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CARBOCUPRATION OF 1-ALKYNES BY BRANCHED ALKYL HETEROCUPRATES($RCuMgX_2$) IN THE PRESENCE OF EXCESS $MgBr_2$

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Abstract: Carbocupration of less reactive 1-alkynes with RMgX/CuCl reagents derived from branched alkyl groups are achieved in the presence of excess magnesium bromide in THF at room temperature.

Carbocupration of 1-alkynes is one of the most attractive and efficient method for obtaining stereospecifically substituted alkenes.[1] Heterocuprates($RCuMgX_2$ or RCuLiX, R = primary alkyl, X = Br, I or SPh) can be readily added to reactive 1-alkynes (RC≡CH, R=Ph, H, Me).[2] However, the addition of branched alkyl group (especially tertiary alkyl) from heterocuprates (tert-$BuCuMgX_2$ or sec-BuCuLiI) to less reactive 1-alkynes (e.g., 1-octyne) were not successful.[2,4] However, tert-$BuCuMgBr_2$ can be added to phenylacetylene and acetylene.[2d] The homocuprates (R_2CuMgX or R_2CuLi, R = primary alkyl) are generally more reactive and add to less reactive 1-alkynes, but only one R is delivered.[3] In the case of secondary or tertiary alkylcuprates, acetylenic proton abstraction was observed.[4,5] Whereas RMgX/CuBr (R = primary or secondary) reagent is known to reduce internal alkynes into cis-alkenes in ether, the tertiary alkyl reagent does not react with internal alkynes.[6] We wish to report the carbocupration of less reactive 1-alkynes using branched heterocuprates (RMgX/CuCl) in the presence of magnesium bromide in THF at room temperature.

It has been reported that the yields of carbocupration of phenylacetylene with $RCuMgBr_2$ reagent increase with addition of $MgBr_2$ in some cases.[7] We have also observed that the "CuH" reagent, generated using $NaBH_4/CuCl/NEt_3$ or NaH/CuCl adds readily into 1-alkynes in the presence of $MgBr_2$.[8] In order to examine whether the addition of branched alkylcopper reagents to 1-alkynes can be facilitated by performing the reaction in the presence of $MgBr_2$, we carried out the following experiment. To a solution of Grignard grade magnesium (60 mmol, 1.5 g) in THF (80 ml) containing t-BuCl (20 mmol, 1.8 g), 1,2-dibromoethane (20 mmol, 3.7 g) was added during a period of 10 min at r.t. under nitrogen atmosphere and the mixture was stirred for 3 h. The contents were cooled to -24°C (liq.N_2 and CCl_4 bath) and CuCl (20 mmol, 2.0 g) was added. The mixture was stirred for 2 h at -24°C and 1-decyne (10 mmol, 1.4 g) was added. The black reaction mixture was brought to r.t. during a period of 3 h and stirred for further 12 h. The mixture was quenched with H_2O, and stirred for further 30 min. and poured into dil.HCl (50 ml, 2 N). After workup and chromatography on a silica gel column 2-tert-butyl-1-decene (65%) and unreacted 1-decyne (30%) were isolated. The results obtained using different branched alkylcuprates with 1-decyne and 1-octyne are summarised in Table 1.

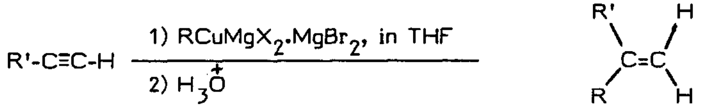

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Table 1. Conversion of 1-alkynes into 2,2-dialkyl olefins.

Entry	R' in **1** (10 mmol)	R in RMgX/CuCl/MgBr$_2^a$ (20/20/ 20 mmol)	Yield (%) 2^b	Recovered 1-alkyne (%)^c
1	n-C_6H_{13}	t-Bu (X = Cl)	60	35
2	n-C_8H_{17}	t-Bu (X = Cl)	65	30
3	n-C_6H_{13}	t-amyl (X = Cl)	40	52
4	n-C_8H_{17}	t-amyl (X = Cl)	40	50
5	n-C_8H_{17}	iso-butyl (X = Br)	55	40
6	n-C_8H_{17}	iso-propyl (X = Br)	57	35

(**a**) All the reactions were carried out under the same conditions as mentioned in the experimental procedure, i.e., reagent quantities, temperature and reaction time. Further increase in the amount of $MgBr_2$ did not have any affect and only small amount (~5%) of addition product was isolated without $MgBr_2$. (**b**) All yields are of isolated products by chromatography on a silica gel column using hexane as eluent and are based on the amount of 1-alkyne initially taken. The actual yields will be high if the amount of recovered 1-alkynes are taken into account. The products were identified by IR, ^1H NMR, ^{13}C NMR and mass spectral data. (**c**) Yields are of recovered starting alkynes.

In order to examine the stability of vinylcopper intermediates produced in the present case, the reaction mixture was treated with D_2O before work-up and stirred for 1 h in the case of t-amylcuprate. Mass spectral data of the isolated alkene showed that deuterium was incorporated to the extent of 75% (M^+ peak at m/e 211 and M^+-1 peak at m/e 210 are in 3:1 ratio) and the recovered 1-decyne did not contain any deuterium. It has been reported that excess LiBr stabilizes vinylcopper reagents.[3] Such solutions are even stable at room temperature.[3] Presumably, the magnesium bromide also has the same affect. In addition, the vinylcopper intermediate in the present case would be highly hindered and this may also help in the unusual stability of the vinylcopper intermediates in the present case.

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References: 1. G.H.Posner, Organic Reactions, 1972, **19**, 1; J.F. Normant, Synthesis, 1972, 63; J.F. Normant and A. Alexakis, Synthesis, 1981, 841. **2.** a/ J.F. Normant, G. Cahiez, M. Bourgain, C. Chuit and J. Villieras, Bull. Soc. Chim. Fr., 1974, 1656; b/ J.F. Normant, G. Cahiez, C. Chuit and J. Villieras, J. Organomet. Chem., 1977, **77**, 269, 281; c/ A. Alexakis, J.F. Normant and J. Villieras, Tett. Lett., 1976, 3461; d/ H. Westmijze, J. Meijer, H.J.T. Bos and P. Vermeer, Recl. Trav. Chim. Pays-Bas.,1976, **95**, 299. **3.** H. Westmijze, J. Meijer, H.J.T. Bos and P. Vermeer, Recl. Trav. Chim. Pays-Bas., 1976, **95**, 304. **4.** H. Westmijze, H. Kleijn and P. Vermeer, Tett. Lett., 1977, 2023. **5.** J.F. Normant and M. Bourgain, Tett. Lett., 1971, 2583. **6.** J.K. Crandall and F. Collonges, J. Org. Chem., 1976, **41**, 4089. **7.** E.C. Ashby, R.S. Smith and A.B. Goel, J. Organomet. Chem., 1981, **215**, C1. **8.** S. Achyutha Rao and M. Periasamy, J. Chem. Soc. Chem. Commun., 1987, 495.

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