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REGIOSPECIFIC ADDITION OF ALKYLSILVER SPECIES TO ENYNYL SULFIDES, -SULFOXIDES, AND -PHOSPHINES

H. WESTMIJZE, H. KLEIJN and P. VERMEER

Department of Organic Chemistry, State University of Utrecht, Croesestraat 79, 3522 AD Utrecht (The Netherlands)

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Summary

The allenes $RCH_2C(R')=C=CHX$ (X = SMe, S(O)Me or PPh_2; R' = H or Me) are formed regiospecifically by reaction of alkylsilver species with the enynes $H_2C=C(R')C\equiv CX$.

Introduction

An important objective in synthesis is to develop regio- and/or stereo-selective methods, and organometallic compounds can often be used successfully for this purpose. Organocopper species, for instance, convert 3-alken-1-ynes, $C=CC\equiv CH$ selectively into 1,3-alkadienes by addition to the triple bond [1,2]. The addition to the triple bond is regiospecific if the triple bond bears an anion stabilizing group like CN or SCH_3 [3,4]. Since the discovery that alkylsilver reagents are stabilized by lithium bromide [5] a number of investigations have shown that both regio- and stereo-chemical results obtained with silver compounds may completely differ from those found using the copper analogues [3, 5—7]. This paper presents some results of our continued research in this field.

Results and discussion

In Table 1 are shown the results of some selected reactions of enynes I—IV (see Scheme 1) with alkylsilver compounds RAg or their ate-derivatives $R_2AgMgCl$. Most of the experiments were carried out using the enynyl sulfides I (R' = H or Me; entries 1—15). It appears that both RAg and $R_2AgMgCl$ may be used to convert I into allenes IV provided that the conditions for the reaction are chosen carefully. For instance, for the transfer of the ethyl group excellent results are obtained when two mole equivalents of EtAg are used (see entries 2 and 9). During this reaction a substantial amount of lithium bromide

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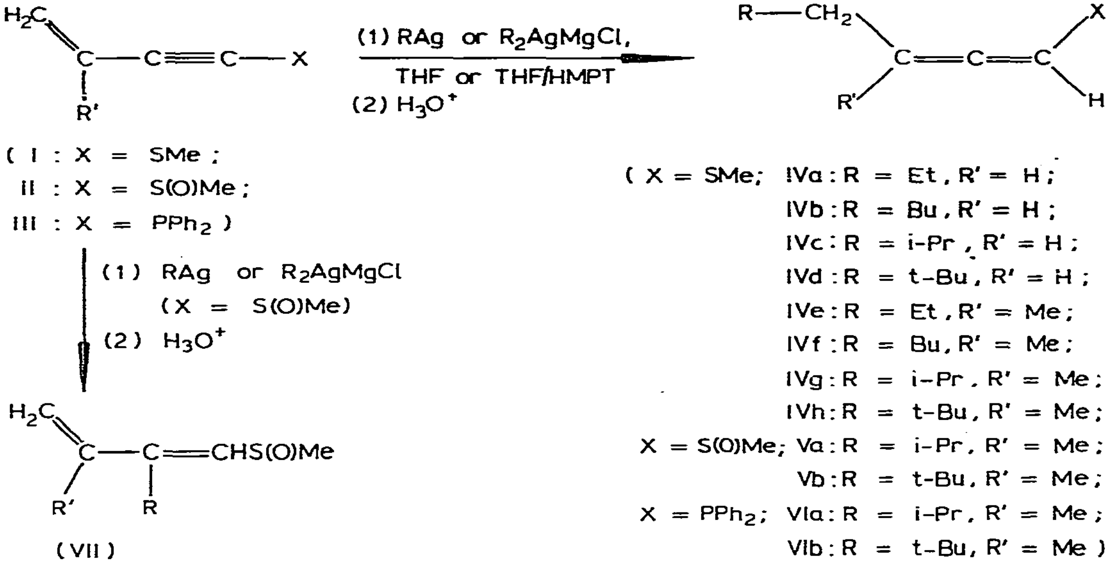

(I : X = SMe ;
II : X = S(O)Me ;
III : X = PPh_2)

(VII)

(X = SMe; IVa : R = Et, R' = H ;
IVb : R = Bu, R' = H ;
IVc : R = i-Pr, R' = H ;
IVd : R = t-Bu, R' = H ;
IVe : R = Et, R' = Me ;
IVf : R = Bu, R' = Me ;
IVg : R = i-Pr, R' = Me ;
IVh : R = t-Bu, R' = Me ;
X = S(O)Me; Va : R = i-Pr, R' = Me ;
Vb : R = t-Bu, R' = Me ;
X = PPh_2; VIa : R = i-Pr, R' = Me ;
VIb : R = t-Bu, R' = Me)

SCHEME 1

must be present, possibly because of marked decomposition of the alkylsilver compound if a smaller amount of lithium bromide is used (compare entries 1 with 2, and 7 with 9). The higher n-alkylsilver homologue BuAg reacts more readily than EtAg (compare entries 7 and 11), and so the amount of lithium bromide can be lower in this case.

The silver compounds RAg, in which R is a branched alkyl group, transfer R much more easily to I than do their primary alkyl analogues. The amount of silver reagent used in these cases can therefore be substantially lower than the two mole equivalents used for n-alkylsilver reagents (see entries 5, 6, 13 and 15). Organosilver species having a branched alkyl group react also faster with unsubstituted enynes [5]. A similar feature has been observed for the reaction of organocopper compounds with 1,3-dienes [8].

From the synthetic point of view, the reaction of I with alkylhomoargentates, $R_2AgMgCl$, is more attractive than the reactions discussed above. Entries 3, 4, 10, 12 and 14 indicate that extensive use can be made of both R groups when such argentates are used. The use of a mixture of THF and HMPT seems to be favourable for the reaction (see note e in Table 1). Unsubstituted 3-alken-1-ynes (X = H) require at least one molar equivalent of the argentate for complete conversion [5]. The MeS group activates the enyne system towards addition, which is consistent with its anion stabilizing ability.

The regiochemistry of the reaction of RAg or $R_2AgMgCl$ with I is wholly similar to that observed for addition of organosilver compounds to unsubstituted enynes [5]. It is known that also organolithium compounds may convert enynyl sulfides into allenes IV by selective transfer of R to the double bond of I [9] *.

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[*] For comparison I (R' = Me) was treated with EtCu. The product obtained was exclusively (Z)-$H_2C{=}C(Me)C(Et){=}CHSMe$.

TABLE 1

REACTION CONDITIONS AND PERCENTAGE CONVERSIONS FOR THE REACTION OF $H_2C{=}C(R')C{\equiv}CX$ (I: X = SMe; II: X = S(O)Me; III: X = PPh_2) WITH RAg OR $R_2AgMgCl$ WITH FORMATION OF $RCH_2C(R'){=}C{=}CHX$ (IV: X = SMe; V: X = S(O)Me; VI: X = PPh_2)

Entry	Starting compound I—III	Silver compound [equiv.] [a]	LiBr [equiv.] [b]	Solvent [c]	Reaction temperature (°C)	Reaction time (min)	Conversion % into IV—VI [d]
1	I (R' = H)	EtAg [1.40]	2.0	THF	−30	60	<5
2	I (R' = H)	EtAg [2.00]	6.0	THF	−30	150	>98
3	I (R' = H)	$Et_2AgMgCl$ [0.75]	2.0	THF/HMPT	+25	60	>98
4	I (R' = H)	$Bu_2AgMgCl$ [0.70]	2.0	THF/HMPT	+25	45	>98
5	I (R' = H)	i-PrAg [1.25]	2.5	THF	−30	60	>98
6	I (R' = H)	t-BuAg [1.20]	2.0	THF	−30	80	>98
7	I (R' = Me)	EtAg [2.00]	3.0	THF	−30	180	<5
8	I (R' = Me)	EtAg [1.25]	6.0	THF	−30	120	66
9	I (R' = Me)	EtAg [2.00]	6.0	THF	−30	150	>98
10	I (R' = Me)	$Et_2AgMgCl$ [0.67]	2.0	THF/HMPT	+25	60	>95
11	I (R' = Me)	BuAg [2.00]	3.0	THF	−30	210	>98
12	I (R' = Me)	$Bu_2AgMgCl$ [0.67]	2.0	THF/HMPT	+25	60	90
13	I (R' = Me)	i-PrAg [1.40]	3.0	THF	−30	210	95
14	I (R' = Me)	$i\text{-}Pr_2AgMgCl$ [0.67]	2.0	THF/HMPT	−10	180	>98 [e]
15	I (R' = Me)	t-BuAg [1.50]	2.0	THF	−30	60	>98
16	II (R' = Me)	i-PrAg [1.10]	3.0	THF	−30	120	>98
17	II (R' = Me)	t-BuAg [1.10]	3.0	THF	−30	120	>98
18	III (R' = Me)	i-PrAg [2.60]	2.5	THF	−30	120	>98
19	III (R' = Me)	t-BuAg [2.60]	2.5	THF/HMPT	−30	180	>98
20	III (R' = Me)	$t\text{-}Bu_2AgMgCl$ [1.25]	4.0	THF	−30	180	>98

[a] The number of mol equivalents of the silver compounds relative to I—III are given in brackets. [b] Mol equivalents relative to the amount of silver compounds. [c] See Experimental section for the THF/HMPT ratio. [d] In experiments in which the % conversion was ≤95%, the allenes were contaminated only with starting material. [e] When the same experiment was performed in THF alone, no IV could be detected (reaction conditions: 30 min at −60°C).

In some experiments we attempted to bring I (R' = Me) into reaction with i-PrMgCl alone or in the presence of a catalytic amount (5 mol%) of AgBr. Only in the latter case was adduct IV obtained, and then only in small yield.

Experiments 16 and 17 involved addition of isopropyl- and t-butyl-silver to the enynyl sulfoxide II (R' = Me), and in these cases pure allenes (compounds V in Scheme 1) were again obtained.

Unfortunately, n-alkylsilver reagents, RAg (R = Et or Bu), do not add to II regioselectively. Instead they convert II into a mixture of V ($\simeq$90%) and 1,3-dienes VII ($\simeq$10%). Attempts to improve the ratio V/VII by using $RAg(AgBr)_2$ in these cases were not successful. Also treatment of II with $R_2AgMgCl$ did not give purer allenes V. The relative amount of 1,3-diene VII in the mixture of V and VII was, in fact, substantially higher (>90%) when the alkylhomoargentates were used *. The behaviour of the enynyl sulfoxide II thus strongly resembles that of the corresponding nitrile $H_2C{=}C(Me)C{\equiv}CCN$, which undergoes addition to the triple bond when treated with $R_2AgMgCl$ but addition to the double bond (to give allenic nitriles) with RAg [3].

Finally, three experiments of Table 1 (entries 18—20) concern the preparation of allenic phosphines (compounds VI) by reaction of the enynyl phosphine III (R' = Me) with RAg or $R_2AgMgCl$. The branched alkyl group R in these cases is only slowly transferred (see Table 1 for relative amounts of the silver species and III and reaction times). So far we have not found conditions which lead to formation of allenic phosphines from n-alkylsilver reagents (RAg or $R_2AgMgCl$).

Conclusion

The work as presented in this report shows that if the group R in RAg or $R_2AgMgCl$ is branched alkyl, a smooth and regiospecific addition to enynyl sulfides I, sulfoxides II, and phosphines III occurs with formation of allenes. The n-alkylsilver species on the other hand are suited for the reaction of enynyl sulfides to give allenes, but seemingly not for those of enynyl sulfoxides and phosphines.

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 IR spectroscopy.

The enynyl substrates I—III were prepared from $H_2C{=}C(R')C{\equiv}CH$ by known procedures [10,11].

The silver reagents RAg and $R_2AgMgCl$ were obtained by stirring RMgCl with $AgBr(LiBr)_n$ (n = 2—6, see Table 1) in THF or THF—HMPT for 20 min at −60°C (see ref. 5).

General procedure for the reaction of I—III with RAg or $R_2AgMgCl$

To a stirred solution of $RAg(LiBr)_n$ (0.030 mol) or $R_2AgMgCl(LiBr)_n$ (0.015

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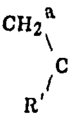
* A 1,3-dienyl sulfoxide is exclusively formed when II is treated with EtCu.

TABLE 2

PHYSICAL CONSTANTS, YIELDS, AND CHARACTERISTIC SPECTROSCOPIC DATA FOR



$\mathrm{R}\overset{a}{\mathrm{CH}_2}\backslash\,\mathrm{C}^3{=}\mathrm{C}^2{=}\mathrm{C}^1\mathrm{H}^b\mathrm{X}$ / R' (IV: X = SMe; V: X = S(O)Me; VI: X = PPh$_2$)

Compound	(°C/mmHg)	n_D^{20}	Yield [a] (%)	IR ν(C=C=C) (cm^{-1})	^{1}H NMR data (CCl$_4$) [b]				^{13}C NMR data (CDCl$_3$)	
					δ(H^a)	δ(R′)	δ(H^b)	δ(X)	δ(C^1, C^3)	δ(C^2)
IVa	70–72/18	1,5144	80	1943	2,01	5,42	5,70	2,08	89.2, 97,8	199.9
IVb	99–101/18	1,5056	88	1941	2,01	5,42	5,70	2,07	89,3, 98,3	200.0
IVc	88–90/24	1,5075	90	1942	1,97	5,39	5,68	2,10	89.2, 96,9	201.0
IVd	91–92/20	1,5004	90	1940	1,96	5,40	5,69	2,10	88.1, 94,9	201.4
IVe	74–75/20	1,5095	90	1945	1,99	1,72	5,63	2,04	88,2, 107,4	197.5
IVf	102–104/18	1,5019	90	1946	1,98	1,73	5,62	2,03	88,3, 107,4	197.4
IVg	85–86/18	1,5042	80	1950	1,90	1,75	5,63	2,04	88,0, 106,3	198.5
IVh	90–91/18	1,5027	85	1948	1,90	1,78	5,57	2,08	87,2, 104,3	199.8
Va	90–93/0,05	1,5083	80	1952	1,95	1,80	5,96	2,64	100.4, 107.2	200.2, 200,3 [c]
Vb	100–102/0,07	1,5098	90	1950	2,00	1,90	5,90	2,57	98,4, 98,7 105,2	201.3, 201,9 [c]
VIa	120–125/0,001	1,5948	85	1950	1,69	1.53	5,52	7,0–7.6	86.1, 98.2	210.3
VIb	123–127/0,001	1,5887	88	1948	1,75	1,63	5,50	7,0–7.6	85.4, 96.6	211,5

[a] After distillation (purity >98%). [b] ^4J(H—C=C=C—H) in Hz: 6.2(IVa); 6.2(IVb); 6,3(IVc); 6.2(IVd). [c] The allenic sulfoxide consisted of a mixture of diastereoisomers.

mol) in dry THF (100 ml) or a mixture of dry THF (100 ml) and HMPT (10 ml), enyne I, II or III (for amounts see Table 1) is added at −60° C. The temperature of the mixture is allowed to rise to that indicated in Table 1, and the mixture is stirred at that temperature for the time shown in Table 1. The mixture is then poured into a saturated solution of ammonium chloride in water (200 ml) containing NaCN (2 g). The allenic sulfides IV and phosphines VI are extracted with pentane (3 × 100 ml) and the allenic sulfoxides V with chloroform (2 × 100 ml). After washing the combined extracts and drying with $MgSO_4$, the solvent is evaporated in vacuo and the residue distilled. Physical constants, yields and characteristic spectroscopic data for pure allenes IV—VI are given in Table 2.

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