

ALKYLSILVER(I) INDUCED 1,5-SUBSTITUTION IN FUNCTIONALLY CONJUGATED ENYNES. A NOVEL ROUTE TO CUMULATED TRIENES

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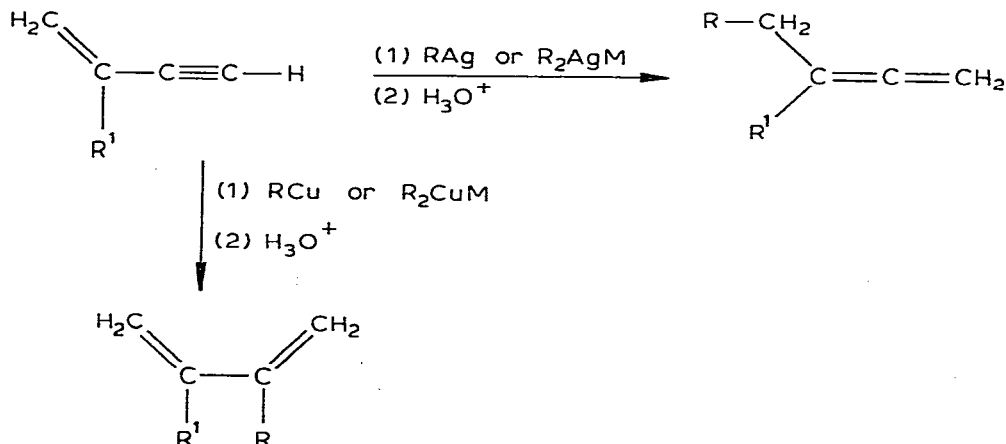
(Received January 2nd, 1980)

Summary

Functionally conjugated enynes, $\text{H}_2\text{C}=\text{C}(\text{R}^1)-\text{C}\equiv\text{C}-\text{CR}^2\text{R}^3\text{OS}(\text{O})\text{Me}$, undergo 1,5-substitution with alkylsilver(I) reagents, $\text{RAg} \cdot 3 \text{LiBr}$. The purity of the produced alkylated butatrienes, $\text{RCH}_2-\text{C}(\text{R}^1)=\text{C}=\text{C}=\text{CR}^2\text{R}^3$ depends on the nature of R in $\text{RAg} \cdot 3 \text{LiBr}$ and on the substituents R^1 , R^2 and R^3 in the substrate.

Introduction

We recently described the stabilization of organosilver(I) compounds by lithium bromide [1]. We further showed that these stabilized silver(I) reagents yield 1,4-adducts with butenyne and 2-methyl-1-buten-3-yne by terminal attack on the double bond. The reaction of these enynes with the corresponding copper(I) compounds is known generally to proceed via a nonterminal attack on the triple bond [2].



In another study we found that *t*-butylcopper(I) exclusively induced a 1,3-substitution in $\text{H}_2\text{C}=\text{C}(\text{Me})-\text{C}\equiv\text{C}-\text{CH}_2\text{OTos}$ with formation of $\text{H}_2\text{C}=\text{C}(\text{Me})-\text{C}(\text{t-Bu})=\text{C}=\text{CH}_2$ [3]. In this copper(I) reaction, attack on the triple bond is thus also involved.

In view of these results it was expected that silver(I) reagents would induce a 1,5-substitution reaction in suitably substituted conjugated enynes by attack at the double bond. The present paper describes the behaviour observed for the reaction of organosilver(I) compounds with a number of enynyl sulfonates of

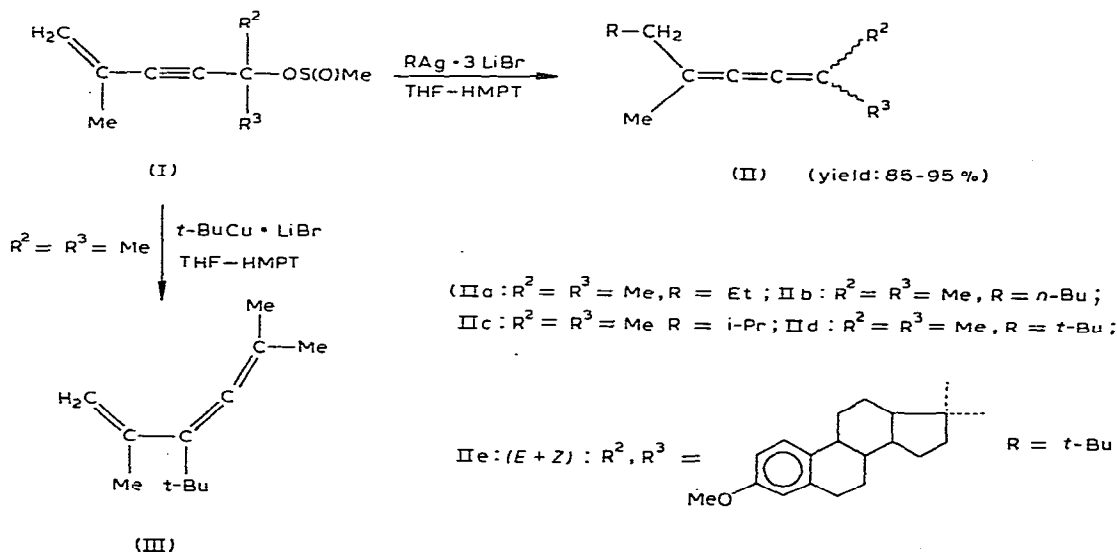
the structure $\text{H}_2\text{C}=\text{C}(\text{Me})-\text{C}\equiv\text{C}-\text{C}(\text{R}^2)(\text{R}^3)-\text{OS}(\text{O})\text{Me}$.

Results and discussion

(a) Preparation of tetra-substituted butatrienes

Our initial experiments involved the reaction of silver(I) compounds with ester I ($\text{R}^2 = \text{R}^3 = \text{Me}$, Scheme 1) in a mixture of tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPT). It appeared that this ester was smoothly converted into the tetra-substituted butatrienes II by various alkylsilver(I) reagents $\text{RAg} \cdot 3 \text{LiBr}$ ($\text{R} = \text{Et}$, *n*-Bu, *i*-Pr and *t*-Bu). The silver(I) compounds used were easily accessible from RMgX and the THF-HMPT soluble complex $\text{AgBr} \cdot 3 \text{LiBr}$ according to the procedure given in reference 1. Under similar conditions no reaction was observed between I and methyl- or phenylsilver(I). These two silver(I) compounds also failed to yield 1,4-adducts with butenyne and 2-methyl-1-buten-3-yne [1]. For comparison we also treated I ($\text{R}^2 = \text{R}^3 = \text{Me}$) with $\text{t-BuCu} \cdot \text{LiBr}$, and found that this reagent exclusively induced a 1,3-substitution. Alkylsilver(I) and alkylcopper(I) thus behave in a complementary fashion towards this functionally conjugated enyne. An interesting butatriene derivative, viz. IIe, was obtained from ester I in which R^2 and R^3 were part of a steroid, both possible geometric isomers were obtained in a ratio of about 60 : 40.

SCHEME 1



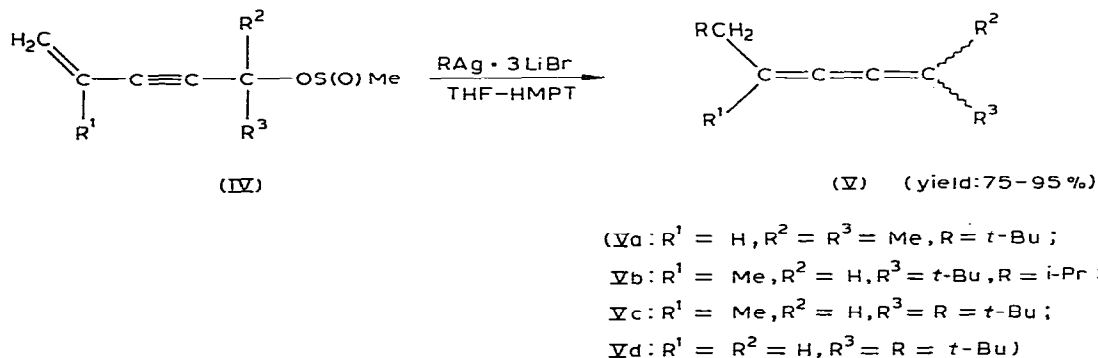
The butatriene structure of II was deduced from Raman and ^{13}C -NMR data. In the Raman spectrum all the products showed amongst others, the characteristic butatriene absorption in the region $2055\text{--}2060\text{ cm}^{-1}$. In the ^{13}C -NMR spectrum the Csp^2 -absorptions were found at $\delta\ 100\text{--}112\text{ ppm}$ and the Csp -ones at $\delta\ 152\text{--}155\text{ ppm}$. The ^{13}C -NMR data reasonably correspond with values reported for unsubstituted butatriene and tetraphenylbutatriene [4].

Table 1 summarizes physical constants, yields and some spectroscopic data found for the cumulenes II.

(b) Preparation of di- and trisubstituted butatrienes

To prepare di- and trisubstituted butatrienes we treated esters IV (given in Scheme 2) with various alkylsilver(I) compounds. From these esters pure di- and trisubstituted butatrienes (V) could be obtained with branched-alkylsilver(I) reagents only. When *n*-alkylsilver(I) compounds were used the desired trienes were contaminated with substantial amounts of higher boiling products. These higher boiling products probably arose from a subsequent attack of unreacted *n*-alkylsilver(I) on the initially formed butatrienes. In a recent paper we reported on an analogous reaction of butatrienes with organocopper(I) compounds [5]. Currently, we are studying the composition of the by-products in more detail. Note that in Vb–Vd *E/Z*-isomerism is possible. In fact, both isomers were obtained in comparable amounts in these cases.

SCHEME 2



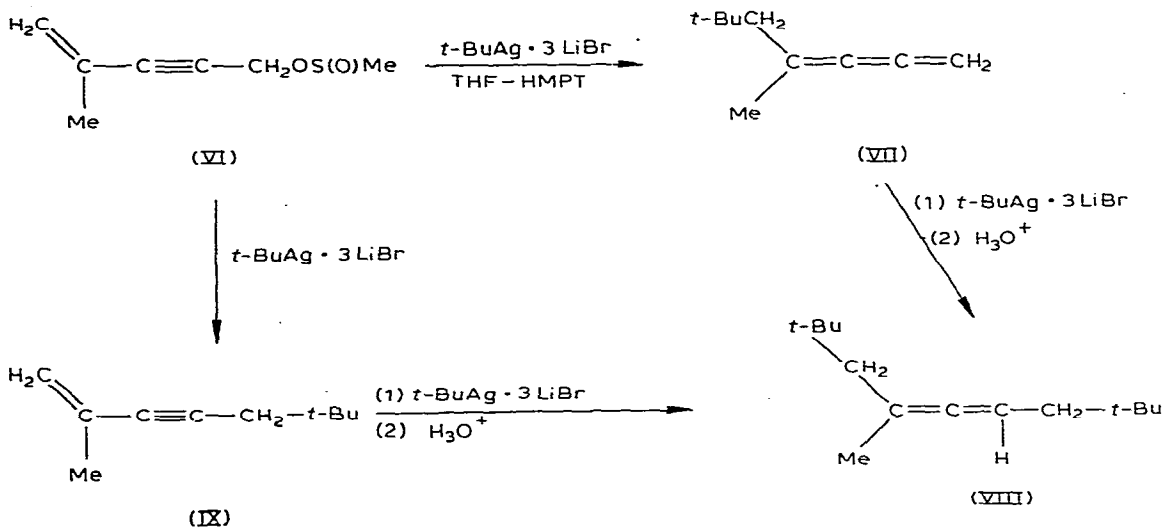
The disubstituted butatriene Vd has the two substituents on C(1) and C(4). Attempts to synthesize a disubstituted butatriene with the two substituents at the same carbon atom from ester VI (Scheme 3) and one mol equiv. of *t*-BuAg · LiBr failed, however. Instead of the desired butatriene derivative VII a mixture of compounds was isolated consisting mainly of the starting ester VI and the allene VIII. When two mol equiv. of *t*-BuAg · 3 LiBr were used, allene VIII was obtained in 50% yield after distillation. In principle, allene VIII can arise via a 1,5-substitution in VI (\rightarrow VII) followed by a 1,2-addition of unreacted alkylsilver(I), or by means of a 1,1-substitution in VI (\rightarrow IX) followed by a 1,4-addition of the silver(I) compound:

TABLE 1
PHYSICAL CONSTANTS, YIELDS AND SOME SPECTROSCOPIC DATA FOR THE BUTADIENES II AND V ^a

II or V ^b	B.p. (°C/mm Hg)	n_D^{20}	Yield (%)	Raman ^c (cm^{-1})	¹³ C- and ¹ H-NMR(CDCl ₃ , δ Me ₄ Si = 0 ppm)		Remarks
					δ C _{sp}	δ C _{sp} ² δ H-C=C=C=C	
IIa	65-66/16	1.5050	95	2060	154.8, 152.6	112.0, 107.2	
IIb	90-98/17	1.5033	90	2055	154.8, 152.4	112.4, 107.3	
IIc	78-80/20	1.5034	85	2060	154.7, 153.5	110.8, 107.1	
II d	87-89/20	1.5037	90	2055	155.2, 154.3	109.9, 107.8	
IIe			87	2050	159.9, 159.8 157.4	111.4, 109.7 109.3	d, e, f, h
Va	85-87/20	1.5021	95	2065	160.0, 155.7	112.0, 100.2	5.19
Vb	88-90/15	1.4942	90	2060	158.2, 157.9 156.4, 156.2	115.5, 115.3 114.6, 114.3	5.27 e, g
Vc	98-99/15	1.4965	90	2055	160.0, 156.2 156.0	115.1, 114.6 114.2, 114.0	5.25 e, g
Vd	95-97/17	1.4901	75	2065	165.3, 164.9 158.2, 158.0	118.6, 103.9	5.22-5.57 e, g

^a Purity of products: >95% (based on GLC and NMR analysis). ^b For the substituents in II and V; see Schemes 1 and 2. ^c Absorption of the 1,2,3-trienyl system. ^d The product was obtained as an oil after purification by column chromatography (Al₂O₃ + 5% H₂O/hexane). ^e A mixture of *E*- and *Z*-isomers was obtained. ^f Ratio of isomers: 60/40 (based on the relative heights of the two t-Bu signals in the ¹H-NMR spectrum). The same value was calculated from the relative intensities of the two signals at δ 159.9 and 159.8 ppm in the ¹³C-NMR spectrum). ^g Ratio of isomers: ~50/50 (based on the relative intensities of t-Bu signals in the ¹H-NMR spectra. From the ¹³C-NMR spectra the same ratio of isomers was calculated. ^h The signal at δ 111.4 ppm is assigned tentatively. A signal with a comparable intensity was present at δ 113.8 ppm.

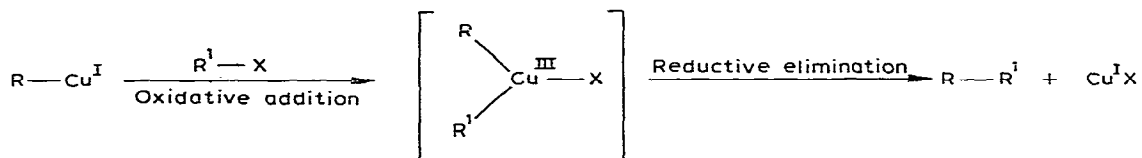
SCHEME 3



Although the conversion IX \rightarrow VIII is indeed possible [6], we were able to exclude the route VI \rightarrow IX \rightarrow VIII as follows: treatment of a mixture of VI and IX (0.01 mol of each) with $t\text{-BuAg} \cdot 3 \text{LiBr}$ (0.02 mol) left IX unchanged within experimental error. This experiment thus indicates that the conversion VI \rightarrow VII was much faster than the conversion VI \rightarrow IX. In addition, the absence of VII in the reaction product shows its high susceptibility to a further addition of the alkylsilver(I). Physical constants, spectroscopic data and yields of the di- and trisubstituted butatrienes V are listed in Table 1.

(c) Proposed mechanism

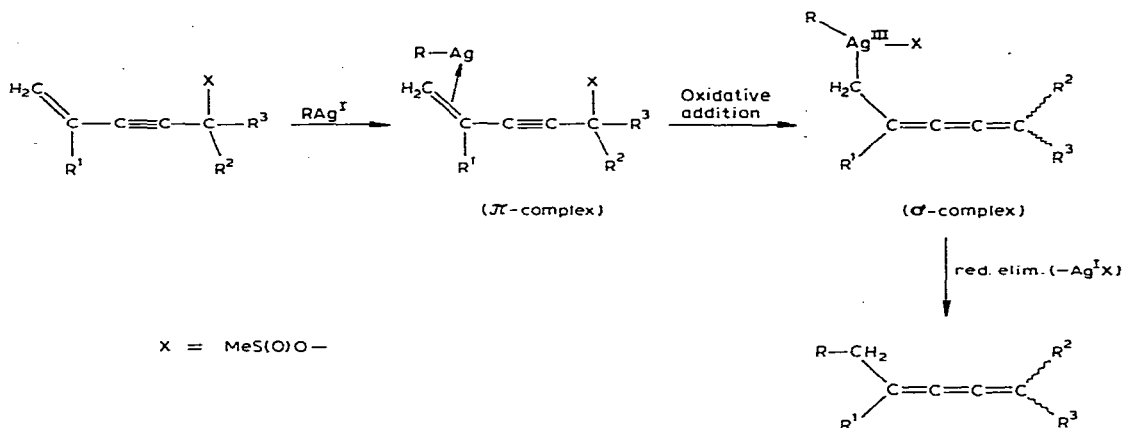
In organocopper chemistry an interesting working-hypothesis is the copper(III)-concept [7,8]. In this concept it is assumed that copper(I) induced substitution reactions proceed via species in which copper formally is present as Cu^{III} . Coupling of RCu with an alkyl halide $\text{R}'\text{-X}$ could thus occur as follows:



Recently, the $\text{Cu}(\text{III})$ -concept has been criticized by Pearson and Gregory from the view point of the HSAB-principle [9]. These authors suggested that Cu^{II} rather than Cu^{III} is involved in copper(I) induced substitution. To our knowledge the problem has not received any attention in silver(I) chemistry. As trialkylgold complexes are known [10], it is reasonable to assume transient formation of Ag^{III} species during the reactions discussed in the present paper. In view of the well-known ability of silver(I) salts to give π -complexes with olefins [11], we assume a formation of a π -complex (see Scheme 4) in the first step of

the reaction. In a subsequent oxidative addition step the proposed silver(III) intermediate is formed as a σ -complex. From this σ -complex the alkyl substituted butatrienes are produced by reductive elimination.

SCHEME 4



Experimental

All reactions with organosilver(I) compounds were performed under dry nitrogen. The products were analysed by GLC (SE 33 column) and by NMR (Varian EM-390 and CFT-20 spectrometers) and Raman spectroscopy.

Preparation of methansulfinates I, IV and VI

Compounds I, IV and VI were obtained from $\text{H}_2\text{C}=\text{C}(\text{R}^1)-\text{C}\equiv\text{C}-\text{CR}^2\text{R}^3\text{OH}$ and methanesulfinyl chloride according to reference 12. The enynyl alcohols were prepared by metalating $\text{H}_2\text{C}=\text{C}(\text{R}^1)-\text{C}\equiv\text{CH}$ with *n*-butyllithium and adding the appropriate carbonyl compound $\text{R}^2\text{R}^3\text{C}=\text{O}$ [13].

General procedure for the preparation of cumulenes II and V

To a stirred suspension of $\text{Ag}^{\text{I}}\text{Br}$ (0.030 mol) in THF (90 ml) was added a solution of lithium bromide (0.090 ml) in THF (45 ml) followed by HMPT (15 ml) at 25°C . The homogeneous solution was cooled to -60°C , and a solution of RMgCl (0.030 ml) in THF (~ 30 ml) was added dropwise. The resulting homogeneous mixture was stirred at -60°C for 20 min, and then the methanesulfinates (0.025 mol) was cautiously added. After stirring at -30°C for 30 min, the temperature of the mixture was allowed to rise to 25°C . The product was isolated by adding an aqueous solution of ammonium chloride containing NaCN (2 g) and extracting the aqueous layer with pentane (3×50 ml). The combined extracts were washed with water (5×100 ml) and dried with MgSO_4 . The solvent was stripped off in vacuo, and the residue was distilled. Physical constants, yields and some spectroscopic data for the cumulenes II and V are listed in Table 1. For the allene VIII (see Scheme 3) the following data were found: B.p. $88-90^\circ\text{C}/15$ mm Hg; n_D^{20} 1.4532; IR(NaCl) 1955 cm^{-1} ($>\text{C}=\text{C}=\text{C}<$); $^1\text{H-NMR}$ (CCl_4 , TMS): δ 4.88 (m, 1H, $\text{H}-\text{C}=\text{C}=\text{C}$), 1.82 (d, 2H,

CH₂), 1.78 (d, 2H, CH₂), 1.62 (d, 3H, CH₃), 0.95 (s, 9H, t-Bu) and 0.90 ppm (s, 9H, t-Bu).

Preparation of allene III

To a stirred solution of t-BuCu · LiBr (0.030 mol; prepared by stirring t-BuMgCl with LiCuBr₂ in THF (90 ml) at -60°C for 20 min) in a mixture of THF (90 ml) and HMPT (15 ml), sulfinate I (0.030 mol, R² = R³ = Me) was added at -60°C. The temperature of the mixture was allowed to rise to 0°C, and the product was isolated as described for the cumulenes II and V (yield of III: 90%). B.p. 55–56°C/14 mm Hg; n_D^{20} 1.4632; IR(NaCl) 1943 cm⁻¹ (>C=C=C<); ¹H-NMR (CCl₄, TMS): δ 4.80–4.95 (m, 2H, H₂C=), 1.78 (dd, 3H, CH₃), 1.67 (s, 6H, 2 × CH₃) and 1.10 ppm (s, 9H, t-Bu).

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