ON THE REACTION OF ALKYLARGENTATES WITH SOME 2- ALKYNENITRILES.

Hans Westmijze , Henk Kleijn and Peter Vermeer .
(Department for Organic Chemistry of the University , Croesestraat 79,
Utrecht , The Netherlands)

 $\frac{Summary}{\alpha} : Alkylargentates add <u>trans</u> to the triple bond of 2-alkynenitriles to furnish$ $<math>\alpha$ -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-alkynenitriles (1) furnishing α -cyanovinylcuprates (3, eq. 1):



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 alkylargentates 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 (cf^2). 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 ($\underline{4}$). 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 R₂AgMgC1.2LiBr (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 ($\underline{6}$) in nearly quantitative yield ($\underline{1} + \underline{4} \Rightarrow \underline{5} \Rightarrow \underline{6}$ in eq. 2; yield of $\underline{6} > 98$ %).



The spectral and physical data of the 2-alkenenitriles $\underline{6}a$ -c were identical to those reported for the same compounds in reference 1. The α,β -unsaturated nitrile $\underline{6}d^4$ has not been described before but its geometric isomer is known (cf¹).

In view of the geometric structure of <u>6</u> we assume that a *trans* addition reaction between <u>1</u> and <u>4</u> took place leading to <u>5</u> from which <u>6</u> was formed with retention of configuration upon protolysis Adducts <u>5</u> could be transformed partially into the isomeric α -cyanovinylargentates <u>7</u> by stirring <u>5</u> for 1 hr at + 30°C. Under the latter conditions a mixture of <u>6</u> and <u>8</u> was obtained in a ratio 21 : 79 (<u>6a:8a</u>) , 27 : 73 (<u>6b:8b</u>) , 40 : 60 (<u>6c:8c</u>) and 63 : 37 (<u>6d:8d</u>).Stirring for longer periods at + 30°C did not influence these ratios. The corresponding α -cyanovinylcuprates have also found to be configurationally unstable at + 30°C (cf¹).

Our results show that , just like organocuprates , stabilized alkylargentates are capable to add to the C-C triple bond of 2-alkynenitriles but the stereochemical course of the alkylargentate reaction is completely *opposite* to that of the cuprate one. This fact makes further work in this field very promising.

Acknowledgement This investigation was supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO).

References and notes.

- 1. H.Westmijze , H.Kleijn and P.Vermeer , Synthesis , 454 (1978).
- 2. H.Westmijze , H.Kleijn and P.Vermeer , J.Organometal.Chem., in press.
- 3. The argentates were prepared by stirring the THF soluble complex $Ag^{I}Br.2LiBr$ with two mole equivalents of RMgCl for 30 min. at $-60^{\circ}C$.
- 4. ¹H NMR data of <u>6</u>d (CDCl₃ solution , δ in ppm (Me₄Si = 0 ppm)) recorded on a Varian EM 390 spectrometer : $\delta = CH-C=N$: 5.18 , $\delta CH_3 -C=$: 2.15 . Physical constants of <u>6</u>d : B.p. 75^oC / 0.5 mmHg , $n_D^{20} = 1.5495$.

(Received in UK 25 June 1979)