

THE BEHAVIOUR OF SOME FUNCTIONALLY SUBSTITUTED α -ALLENIC ALCOHOL DERIVATIVES TOWARD ORGANOCOPPER(I) SPECIES

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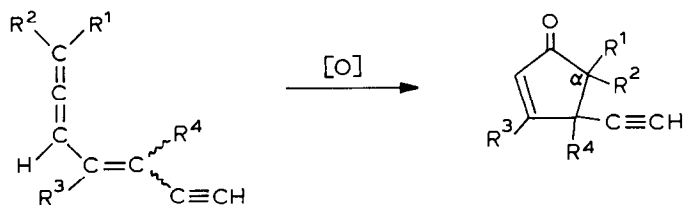
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Summary

Trimethylsilyl ethers of 2,3-hexadien-5-yn-1-ols (**1**) undergo carbocupration at the terminal triple bond, and this reaction has been used to prepare, among other species, the trimethylsilyl ethers of 8-trimethylsilyl-2,3,5-octatrien-7-yn-1-ols (**6a** and **7a**). When the terminal triple bond of **1** is protected with a trimethylsilyl group S_N2' -like displacements take place upon addition of RCu , with predominant formation of *E*-dienynes in which H is present instead of R, especially when *s*-BuCu is used. Only when R is methyl is the R group transferred. On the other hand, smooth formation of dienynes bearing the R group are observed upon reaction of methanesulfonates with RCu ; in this case, however, the configuration of the dienynes is mainly *Z*. A mechanistic rationalization of the results is proposed.

Introduction

Vinylallenes are versatile starting compounds for cyclopentenones. It has been shown that such allenes undergo ring closure upon treatment with peracids [1]. This route to cyclopentenones constitutes an interesting entry to the synthesis of prostaglandins and the like. Efforts in that direction have been undertaken by epoxidizing derivatives of vinylallenes, viz. the so-called allenynes [2]. The presence of the triple bond gives rise to formation of cyclopentenones which carry this triple bond in a suitable position for further derivatization, e.g. into prostaglandine systems.



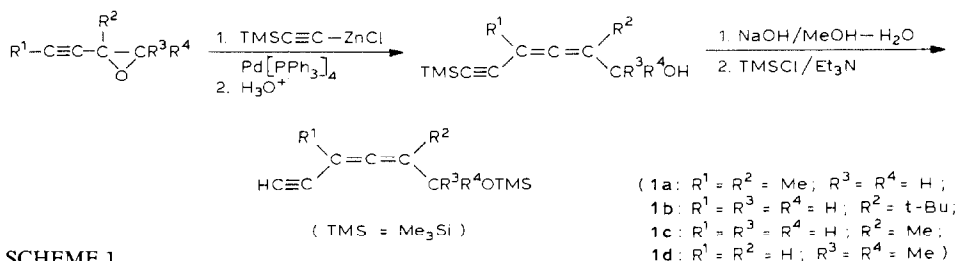
($R^1 - R^4$ = alkyl group)

The required allenynes were prepared by a rather laborious route in 22–46% overall yield and were obtained as *Z/E*-mixtures [2]. In view of these results we felt that it would be worthwhile to find an easier method of preparing such allenynes. Furthermore, it was anticipated that the presence of a hydroxymethyl group at C_α in the cyclopentenone would be attractive for further conversions.

It is shown in part I of this paper that a number of allenynes are readily accessible through carbocupration of the triple bond of 2,3-hexadien-5-yn-1-ols. In part II some quite unexpected results are presented; these were obtained upon addition of organocopper(I) species to similar substrates in which the triple bond was protected against carbocupration.

I. Carbocupration of trimethylsilyl ethers of 2,3-hexadien-5-yn-1-ols

It was observed recently in our laboratory that α -acetylenic epoxides undergo S_N2'-like displacements smoothly and in excellent yields upon treatment with 1-alkynylzinc compounds in the presence of a palladium(0) catalyst [3]. It was therefore not difficult to prepare the allenynes **1** required for our study from the readily available α -acetylenic epoxides (overall yield of **1** > 80%).



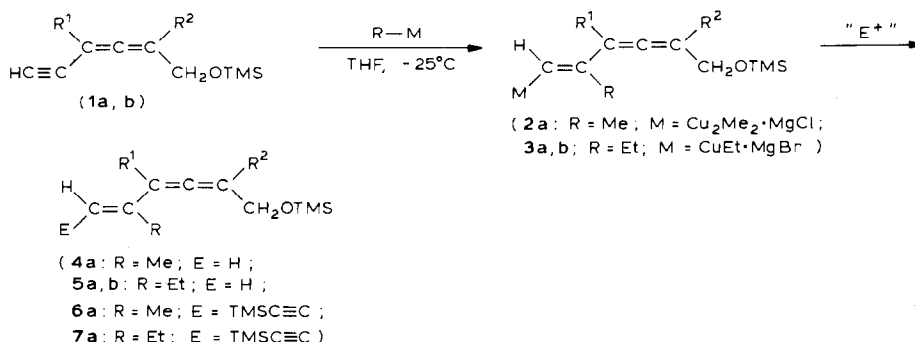
SCHEME 1

With compounds **1** available we then studied carbocupration of the terminal triple bond. We confined ourselves to reactions of **1** with methyl- and ethylcopper(I) species (solvent, tetrahydrofuran). First we investigated the reaction of **1a** with the trimethyldicuprate Me₃Cu₂MgCl. From other work it had appeared that this cuprate is excellent for conversion of 1-alkynes stereo- and regio-specifically into 2-methyl substituted 1-alkenes [4,5].

We were pleased to find that also allenyne **1a** underwent a smooth *cis* addition by a selective transfer of one of the three available methyl groups. The resulting intermediate **2a** (Scheme 2) gave vinylallene **4a** (75% yield after distillation) upon protolysis. More importantly, addition of (trimethylsilyl)ethynyl iodide to **2a** gave the desired allenyne **6a** in 85% yield after purification over Florisil (see Scheme 2) [6].

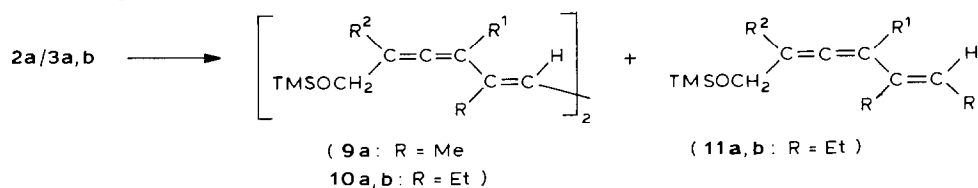
The use of MeCu, prepared from MeMgCl and copper(I) bromide, gave disappointing results. Its reactivity is low so that under the conditions which had to be used the initially formed adduct dimerized into the polyene **9a** (Scheme 3) [7,8]. Experiments in which the homocuprate Me₂CuMgCl was used also gave results poorer than those obtained with Me₃Cu₂MgCl. The homocuprate is too basic so that substantial deprotonation of **1a** occurred as was shown by deuteriolysis of the reaction mixture: in addition to the desired adduct, ca. 30% of monodeuterated **1a** (–C≡C–D) was recovered. Deprotonation of 1-alkynes by dimethylcuprates has been known for a long time [9,10].

Ethylation of the allenyne **1a** and **1b** was brought about smoothly by Et_2CuMgBr . When this homocuprate was used, no deprotonation of the acetylenic function occurred. One of the two available ethyl groups was transferred to **1** in these cases. Protonation of the intermediate adducts **3a,b** gave vinylallenenes **5a,b** whilst addition of (trimethylsilyl)ethynyl iodide gave the desired allenenyne **7a** (see Scheme 2) in 75% yield after purification. Physical constants and spectroscopic data for **4–7** are given in the Experimental section.



SCHEME 2

The reaction temperature during the carbocuprations appeared to be rather critical. Above -25°C , especially adduct **2a** tended to dimerize into the polyene **9a** in Scheme 3. The choice of starting reagents from which the cuprates were prepared appeared to be important. Thus, the best results in, e.g., the ethylation reaction were obtained when the cuprate was prepared from EtMgBr and copper(I) chloride. The use of copper(I) bromide in these cases gave some dimer **10** and some double ethylated product **11** (see Scheme 3).



SCHEME 3

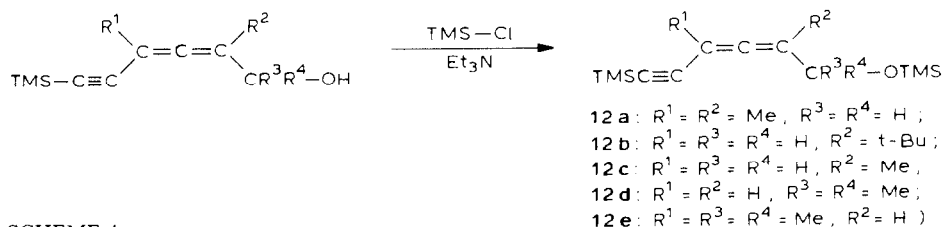
The regioselectivity of the carbocupration reaction depended on the nature of R^1 and R^2 . It was high (> 98%) when R^1, R^2 were Me, Me or H, t-Bu (compounds **1a** and **1b**) but poor when R^1, R^2 were H, H or H, Me (compounds **1c** and **1d**). In the latter two cases mixtures of the desired adducts and unidentified contaminants were obtained. For the time being, we assume that these contaminants arose by attack of the copper(I) reagents on the central C-atom of the allenic moiety of **1**. Further work will be carried out to determine the structure of the contaminants.

In any case, sufficient steric protection of the allenic moiety of **1** seems to be a prerequisite for a highly regioselective reaction at the triple bond. The low regioselectivity in the case of **1c** and **1d** raised the question of whether it would be possible to direct the attachment of R entirely to the central C-atom of the allenic system. It was therefore decided to make the triple bond unattractive to attack of organo-copper(I) species by protecting it with a trimethylsilyl group. The results of this study are presented in part II, below.

II. Reactions of derivatives of 6-trimethylsilyl-2,3-hexadien-5-yn-1-ols with organo-copper(I) species

a. Conversion of the trimethylsilyl ethers **12a-e**

The allenynes **12a-e** used for this part of our study were readily prepared as follows.

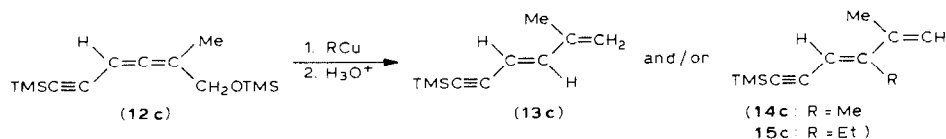


SCHEME 4

Our initial experiments concerned the reactions of **12c** with the cuprate Et₂CuMgBr. Treatment of **12c** with this cuprate in THF gave a mixture of two dienyne, viz. **13c** (*E/Z* ≈ 85/15) and **15c** (*E/Z* ≈ 85/15) in the ratio 75/25 (See Scheme 5). Dienyne **15c** is the normal S_N2' product, dienyne **13c**, however, is a "reductive" substitution product. It contains a hydrogen atom instead of an alkyl group on the original central C-atom of the allenic moiety.

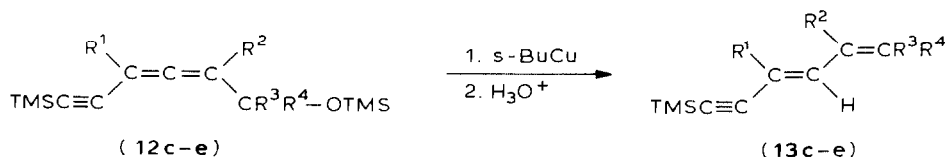
When ethylcopper, EtCu, was used the ratio **13c/15c** was not much changed viz. 80/20, but the stereoselectivity of the formation of **13c** improved considerably: only the *E* isomer of **13c** was detected. Use of phenylcopper(I) did not lead to conversion of **12c** into dienyne. The allenyne **12c** was completely recovered.

Methylcopper(I) brought about a normal S_N2' displacement on **12c** with formation of dienyne **14c** (*E/Z* ≈ 92/8). No "reductive" substitution product was observed, even not when the reaction was carried out at -60°C. For complete conversion of **12c** by MeCu a fourfold excess of the copper(I) compound was used.



SCHEME 5

Initially, we explained these results by assuming that ethylcopper, and also its cuprate, mainly decomposes into copper(I) hydride [11] under the conditions of the reaction, whereupon an S_N2' displacement in **12c** by copper(I) hydride would give **13c**. Such a process cannot occur with methylcopper(I) since this reagent lacks β-hydrogen atoms. We were supported in this opinion by the observation that not only allenyne **12c** but also **12d** and **12e** could be converted stereospecifically and in excellent yields (80–90%) into pure *E*-dienynes **13d-e** (Scheme 6) by use of *s*-BuCu.

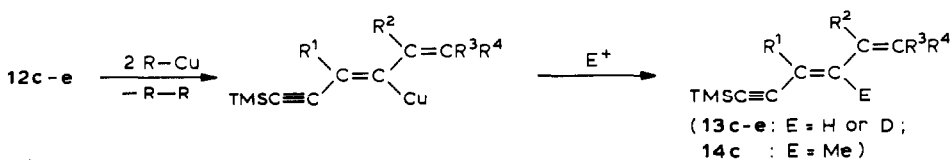


SCHEME 6

From other work it is known that an *s*-butyl group is an excellent hydride donor [12].

However, there was one point that made us suspicious: For a complete conversion of **12** into **13** a twofold excess of *s*-BuCu was required *. Why should such an excess be necessary? The answer to this question appeared to be the occurrence of an almost quantitative dimerization of the R group to R-R. Thus, treatment of **12c** with 2.0 mole equivalents of *n*-pentylcopper(I) produced mainly **13c** and an equimolar amount of *n*-decane. Apparently, the alkyl group in the copper(I) reagent had not served as a hydride donor. Further support for this conclusion was obtained from the following experiments.

Treatment of **12c** with 2.0 mole equivalents of *s*-BuCu followed by addition of D₂SO₄/MeOD gave over 90% deuterium incorporation in **13c** (Scheme 7). Addition of methyl iodide instead of D₂SO₄/MeOD led to the formation of *E*-**14c** in 85% yield. These results are consistent with a reaction proceeding through the *Z*-vinyl-copper(I) compounds indicated in Scheme 7.

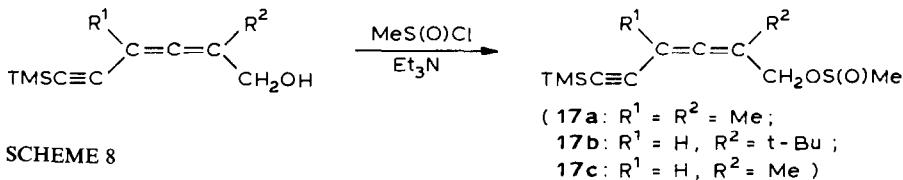


SCHEME 7

Not all the allenynes **12** could be converted into **13** or derivatives thereof. Thus, the attempted conversion of **12a** and **12b** into **13a,b** by *s*-BuCu failed completely. Possibly, the steric hindrance exerted by R¹ and R² is too large for *s*-BuCu to approach the central C-atom of the allenic moiety in these cases. Decomposition of the copper(I) reagent will then be the main process. Finally we must mention another point which is important for mechanistic considerations, namely that the acetylenic function in **12** is essential for a smooth conversion of **12** into **13**. When an alkyl or a 1-alkenyl group is present instead of the (trimethylsilyl)ethynyl function no formation of **13** took place (studied for *s*-BuCu). At this stage of the study, it was decided to vary another parameter, viz. the leaving group. The reason for this was that in organocopper(I) chemistry the (trimethylsilyl)oxy group is not as good a leaving group as for instance a methanesulfinate group, and so it seemed likely that allenynes like **12a** and **12b** containing the methanesulfinate function would be more susceptible to substitution. It will be shown below that the results obtained with the sulfonates were quite different from those with **12**.

b. Conversion of the esters **17a-c**

The allenynes **17a-c** were prepared by treatment of the corresponding alcohols with methanesulfinyl chloride and triethylamine [13]. The esters formed were used without further purification.

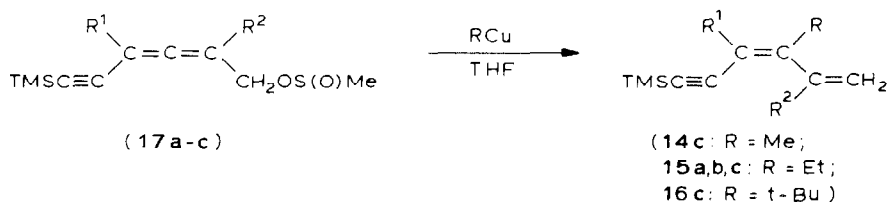


SCHEME 8

* Similar observations were made when EtCu was used. When half the amount of the RCu reagent was used (R ≠ Me), the yield of **13** was ca. 50%.

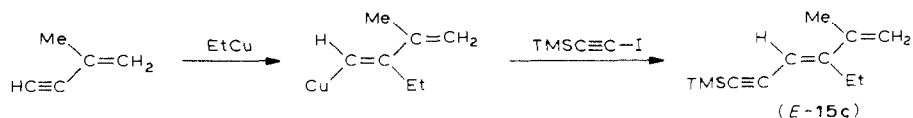
When the allenynes **17** were treated with MeCu, EtCu and *t*-BuCu, a smooth S_N2' reaction took place in all cases, with formation of dienynes **14**–**16** in 80–90% yield. No “reductive substitution products” **13** were formed in these reactions*.

Another interesting point is the stereochemistry of the reaction. In section II.a it was noted that **14c** and **15c** mainly consisted of the *E* isomers. However, the dienynes **14**, **15** and **16** obtained from **17** were more than 92% *Z*-isomer. This influence of the leaving group is very remarkable.



SCHEME 9

It should be noted that the allenynes of the **a** and **b** series all reacted very well. The *Z*-stereochemistry of **14**–**16** was proven in one case by an independent synthesis as outlined in Scheme 10. Isoprenylacetylene was converted by EtCu into the adduct indicated. Such addition reactions proceed *cis* [14]. Addition of (trimethylsilyl)ethynyl iodide to the adduct gave pure *E*-**15c**. The same compound has already been described in Scheme 5. The 1H NMR data for dienyne **15c** out of Scheme 9 differed from those recorded for *E*-**15c**, so that the configuration of **15c** being prepared from the methanesulfinate must be *Z*. In the next section a rationalization of these results is given.



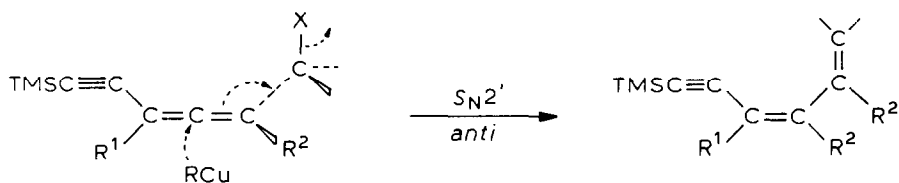
SCHEME 10

c. Mechanistic considerations

From a mechanistic point of view it is most convenient to discuss first the conversion of the sulfonates **17**. It was shown that mainly *Z*-dienynes were obtained from **17** (see Scheme 9). From other work it was known that the acetylenic substituent is not necessary for conversion of α -allenic sulfonates into 1,3-dienes [cf. 15]. In our opinion the conversion of **17** into *Z*-**14**, **15**, **16** can be rationalized as indicated in Scheme 11. The reaction depicted involves a direct S_N2' displacement by attack of the copper(I) reagent on the allylic sulfinate moiety. *Z*-Dienynes are

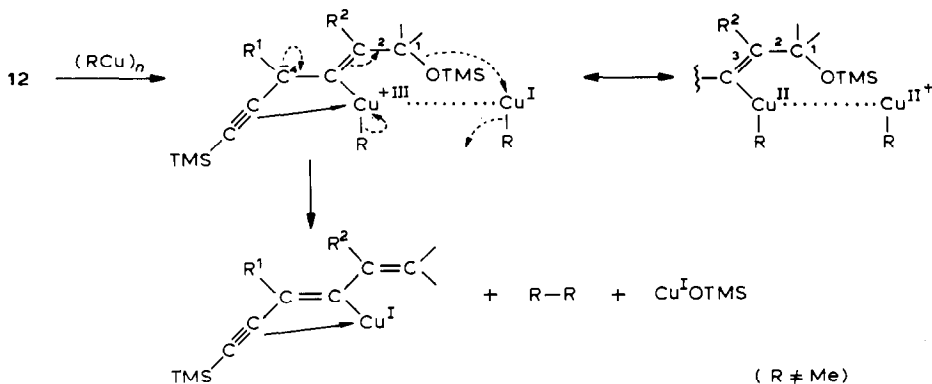
* Treatment of the acetate analogue of **17c** with EtCu produced after protic work-up a mixture of **13c** (30%) and **15c** (70%). The leaving group character of an acetate function is between that of a sulfinate and a TMSO group.

formed because the steric hindrance between RCu and R^1 (H or Me) will be smaller than between RCu and the (trimethylsilyl)ethynyl group. In the light of other observations [16] we assume that the $\text{S}_{\text{N}}2'$ displacement proceeds *anti*.



SCHEME 11

The exact mechanism of such organocopper(I) induced substitutions is not yet known. Copper(III) intermediates are usually proposed [17], although the participation of copper(II) species cannot be excluded [18]. It is more difficult to rationalize the behaviour of **12** towards RCu . It is necessary to account for four observations, viz. (i) that the reaction of **12** with RCu ($\text{R} \neq \text{Me}$) proceeds through vinylcopper(I) compounds, (ii) that formation of the *Z*-vinylcopper(I) compounds is preferred, (iii) that the acetylenic substituent is essential, and (iv) that MeCu transfers its methyl group to *E*-dienynes. We believe that a mechanism as outlined in Scheme 11 satisfactorily accounts for the results for $\text{R} \neq \text{methyl}$. The first step involves the addition of the $(\text{RCu})_n$ reagent to the enyne moiety of **12** as a direct allylic substitution reaction and is unlikely in view of the fact that a (trimethylsilyl)oxy group is not as good a leaving group. It should be noted that the RCu reagent is represented as $(\text{RCu})_n$; it is well known that organocopper(I) species exist as cluster compounds [19] and for our purpose we make use of only two RCu units of the cluster. When the $(\text{RCu})_n$ reagent adds to the enyne system, an intermediate of the type $[(\text{RCu}^{\text{I}})_{n-1}\text{RCu}^{\text{III}} \cdot \text{substrate}]$ will be formed. (As indicated in Scheme 12, a mesomeric form containing two Cu^{II} atoms can be written.)



SCHEME 12

The conformation around C(3)–C(4) in the initial adduct will be such that a favourable complexation of the copper(III) atom with the triple bond can occur. The negative charge is shown as localized at C(4) in Scheme 12, but in practice it will be delocalized over the whole π -system. Because of the presence of this negative charge the TMSO group can now be expelled, as indicated by the arrows, to give the vinylcopper(I) compound, $\text{R}-\text{R}$, and $\text{Cu}^{\text{I}}\text{OTMS}$. This Scheme does not account for

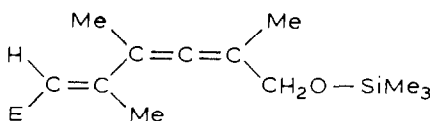
the behaviour of MeCu. Initially, we thought that in this case the liberated TMSO⁻ group would attack the group R instead of a copper atom of the cluster; this seemed reasonable in view of the fact that S_N2'-reactions occur much more rapidly with methyl groups than with higher homologues. However, experiments in which PhMe₂SiO or Ph₃SiO groups were used instead of the TMSO group gave no MeOSiMe₂Ph or MeOSiPh₃. The explanation of the behaviour of MeCu must await further studies.

Experimental

All operations with organometallic reagents were carried out under dry nitrogen. The products were analyzed by NMR (Varian EM-390 and CFT-20 spectrometer) and IR spectroscopy. The allenynes **1**, **12** and **17** were obtained by standard procedures [3,13].

1. Conversion of **1a** into **4a**, **6a**

A solution of MeMgCl (0.045 mol) in THF (50 ml) was added dropwise to a stirred solution of copper(I) bromide (0.030 mol) and lithium bromide (0.060 mol) in dry THF (40 ml) at -25°C. The mixture was stirred for 15 min at this temperature, then silyl ether **1a** (0.015 mol) was added, and the mixture was stirred for a further 3 h at -25°C. Compound **4a** was isolated by pouring the mixture into saturated aqueous ammonium chloride (200 ml) containing NaCN (2 g), extracting with pentane, washing the combined extracts with water and drying them over MgSO₄, and subsequent evaporation of the solvent in vacuo. Compound **6a** was isolated by adding (trimethylsilyl)ethynyl iodide (0.045 mol) and stirring of the mixture for 1 h at 20°C before hydrolytic work-up. Compound **4a** was distilled in vacuo, and **6a** was purified by column chromatography on Florisil with n-pentane as eluent. Physical constants, yields and characteristic spectroscopic data for **4a** and **6a** are listed below (purity ≥ 95%).



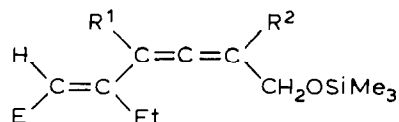
Compound 4a: E = H. B.p. 43°C/0.005 mmHg; n_D^{20} 1.4722; yield 75%. ¹H NMR (CCl₄, TMS): δ(ppm) 4.85 (H₂C=C), 4.05 (CH₂O), 1.82 (MeC=C=C), 1.75 (MeC=C), 1.70 (MeC=C=C), 0.10 (Me₃Si). ¹³C NMR (CDCl₃, TMS): δ(ppm) 202.4 (=C=). IR (NaCl): 1950 cm⁻¹ (C=C=C).

Compound 6a: E = C≡CSiMe₃. n_D^{20} 1.5055; yield 85%. ¹H NMR (CCl₄, TMS): δ(ppm) 5.35 (=CHC≡C), 4.02 (CH₂O), 1.89 (MeC=C), 1.82 (MeC=C=C), 1.72 (MeC=C=C), 0.17 (Me₃Si), 0.09 (Me₃Si). ¹³C NMR (CDCl₃, TMS): δ(ppm) 203.3 (=C=). IR (NaCl) 1949 cm⁻¹ (C=C=C).

2. Conversion of **1a,b** into **5a,b** and **7a**

A solution of EtMgBr (0.020 mol) in THF (20 ml) was added, dropwise at -60°C, to a stirred solution of copper(I) chloride (0.010 mol) and lithium bromide (0.030 mol) in dry THF (25 ml). The mixture was stirred for 15 min to complete the formation of the cuprate, then, silylether **1a** or **1b** (0.010 mol) was added and stirring

was continued for 1 h at -60°C . Adducts **5a** and **5b** were isolated as described for **4a** whilst allenenyne **7a** was formed by reaction with (trimethylsilyl)ethynyl iodide (0.022 mol) as described above. Compounds **5a** and **5b** were distilled in vacuo, and compound **7a** was purified by column chromatography on Florisil with n-pentane as eluent. Physical constants, yields and characteristic spectroscopic data are listed below (purity $\geq 95\%$).



Compound 5a: $E = H$, $R^1 = \text{Me}$, $R^2 = \text{Me}$. B.P. $50\text{--}55^{\circ}\text{C}/0.01$ mmHg; n_{D}^{20} 1.4740; yield 85%. ^1H NMR (CCl_4 , TMS): δ (ppm) 4.82 ($\text{H}_2\text{C}=\text{C}$), 4.01 (CH_2O), 2.11 ($\text{CH}_2\text{C}=\text{C}$), 1.82 ($\text{MeC}=\text{C}=\text{C}$), 1.70 ($\text{MeC}=\text{C}=\text{C}$), 1.02 (CH_3), 1.00 (Me_3Si). ^{13}C NMR (CDCl_3 , TMS): δ (ppm) 201.7 ($=\text{C}=\text{C}$). IR (NaCl): 1951 cm^{-1} ($\text{C}=\text{C}=\text{C}$).

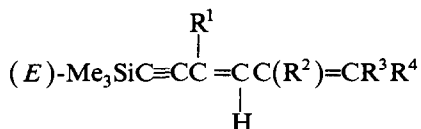
Compound 5b: $E = H$, $R^1 = H$, $R^2 = t\text{-Bu}$. B.p. $60\text{--}65^{\circ}\text{C}/0.1$ mmHg; n_{D}^{20} 1.4718; yield 90%. ^1H NMR (CCl_4 , TMS): δ (ppm) 5.84 ($\text{HC}=\text{C}=\text{C}$), 4.85 + 4.72 ($\text{H}_2\text{C}=\text{C}$), 4.17 (CH_2O), 2.05 ($\text{CH}_2\text{C}=\text{C}$), 1.10 ($t\text{-Bu}$), 1.02 (CH_3), 0.09 (Me_3Si). ^{13}C NMR (CDCl_3 , TMS): δ (ppm) 202.0 ($=\text{C}=\text{C}$). IR (NaCl): 1944 cm^{-1} ($\text{C}=\text{C}=\text{C}$).

Compound 7a: $E = \text{C}\equiv\text{CSiMe}_3$, $R^1 = \text{Me}$, $R^2 = \text{Me}$. n_{D}^{20} 1.4987; yield 75%. ^1H NMR (CCl_4 , TMS): δ (ppm) 5.30 ($\text{HC}=\text{C}$), 4.07 (CH_2O), 2.36 ($\text{CH}_2\text{C}=\text{C}$), 1.79 ($\text{MeC}=\text{C}=\text{C}$), 1.72 ($\text{MeC}=\text{C}=\text{C}$), 0.97 (CH_3), 0.18 (Me_3Si), 0.09 (Me_3Si). ^{13}C NMR (CDCl_3 , TMS): δ (ppm) 203.1 ($=\text{C}=\text{C}$). IR (NaCl): 1950 cm^{-1} ($\text{C}=\text{C}=\text{C}$).

3. General procedure for the reaction of **12c–e** with *s*-BuCu *

A solution of *s*-BuMgCl (0.020 mol) in THF (20 ml) was added at -60°C , to a stirred solution of copper(I) bromide (0.020 mol) and lithium bromide (0.020 mol) in dry THF (25 ml). The formation of the organocopper(I) compound was complete after 15 min stirring at -60°C .

Allenyne **12** (0.010 mol) was then added at -60°C and the mixture was stirred for 1 h at -30°C . Work-up as described under 1 followed by distillation of the crude products gave dienyne (*E*)-**13c–e** in 80–90% yield (purity $\geq 95\%$). Physical constants and characteristic ^1H NMR data for **13c–e** are as follows **.



Compound 13c: $R^1 = H$, $R^2 = \text{Me}$, $R^3 = H$, $R^4 = H$. B.p. $85^{\circ}\text{C}/20$ mmHg; n_{D}^{20} 1.5006. ^1H NMR (CCl_4 , TMS): δ (ppm) 6.62 ($\text{HC}=\text{C}$; $^3J(\text{H},\text{R}^1)$ 15.6 Hz), 5.50 (R^1), 5.01 ($\text{R}^3 + \text{R}^4$), 1.79 ($\text{MeC}=\text{C}$), 0.15 (Me_3Si).

Compound 13d: $R^1 = H$, $R^2 = H$, $R^3 = \text{Me}$, $R^4 = \text{Me}$. B.p. $130^{\circ}\text{C}/40$ mmHg, n_{D}^{20} 1.5218. ^1H NMR (CCl_4 , TMS): δ (ppm) 6.76 ($\text{HC}=\text{C}$; $^3J(\text{H},\text{R}^1)$ 15.6 Hz; $^3J(\text{H},\text{R}^2)$ 11.8 Hz), 5.82 (R^2), 5.37 (R^1), 1.78 ($\text{R}^3 + \text{R}^4$), 1.18 (Me_3Si).

* Similar conditions were used in the case of EtCu and $n\text{-C}_5\text{H}_{11}\text{Cu}$.

** In the IR spectrum no allenic absorption was present. All three compounds showed the $\text{C}\equiv\text{C}$ absorption in the region $2100\text{--}2200\text{ cm}^{-1}$.

Compound 13e: $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^3 = \text{Me}$, $R^4 = \text{Me}$. B.p. 108–111°C/20 mmHg, n_{D}^{20} 1.5249. ^1H NMR (CCl_4 , TMS): δ (ppm) 6.53 ($\text{HC}=\text{C}$; $^3J(\text{H}, \text{R}^2)$ 11.7 Hz), 5.96 (R^2), 1.84 ($\text{R}^3 + \text{R}^4$), 1.77 (R^1), 0.18 (Me_3Si).

4. Reaction of 12c with MeCu

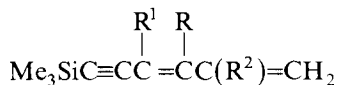
Allenyne **12c** (0.010 mol) was added with stirring at 0°C during 10 min to a suspension of MeCu (0.040 mol) (prepared in situ by stirring MeMgCl (0.040 mol) with a mixture of copper(I) chloride (0.040 mol) and lithium bromide (0.050 mol)) in THF (90 ml) at 0°C. Stirring was continued for 1 h at 0°C. Work-up in the usual way followed by distillation of the crude product at reduced pressure gave the pure dienyne **14c** as a *E/Z*-mixture (ratio \approx 92/8).

Physical constants for the mixture of isomers and ^1H NMR data for *E*-**14c** are as follows.

$$\begin{array}{c} \text{H} \\ | \\ \text{Me}_3\text{SiC}\equiv\text{CC}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2 \end{array}$$
(14c; E/Z \approx 92/8). B.p. 92–94°C/20 mmHg, n_{D}^{20} 1.5078. ^1H NMR (CCl_4 , TMS): δ (ppm) for the *E*-isomer: 5.55 ($\text{HC}=\text{C}$), 5.14 + 5.01 ($\text{H}_2\text{C}=\text{C}$), 2.02 ($\text{MeC}=\text{C}$), 1.88 ($\text{MeC}=\text{C}$), 0.20 (Me_3Si).

5. General procedure for the reaction of 17a–c with RCu

Methanesulfinate **17** (0.020 mol) was added to a stirred suspension of RCu (0.020 mol) (prepared as described above) in THF (45 ml) at –60°C. The mixture was stirred for 1 h at –30°C then worked-up as indicated under 1. The isolated products were distilled at reduced pressure to give dienyne **14–16**, mainly as *Z* isomers in 80–90% yield (purity \geq 95%)*. Physical constants and characteristic ^1H NMR data for compounds **14–16** are listed below.



Compound 14c: $R = \text{Me}$, $R^1 = \text{H}$, $R^2 = \text{Me}$, $Z/E \approx 92/8$. B.p. 45–47°C/35 mmHg; n_{D}^{20} 1.4950. ^1H NMR (CCl_4 , TMS): δ (ppm) for the *Z*-isomer: 5.33 (R^1), 5.13 + 5.00 ($\text{H}_2\text{C}=\text{C}$), 2.86 ($\text{HC}\equiv\text{C}$), 2.04 (R^2), 1.91 (R). The signal for $\text{HC}\equiv\text{C}$ of the *E*-isomer was present at 3.12 ppm (cf. [20]). IR (NaCl): 3305 cm^{-1} ($\text{HC}\equiv$).

Compound 15a: $R = \text{Et}$, $R^1 = \text{Me}$, $R^2 = \text{Me}$; $Z/E \approx 84/16$. B.p. 95–98°C/20 mmHg; n_{D}^{20} 1.4786. ^1H NMR (CCl_4 , TMS): δ (ppm) for the *Z*-isomer: 4.98 + 4.86 ($\text{H}_2\text{C}=\text{C}$), 2.19 ($\text{CH}_2\text{C}=\text{C}$), 1.87 (R^2), 1.82 (R^1), 0.95 (CH_3), 0.14 (Me_3Si).

Compound 15b: $R = \text{Et}$, $R^1 = \text{H}$, $R^2 = t\text{-Bu}$; $Z/E > 98/2$. B.p. 115–117°C/20 mmHg; n_{D}^{20} 1.4750. ^1H NMR (CCl_4 , TMS): δ (ppm) 5.32 (R^1), 5.12 + 5.74 ($\text{H}_2\text{C}=\text{C}$), 2.20 ($\text{CH}_2\text{C}=\text{C}$), 1.13 (R^2), 1.00 (CH_3), 0.13 (Me_3Si).

Compound 15c: $R = \text{Et}$, $R^1 = \text{H}$, $R^2 = \text{Me}$; $Z/E \approx 97/3$. B.p. 41–42°C/20 mmHg; n_{D}^{20} 1.4839. ^1H NMR (CCl_4 , TMS): δ (ppm) for the *Z*-isomer: 5.26 (R^1), 5.02 ($\text{H}_2\text{C}=\text{C}$), 2.78 ($\text{HC}\equiv\text{C}$), 2.24 ($\text{CH}_2\text{C}=\text{C}$), 1.95 (R^2), 1.02 (CH_3). The δ signal for the acetylenic proton of the *E*-isomer was found at 3.10 ppm (cf. [20]). IR (NaCl): 3315 cm^{-1} ($\text{HC}\equiv$).

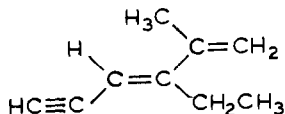
* In two cases, **14c** and **15c**, the trimethylsilyl group was removed prior to distillation by treatment of **14c** and **15c** with sodium hydroxide (0.4 g) in a mixture of water (5 ml) and methanol (50 ml) for 1 h at 25°C. The physical constants and ^1H NMR data refer to the desilylated compounds.

Compound 16c: $R = t\text{-Bu}$, $R^1 = H$, $R^2 = Me$, $Z/E \approx 96/4$. B.p. 103–105°C/20 mmHg; n_D^{20} 1.4755. $^1\text{H NMR}$ (CCl_4 , TMS): δ (ppm) for the *Z*-isomer: 5.37 (R^1), 5.06 + 4.65 ($\text{H}_2\text{C}=\text{C}$), 1.90 (R^2), 1.10 (R), 1.13 (Me_3Si). The signal for R present in the *E*-isomer is found at 1.29 ppm.

6. Preparation of desilylated *E*-15c

Isopropenylacetylene (0.025 mol) was added to a stirred suspension of EtCu (0.020 mol) (prepared as described above) in THF (45 ml) at -60°C . The mixture was stirred for 30 min at -20°C then cooled to -60°C , and (trimethylsilyl)ethynyl iodide (0.020 mol) was added. Stirring was continued for an additional hour at 25°C . The product was isolated in the usual way and desilylated as described under 5. The yield of the purified diyne was about 80% (purity $\geq 90\%$).

Physical constants and characteristic spectroscopic data are as follows.



B.p. 64–65°C/30 mmHg; n_D^{20} 1.5061. $^1\text{H NMR}$ (CCl_4 , TMS): δ (ppm) 5.47 ($\text{HC}=\text{C}$), 5.20 + 5.05 ($\text{H}_2\text{C}=\text{C}$), 3.12 ($\text{HC}\equiv\text{C}$), 2.57 ($\text{CH}_2\text{C}=\text{C}$), 1.88 ($\text{CH}_3\text{C}=\text{C}$), 1.08 (CH_3). IR (NaCl): 3312 cm^{-1} ($\text{HC}\equiv$).

References

- 1 J. Grimaldi and M. Bertrand, *Bull. Soc. Chim. Fr.*, (1971) 957.
- 2 A. Doutheau, J. Gore and M. Malacria, *Tetrahedron*, 33 (1977) 2393.
- 3 H. Kleijn, J. Meijer, G.C. Overbeek and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 101 (1982) 97.
- 4 H. Westmijze, H. Kleijn, J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 100 (1981) 98.
- 5 H. Kleijn, H. Westmijze, J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 100 (1981) 249.
- 6 See for the preparation of conjugated enynes following this method: A. Commerçon, J.F. Normant and J. Villieras, *Tetrahedron*, 36 (1980) 1215.
- 7 J.F. Normant, G. Cahiez, M. Bourgain, C. Chuit and J. Villieras, *Bull. Soc. Chim. Fr.*, (1974) 1656.
- 8 H. Westmijze, J. Meijer, H.J.T. Bos and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 95 (1976) 299.
- 9 J.F. Normant and M. Bourgain, *Tetrahedron Lett.*, (1971) 2583.
- 10 H. Westmijze, J. Meijer, H.J.T. Bos and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 95 (1976) 304.
- 11 J.F. Normant, *Synthesis*, (1972) 63 and references cited therein.
- 12 For instance, see: F. Sato, H. Watanabe, Y. Tanaka and M. Sato, *J. Chem. Soc., Chem. Commun.*, (1982) 1127.
- 13 P. Vermeer, H. Westmijze, H. Kleijn and L.A. van Dijck, *Recl. Trav. Chim. Pays-Bas*, 97 (1978) 56.
- 14 (a) H. Westmijze, H. Kleijn, J. Meijer and P. Vermeer, *Tetrahedron Lett.*, (1977) 869; (b) F. Scott, G. Cahiez, J.F. Normant and J. Villieras, *J. Organomet. Chem.*, 144 (1978) 13.
- 15 H. Kleijn, H. Westmijze, J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 99 (1980) 340.
- 16 For instance, see: C.J. Elsevier, J. Meijer, H. Westmijze, P. Vermeer and L.A. van Dijck, *J. Chem. Soc., Chem. Commun.*, (1982) 84.
- 17 B.H. Lipshutz, R.S. Wilhelm and J.A. Kozlowski, *Tetrahedron*, 40 (1984) 5005 and references cited therein.
- 18 R.G. Pearson and C.D. Gregory, *J. Am. Chem. Soc.*, 98 (1976) 4098.
- 19 See, for instance: (a) G. van Koten, A.J. Leusink and J.G. Noltes, *J. Chem. Soc., Chem. Commun.*, (1970) 1107; (b) J.A.J. Jarvis, B.T. Kilbourn, R. Pearce and M.F. Lappert, *ibid.*, (1973) 475; (c) H.K. Hofstee, J. Boersma and G.J.M. van der Kerk, *J. Organomet. Chem.*, 144 (1978) 255.
- 20 H. Kleijn, M. Tigchelaar, J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, 100 (1981) 337.