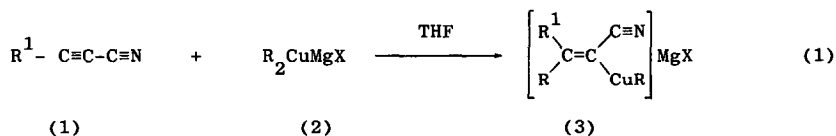


ON THE REACTION OF ALKYLARGENTATES WITH SOME 2-ALKYNE-NITRILES.

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Summary : Alkylargentates add *trans* to the triple bond of 2-alkynenitriles to furnish α -cyanovinylargentates in a high yield. The adducts are configurational unstable at higher temperature.

In a recent paper¹ we reported on the smooth *cis* addition of organocuprates (2) to 2-alkyne-nitriles (1) furnishing α -cyanovinylcuprates (3, eq. 1) :



R¹ = Alkyl, phenyl
 R = Alkyl, phenyl
 X = Cl or Br

A *cis* stereochemistry has also been observed for the addition of organocopper(I) reagents to a large number of other acetylenic substrates. Hitherto the reactivity of the corresponding alkyl-argentates towards C-C triple bonds has received little attention in the literature. This is due mainly to the generally high thermal instability of alkylsilver(I) reagents. Recently² we found, however, that the stability of alkylsilver, RAg, and alkylargentates, R₂AgMgX, could be improved considerably by preparing them in the presence of lithium bromide. Moreover it appeared that such stabilized alkylsilver(I) species were capable to react with conjugated enynes to afford addition products (cf²). Currently we are continuing our study concerning the applicability of these reagents in synthesis. The present paper describes our results obtained for the reaction of 2-alkynenitriles 1 with stabilized alkylargentates of the type R₂AgMgX.2LiBr (4). We shall show that the latter reagents are capable to convert 2-alkynenitriles into 2-alkenenitriles in excellent yields. Thus reaction of 1 (0.030 mol; R¹ = Ph or 1-cyclohexenyl) in THF (150 ml) with R₂AgMgCl.2LiBr (0.030 mol)³ for 0.5 hr at -50° (R = Et or Bu) or 2 hrs at -35° (R = Me) and subsequent protolysis at -50° and -35° respectively furnished 2-alkenenitriles (6) in nearly quantitative yield (1 + 4 ⇒ 5 ⇒ 6 in eq. 2; yield of 6 > 98%).

