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ON THE HOMOPROPARGYLATION OF ALKYLVINYLCUPRATES.
A NEW ENTRANCE TO THE CHEMISTRY OF JUVENILE HORMONES AND THEIR ANALOGS.

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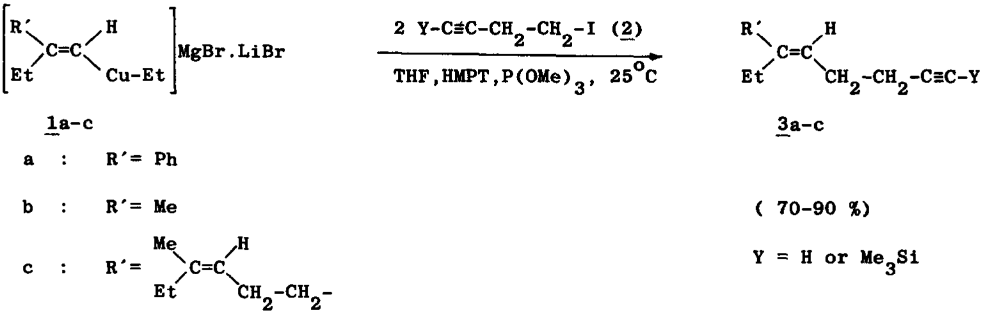
Alkylation of vinylheterocuprates in diethyl ether has been shown to proceed with retention of configuration and with satisfactory yields in many cases[1]. However , the reaction of vinylheterocuprates with homopropargylating reagents like 2 has been very troublesome thusfar[1-3]. Recently[4],we reported on the stereospecific synthesis of alkylvinylcuprates like 1a-c from 1-alkynes and dialkylcuprates in a high yield, using tetrahydrofuran (THF) as a solvent. We decided to study the behaviour of such mixed homocuprates towards homopropargylating reagents 2 (Y = H or Me_3Si) in more detail , as a smooth homopropargylation of the vinyl part of these cuprates would be an interesting new entrance to the preparation of natural compounds and their analogs (*vide infra*). In this paper we wish to present our preliminary results .

Treatment of the alkylvinylcuprates 1a-c (cf 4) with two mole equivalents of 2 (Y = H or Me_3Si) produced the desired homopropargylated compounds 3 a-c in good yields (70-90 %), provided that the alkylation was carried out in the presence of hexamethylphosphoric triamide (HMPT) and trimethyl phosphite [5] :



Recently [6] we found that the alkylgroup of a number of alkylvinylcuprates reacted much faster with methyl iodide than the vinyl group. We were therefore very surprised to obtain compounds 3 in reasonable yields (~ 60 %) from the reaction of 1 with <u>one</u> equivalent of 2 .

Our present study shows that we now have a method at hand which leads , starting from simple 1-alkynes (e.g. : propyne $\longrightarrow$ [1b] $\longrightarrow$ 3b $\longrightarrow$ [1c] $\longrightarrow$ 3c) in a few steps and in a good overall yield to compounds of type 3c , which are very useful precursors for juvenile hormones and their analogs (cf [3]).
Currently , an extensive study concerning the homopropargylation and other alkylations of alkylvinylcuprates is in progress.
The results will be applied to the synthesis of juvenile hormones.

A typical procedure is as follows :

To a stirred suspension of 1 (0.01 mol)[4] in a mixture of THF (35 ml) and HMPT (5 ml) we added trimethyl phosphite (0.02 mol for R′= Ph ; 0.04 mol for R′= Me or (Z)-Me(Et)C=CH-$(CH_2)_2$) at -50°. After stirring the reaction mixture during 15 min at - 50° two equivalents of 2 (0.02 mol) were cautiously added at - 50°. The temperature of the reaction mixture was raised within 30 min to + 25° followed by stirring during 6 hours at this temperature. Subsequently, the alkylated products 3 were isolated in the usual manner. The yields, which are not optimalized , were determined by GLC and ^{1}H-NMR analysis.
The spectroscopic data of the purified products were in agreement with the proposed structures 3a-c and will be published in a full paper.

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References and notes.

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3. C.Chuit , G.Cahiez . J.Normant , J.Villieras , Tetrahedron , 32 , 1675 (1976).
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5. If HMPT and $P(OMe)_3$ were omitted , the results were disappointing .
   Alkylation of vinylcopper(I)compounds in diethyl ether has also been reported to give better results in the presence of HMPT and $P(OMe)_3$ (cf [1]).
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