

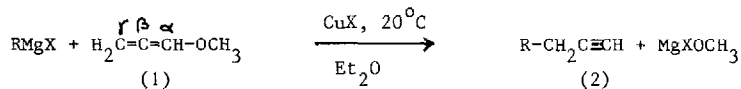
FORMATION OF VINYLIC ETHERS FROM METHOXYALLENE AND ORGANOCOPPER(I) COMPOUNDS

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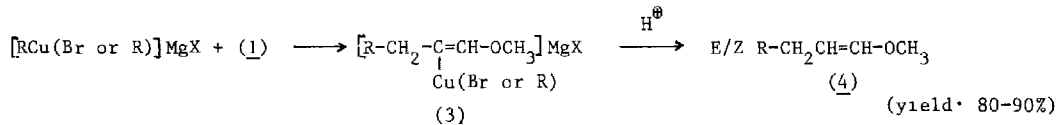
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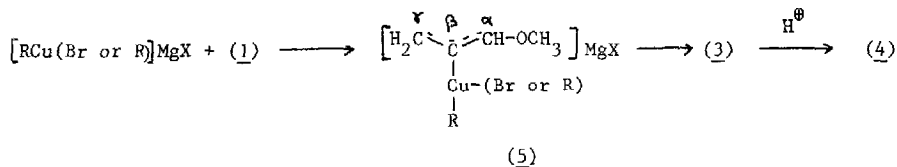
Recently we reported an efficient synthesis of 1-alkynes R-CH<sub>2</sub>C≡CH (2) by reaction of Grignard reagents RMgX with methoxyallene (1) in diethyl ether under the influence of catalytic amounts of copper(I) halides<sup>1</sup>



We found that similar results can be obtained when this reaction is carried out in tetrahydrofuran (THF) with catalytic amounts of CuBr. In order to get more insight in this reaction we treated (1) with preformed homocuprates R<sub>2</sub>CuMgX and heterocuprates [RCuBr]MgX in THF and we observed a smooth reaction leading to the adducts (4) in excellent yields (after protonation)



As is seen in the Table the E/Z ratio in (4) is in two cases strongly influenced by the type of organocopper(I) reagent used, viz R=1-Pr or n-Bu. An explanation for these remarkable differences has still to be given. The assumption of the adduct (3) as intermediate in the formation of (2) from (1) seems reasonable as treatment of (3) with excess RMgX in THF leads quantitatively to (2). The most probable reaction path for the formation of (3) from (1) seems to us a primary attack by the cuprate on the α,β-double bond in (1) leading to a copper (III) intermediate in which rotation will occur to an allylic anion (5). A subsequent 1,3-shift of the R radical in (5) from Cu to C(γ) results in the adduct (3).



This is supported by the fact that with  $(C_6H_5)_2CuMgBr$  also amounts (4-7%) of  $C_6H_5CH=C=CH_2$  are found (see Table) resulting from partially transfer of  $R=C_6H_5$  in (5) to C( $\alpha$ ), followed by loss of  $(C_6H_5CuOCH_3)MgX$ . The mechanism presented above is different from that reported for additions of organocopper(I) compounds to allenes  $-C=C=C-X$  with an electron withdrawing substituent ( $X=P(O)(C_6H_5)_2, S(O)Ar, SO_2Ar$ ) in which reactions the organocopper(I) reagent seems to attack primarily the  $\alpha$ -C atom<sup>2,3</sup>. Alkylation of intermediates (3), being an equivalent of an enolate, with MeI and allylbromide gives good results.

#### General Procedure

To 0.050 mole of  $R_2CuMgX$  or  $[RCuBr]MgX$  (prepared from  $RMgX$  and appropriate amounts of  $CuBr$ ) in 150 ml of THF was added 0.025 mole of methoxyallene (1) at  $-60^\circ C$  (for  $R=C_6H_5$  at  $0^\circ C$ ). After stirring during 30 minutes at  $-30^\circ C$  (in the case  $R=C_6H_5$   $0^\circ C$ ) the reaction temperature was raised to  $0^\circ C$  (for  $R=C_6H_5$  to  $30^\circ C$ ). Subsequently the reaction mixture was poured into 100 ml of an aqueous solution of 5 g of NaCN and 20 g of  $NH_4Cl$ . The adduct (4) was isolated by extraction with pentane. After washing the extracts with water and drying over  $K_2CO_3$  the solvent was distilled off and the residue was distilled at diminished pressure. The purity of the adducts (4) appeared to be >95% according to  $^1H$ -NMR and GLC analysis. (For physical constants see Table).

Table

Cuprate	E/Z ratio of $R-CH_2CH=CH-OCH_3$ (4)	B p ( $^\circ C/mm$ Hg)	$n_D^{20}$
$i-Pr_2CuMgCl$	30/70	47-49/50	1.4154
$t-Bu_2CuMgCl$	12/88	59-61/50	1.4195
$n-Bu_2CuMgCl$	42/58	46-48/18	1.4237 <sup>a</sup>
$(C_6H_5)_2CuMgBr$	43/57	94-98/18	1.5230
$[i-PrCuBr]MgCl$	0/100	50/50	1.4149
$[t-BuCuBr]MgCl$	13/87	58-60/50	1.4194
$[n-BuCuBr]MgCl$	15/85	47-49/18	1.4233
$[C_6H_5CuBr]MgBr$	39/61	94-98/18	1.5234

<sup>a</sup>The undistilled product contained 4-7% of  $C_6H_5CH=C=CH_2$ .

#### References

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