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# AN ORGANOCOPPER MEDIATED SYNTHESIS OF (*E*)-1,4-DI-TERT-BUTYLBUTATRIENE.

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*Summary* *In the paper a highly stereoselective route to trans-1,4-di-tert-butylbutatriene via t-BuCu induced 1,3-substitution in (Z)-t-BuCH=C(Br)-C≡CH is described.*

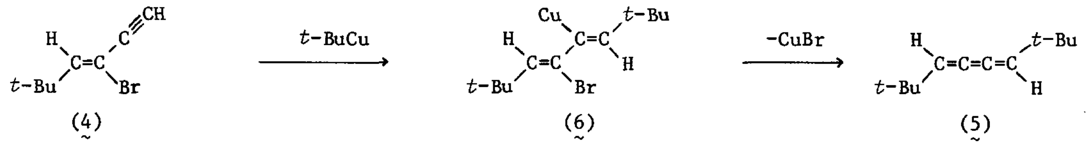
In the literature a number of reports concern the reaction of conjugated enynes with organocopper compounds. The available data show that the reaction gives adducts **2** (see eq.1) when the group R is small, and mixtures of adducts **2** and **3** when the group R is bulky.[1,2] Both adducts **2** and **3** arise by addition of the copper reagent to the triple bond.

R'= H or alkyl

It is noteworthy in this connection that in one case addition of a copper reagent to the double bond of a conjugated enyne has been observed.[3]

At the moment that this study was initiated it was not known how copper reagents react with conjugated enynes in which on C(3) instead of R' a good leaving group (*e.g.* Br) is present. If the reaction of copper reagents with such functionalised enynes should give adducts of type **3**, a subsequent elimination of CuX from these adducts should give cumulated trienes.

To investigate this potential route to butatriene derivatives it was decided to treat a suitably substituted 3-bromo-3-alken-1-yne with an organocopper compound. 3-Bromo-3-alken-1-ynes are readily available by reaction of 1,3-diynes with alkylsilver compounds and subsequent reaction of the produced adducts with *N*-bromosuccinimide.[4] For our purpose we prepared the 3-bromo-3-alken-1-yne **4** (see eq.2). We were very pleased to find that treatment of **4** with an equimolar amount of *t*-BuCu during 15 min at -50°C in tetrahydrofuran gave in a regiospecific reaction pure triene **5** (see eq.3) in excellent yield (95%). $^1H$ NMR analysis (see below) showed that this regiospecific reaction was also highly stereoselective, if not stereospecific. Thus starting from **4** (*E*/*Z*=7/93) compound **5** has been obtained as a mixture consisting of 93% *trans* and 7% *cis* isomer. This stereochemical course is conceivable by assuming that the overall substitution follows the two-step reaction sequence depicted in eq.2:



(2)

The first step of the reaction is proposed to be a *cis* addition of *t*-BuCu to the triple bond in 4. This proposal is quite reasonable in view of the well-known *cis* addition of organocopper reagents to other 1-alkynes.[1,2,5] The second reaction step in eq.2 must then involve an *anti* elimination of CuBr from adduct 6. Unfortunately, attempts to intercept adduct 6 by protolysis at -60°C have failed thus far, so that a synchronous 1,3-substitution path cannot be excluded.

The *trans* geometry proposed for 5 is based on the comparison of the $^1$H NMR data recorded for this compound with those found for *cis*-1,4-di-*tert*-butylbutatriene. The *cis* butatrienyl compound is readily available from ethynyl methyl sulfide and *t*-BuCu.[6,7] Its $^1$H NMR spectrum ($CCl_4$; $\delta(Me_4Si)$= 0 ppm) shows two sharp singlets, one at $\delta$ 5.44(=CH) and the other at $\delta$ 1.11 (*t*-Bu). Our compound 5 on the other hand shows sharp singlets at $\delta$ 5.48(=CH) and $\delta$ 1.09(*t*-Bu). A mixture of both compounds shows the expected four signals in the $^1$H NMR spectrum. The overall stereochemistry of the conversion of 4 into 5 is therefore *anti*. To our best knowledge this is the first example of an organocopper induced 1,3-substitution in a propargylic compound in which the carbon bearing the leaving group is $sp^2$-hybridized. Also organocopper induced 1,3-substitution reactions in propargylic esters in which the propargylic carbon is $sp^3$-hybridized generally proceed *anti*.[8]

Currently the scope of the presented reaction principle is investigated.

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7. That this reaction indeed gives *cis*-butatriene derivatives has been established by X-ray analysis of another butatriene compound which was prepared *via* the same method: W.G.M. van den Hoek, J. Kroon, H. Kleijn, H. Westmijze and P. Vermeer, and H.J.T. Bos, J. Chem. Soc., Perkin II, 1979, 4231.
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