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

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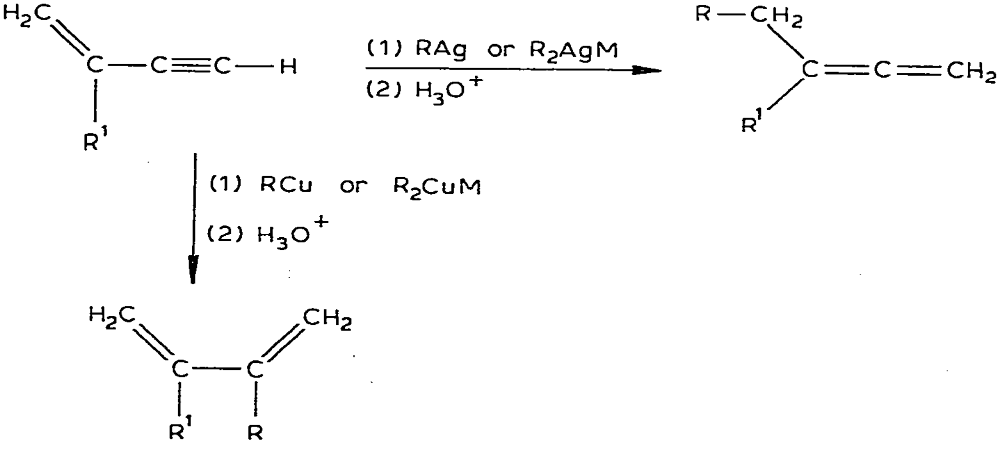
Summary

Functionally conjugated enynes, $H_2C{=}C(R^1){-}C{\equiv}C{-}CR^2R^3OS(O)Me$, undergo 1,5-substitution with alkylsilver(I) reagents, $RAg \cdot 3\ LiBr$. The purity of the produced alkylated butatrienes, $RCH_2{-}C(R^1){=}C{=}C{=}CR^2R^3$ depends on the nature of R in $RAg \cdot 3\ LiBr$ 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 $H_2C{=}C(Me){-}C{\equiv}C{-}CH_2OTos$ with formation of $H_2C{=}C(Me){-}C(t\text{-}Bu){=}C{=}CH_2$ [3]. In this copper(I) reaction, attack on the triple bond is thus also involved.

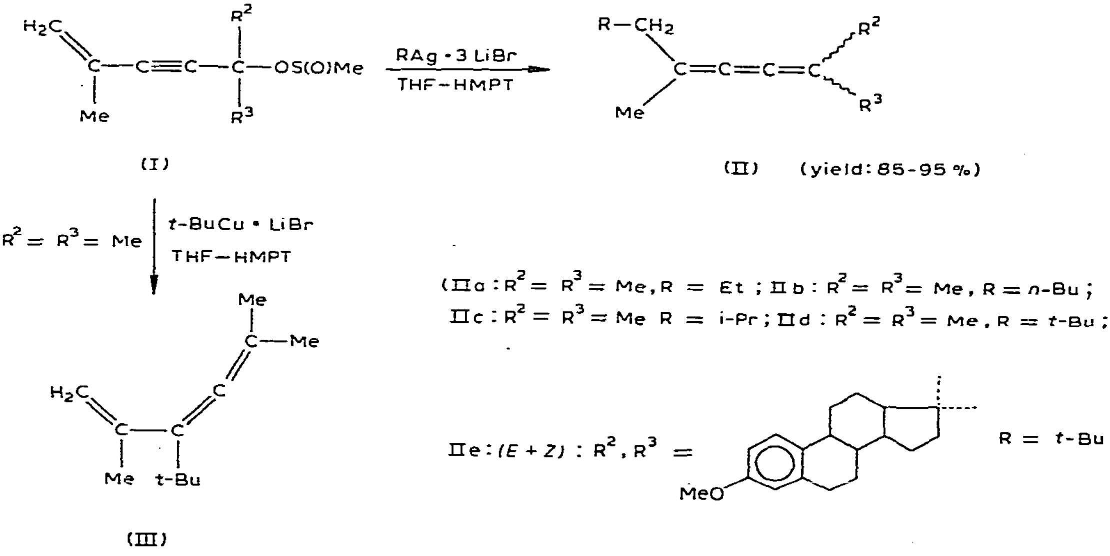
In view of these results it was expected that silver(I) reagents would induce a 1,5-substitution reaction in suitably substituted conjugated enynes by attack at the double bond. The present paper describes the behaviour observed for the reaction of organosilver(I) compounds with a number of enynyl sulfinates of the structure $-\overset{|}{C}{=}\overset{|}{C}{-}C{\equiv}C{-}\underset{|}{\overset{|}{C}}{-}OS(O)Me$.

Results and discussion

(a) Preparation of tetra-substituted butatrienes

Our initial experiments involved the reaction of silver(I) compounds with ester I ($R^2 = R^3 = Me$, 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 RAg · 3 LiBr (R = Et, n-Bu, i-Pr and t-Bu). The silver(I) compounds used were easily accessible from RMgX and the THF-HMPT soluble complex AgBr · 3 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 ($R^2 = R^3 = Me$) with t-BuCu · 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



(IIa : $R^2 = R^3 = Me$, R = Et ; IIb : $R^2 = R^3 = Me$, R = n-Bu ;
IIc : $R^2 = R^3 = Me$ R = i-Pr ; IId : $R^2 = R^3 = Me$, R = t-Bu ;
IIe : (E + Z) : R^2, R^3 =

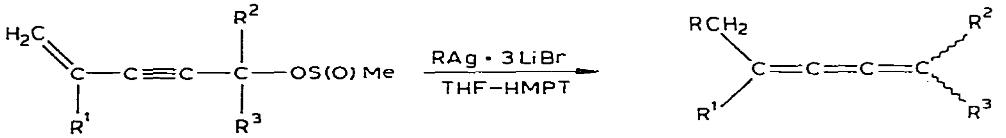
The butatriene structure of II was deduced from Raman and ^{13}C-NMR data. In the Raman spectrum all the products showed amongst others, the characteristic butatriene absorption in the region 2055—2060 cm^{-1}. In the ^{13}C-NMR spectrum the Csp^2-absorptions were found at δ 100—112 ppm and the Csp-ones at δ 152—155 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



(IV)

(V) (yield:75–95%)

(Va : R^1 = H, R^2 = R^3 = Me, R = *t*-Bu ;
Vb : R^1 = Me, R^2 = H, R^3 = *t*-Bu, R = i-Pr ;
Vc : R^1 = Me, R^2 = H, R^3 = R = *t*-Bu ;
Vd : R^1 = R^2 = H, R^3 = R = *t*-Bu)

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 (→ VII) followed by a 1,2-addition of unreacted alkylsilver(I), or by means of a 1,1-substitution in VI (→ IX) folled by a 1,4-addition of the silver(I) compound:

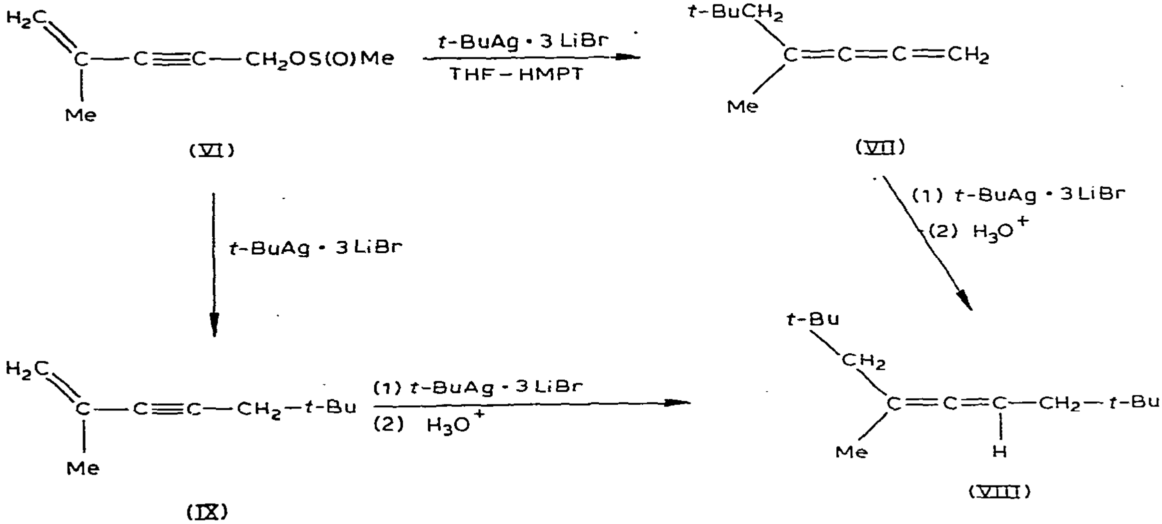
TABLE 1

PHYSICAL CONSTANTS, YIELDS AND SOME SPECTROSCOPIC DATA FOR THE BUTATRIENES 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)			
					δ C_{sp}	δ C_{sp^2}	δ $H{-}\overset{|}{C}{=}C{=}C{=}C$	Remarks
IIa	65–66/16	1.5050	95	2060	154.8, 152.6	112.0, 107.2		
IIb	96–98/17	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		
IId	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 (Al_2O_3 + 5% H_2O/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 ^{1}H-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 ^{13}C-NMR spectrum). [g] Ratio of isomers: ~50/50 (based on the relative intensities of t-Bu signals in the ^{1}H-NMR spectra. From the ^{13}C-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.

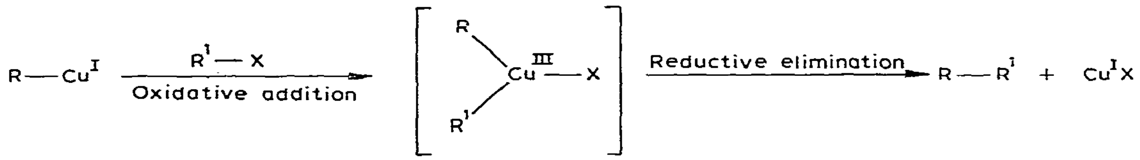
SCHEME 3



Although the conversion IX → VIII is indeed possible [6], we were able to exclude the route VI → IX → VIII as follows: treatment of a mixture of VI and IX (0.01 mol of each) with t-BuAg · 3 LiBr (0.02 mol) left IX unchanged within experimental error. This experiment thus indicates that the conversion VI → VII was much faster than the conversion VI → 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.

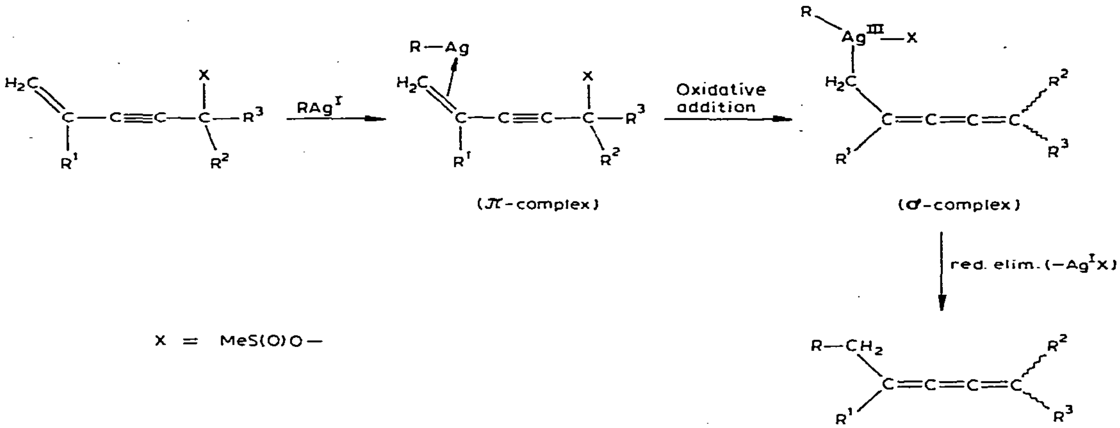
(c) Proposed mechanism

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 R′—X could thus occur as follows:



Recently, the Cu(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 $H_2C{=}C(R^1){-}C{\equiv}C{-}CR^2R^3OH$ and methanesulfinyl chloride according to reference 12. The enynyl alcohols were prepared by metalating $H_2C{=}C(R^1){-}C{\equiv}CH$ with n-butyllithium and adding the appropriate carbonyl compound $R^2R^3C{=}O$ [13].

General procedure for the preparation of cumulenes II and V

To a stirred suspension of Ag^IBr (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 methanesulfinate (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°C/15 mm Hg; n_D^{20} 1.4532; IR(NaCl) 1955 cm^{-1} (>C=C=C<); ^{1}H-NMR (CCl_4, TMS): δ 4.88 (m, 1H, H—C=C=C), 1.82 (d, 2H,

CH_2), 1.78 (d, 2H, CH_2), 1.62 (d, 3H, CH_3), 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 $LiCuBr_2$ 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, $R^2 = R^3 =$ 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} ($>C=C=C<$); ^{1}H-NMR (CCl_4, TMS): δ 4.80—4.95 (m, 2H, $H_2C=$), 1.78 (dd, 3H, CH_3), 1.67 (s, 6H, 2 × CH_3) and 1.10 ppm (s, 9H, t-Bu).

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