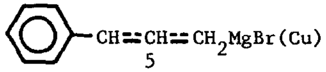
1a, R = Me
b, R = Ac

The only reasonable structure of the yellow intermediate seems to be the MgBr or Cu^{I}-bound mesomeric anion 5 which is hydrolysed to the mixture of 2 and 3. A Cu^{III}-intermediate as the

Compound	mol% CuBr rel. EtMgBr	% reduction products (2+3)	% substitution product (4)	Total yield (%)
1a	10	90	10	>90
1a	10	87[a]	13[a]	>90
1a	25	78	22	90
1b	25	16	84	70

[a] Run with Mg containing <5 ppm of other metals and with purified $CuBr\cdot Me_2S$.

immediate precursor of 2 and 3, which has been suggested in similar reactions,[1,2] can be ruled out primarily for one practical reason *i.e.* there is not enough copper present to bind all the allyl ligands as Cu^{III}. From a theoretical point of view it would also be disturbing if an allyl and alkyl-containing Cu^{III}-complex would be stable for hours at -25° (the product composition is not altered by raising the temperature to 0° before hydrolysis). In summary, our experiments show that there are at least two factors which determine the ratio between substitution and reduction for allylic derivatives in their reactions with the present organocuprate: (i) the structure of the allylic part of the molecule; simple 2-alkenyl methyl ethers do not give rise to reduction products,[6] (ii) the type of leaving group; methoxy giving rise to much more reduction product than acetoxy (Table). We will discuss probable causes of these effects at a later date.[7]



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5. It has been shown that allyl phenyl ether is cleaved (reduced) by BuMgBr in the presence of minute amounts of $CoCl_2$, M.S. Kharasch and R.L. Huang. J. Org. Chem. 17, 669 (1952).
6. A. Commercon, M. Bourgain, M. Delaumeny, J.F. Normant and J. Villieras. Tetrahedron Lett. 3837 (1975); we have specifically looked for reduction products in the reaction of 1-pentyl-2-propenyl methyl ether with EtMgBr-CuBr but have been unable to find any.
7. A grant (to A.C.) from the C.W. Scheele Foundation, administered by the Swedish Academy of Science, is gratefully acknowledged.

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