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APPLICATION OF ALLENYLSILVER(I) COMPOUNDS IN ORGANIC SYNTHESIS. A SIMPLE ROUTE TO SUBSTITUTED ALLENES

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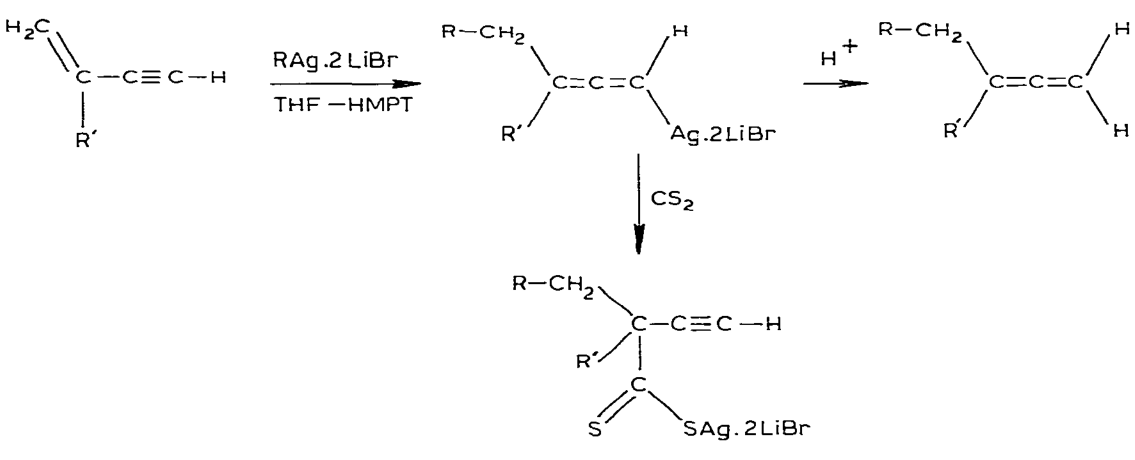
Summary

Allenylsilver(I) compounds, prepared in situ by addition of alkylsilver(I)-lithium bromide complexes to butenynes, readily react with a variety of electrophiles. The produced compounds are usually almost pure allenes, but in some cases substantial amounts of the isomeric acetylenes are also formed.

Introduction

In the literature considerable attention has been focussed on reactions of allenyl-metal compounds, $>C{=}C{=}C{-}M$, with electrophiles, "E^+". The reported data do not establish a general pattern of reactivity, however. In some reactions acetylenes, $>C(E){-}C{\equiv}C{-}$, are mainly produced, in other reactions formation of



allenes, >C=C=C—E, is preferred [1].

Allenylsilver(I) reagents have not received much attention, thus far. We recently showed that these allenyl-metal compounds can be readily obtained by treating conjugated enynes with alkylsilver(I)-lithium bromide complexes, RAg · 2 LiBr [2]. Protolysis of such allenylsilver(I) compounds gives allenes. On the other hand, acetylenes were produced when these silver(I) reagents were allowed to react with carbon disulfide [3].

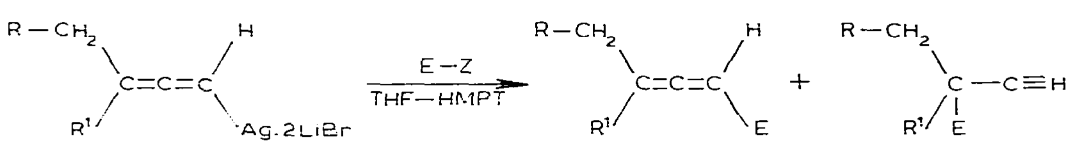
The present paper deals with a more extensive study of the behaviour of allenylsilver(I) compounds towards electrophiles.

Results and discussion

The allenylsilver(I) compounds I, obtained from $H_2C{=}C(R'){-}C{\equiv}CH$ (R′ = H or Me) and RAg · 2 LiBr [1] *, appeared to react regioselectively with a large variety of electrophiles E—Z, viz. cyanogen bromide, iodine, methyl methanethiolsulfonate, allyl bromide, and the halides $Me_3M{-}Cl$ (M = Si, Ge, and Sn). Analysis of the products showed that these electrophiles strongly preferred to react at the allenic end of I to give allenes II (see Scheme 1; E in II: Br, I, MeS, $H_2C{=}CH{-}CH_2{-}$, and Me_3M, respectively). Generally, the amount of isomeric 1-alkynes III, compounds resulting from propargylic attack by the electrophile, was less than 5%; in case of bromination of I (R = t-Bu, R′ = H) by cyanogen bromide the ratio II/III was somewhat lower, viz. 90/10. The total yield of II + III in all cases was in the range 80—90% (calculated on RAg · 2 LiBr).

In the same study we also attempted to prepare allenyl bromides by allowing I to react with *N*-bromosuccinimide (NBS). Although this reaction also proceeded smoothly, the ratio II/III was not as high as that in the corresponding reaction with cyanogen bromide. For instance, treatment of I (R = t-Bu, R′ = Me) with NBS led to a mixture of II and III in a ratio 80/20, while that with cyanogen bromide gave almost exclusively II (ratio II/III: >95/5). Reaction of the same silver(I) compound with *N*-chlorosuccinimide (NCS) gave mainly acetylene III (E = Cl; ratio II/III: 25/75).

SCHEME 1



(I) (II) (III)

(R = Bu, i-Pr, t-Bu;

R¹ = H or Me; E—Z = Br—CN, I_2, $MeS{-}SO_2Me$,

$H_2C{=}CH{-}CH_2Br$, $Me_3Si{-}Cl$, $Me_3Ge{-}Cl$, $Me_3Sn{-}Cl$, NBS, NCS)

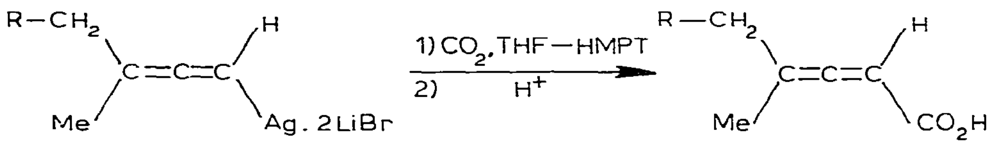
Attempts to alkylate I in THF-HMPT by methyl iodide were not successful. For instance, when I(R = t-Bu, R′ = Me) was allowed to react with methyl iodide,

* These additions were performed in a mixture of tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPT).

a mixture of high-boiling products was obtained, presumably consisting of dimers derived from I. So, allenylsilver(I) compounds are considerably less prone to alkylation than their lithium and copper analogs, which can be alkylated readily [4—5].

In the introduction it was noted that carbon disulfide is introduced at the propargylic site of I. In contrast, carbon dioxide appears to react at the allenic site of I, with formation of nearly pure allenyl carboxylic acids (compounds IV in Scheme 2):

SCHEME 2



(I) (IV)

(R = i—Pr, yield of IV : 85%;
R = t—Bu, yield of IV : 90%)

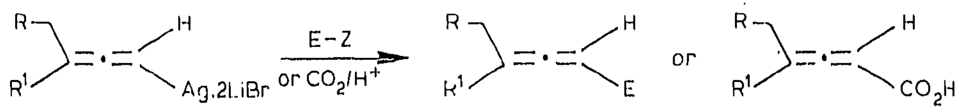
Physical constants and some characteristic spectroscopic data for allenes II and IV are given in Table 1.

The results show that most of the electrophiles studied are preferentially introduced at the allenic end of compounds I, although in some cases, viz. reaction of I with NCS and carbon disulfide, introduction of the electrophile at the propargylic site is favoured. This implies that the regiochemistry observed for reactions of I with electrophiles, cannot fully be rationalized with Pearson's hard and soft acid and base principle (HSAB, [6]). Using this principle, one would namely predict that soft electrophiles (e.g. CS_2, I_2, allyl bromide, MeS—SO_2Me etc.) are preferentially introduced at the "soft" end of I and hard ones (e.g. H_2O, CO_2, Me_3Si—Cl etc.) at the "hard" end of I. Most likely, the propargylic site of I is, in HSAB-terms, softer than its allenic one because of higher *p* character at the propargylic site. (This assumption was also made for allenyllithium compounds [1].)

For reactions with electrophiles of the soft series, only that of I with carbon disulfide (see Introduction), would fit the HSAB-principle; reaction of I with the other electrophiles does not. Most of the hard electrophiles used in this paper, and also H_2O (see ref. 2), react preferentially at the "hard", allenic end of I, but NCS (which is undoubtedly "hard") mainly gives the product which would be predicted for soft electrophiles. With respect to the latter reaction is it noteworthy that NBS, which is softer than NCS, gives more allenic product than NCS.

These data show that when used alone the HSAB-explanation breaks down, especially when applied to reactions of I with soft electrophiles. Creary [1] has also observed an inconsistency with the HSAB-principle for reactions of 3,3-dimethylallenyllithium with certain electrophiles. He suggested that other factors such as steric hindrance, charge distribution in the allenylmetal compounds, and the stability of the allene relative to the acetylenic product, can play a large part in determining the acetylene-allene ratios.

TABLE 1



(I) (II) (IV)

(I) R	(I) R^1	E—Z or CO_2/H^+	Product II/IV [a] B.p. (°C/mmHg)	n_D^{20}	NMR-data [$\delta(Me_4Si) = 0$ ppm] [b] of $>C=C=C(H^a)(E, CO_2H)$ $\delta(H^a)$	$\delta(C_{sp})$	$\delta(C_{sp}2)$	IR(film) $\nu(C=C=C)$ (cm^{-1})
t-Bu	H	Br—CN	33—35/0.6 [c]	1.4875	5.83 [d]	203.1	71.1, 97.8	1958
		Me_3Sn—Cl	100—101/16	1.4922	4.94 [e]	209.0	75.6, 77.2	1933
Bu	Me	Br—CN	42—44/0.5	1.4940	5.80	199.6	71.3, 110.9	1955
		Me_3Ge—Cl	44—45/0.6	1.4668	4.85	206.3	82.0, 92.1	1945
		Me_3Sn—Cl	64—65/0.5	1.4915	4.98	207.2	76.9, 89.2	1938
		$CH_2=CHCH_2$—Br	94—96/16	1.4616	[f]	202.2	88.4, 99.7	1965
i-Pr	Me	Br—CN	28—30/0.5	1.4981	5.79	199.6	70.6, 109.9	1955
		I_2	42—43/0.5	1.5432	5.53	203.4	35.0, 105.6	1944
		Me_3Si—Cl	70—71/20	1.4485	4.73	209.6	81.5, 90.4	1942
		Me_3Sn—Cl	51—53/0.5	1.4925	4.94	207.9	78.5, 87.9	1936
		CO_2/H^+	93—95/0.4	1.4824	5.39	212.0	86.1, 103.3 [g]	1963
t-Bu	Me	Br—CN	32—33/0.4	1.4991	5.78	201.0	70.6, 108.5	1953
		I_2	53—55/0.5	1.5588	5.55	204.6	35.2, 104.2	1940
		MeS—SO_2Me	90—91/18	1.5027	5.58	199.8	87.2, 104.3	1946
		Me_3Si—Cl	85—86/20	1.4510	4.73	210.9	80.6, 89.0	1940
		Me_3Ge—Cl	80—82/18	1.4675	4.83	208.7	80.9, 89.5	1942
		Me_3Sn—Cl	48—49/0.5	1.4937	4.90	209.3	78.5, 86.6	1932
		$CH_2=CHCH_2$—Br	71—72/16	1.4680	[h]	204.3	86.9, 996.8	1965
		CO_2/H^+	99—100/0.4	1.4841	5.38	213.2	85.8, 101.8 [i]	1958

[a] The purity of the distilled products was at least 95%, unless otherwise stated; yield of II and IV: 80—90%; The amount of acetylenic products was less than 5%, except for the reaction of I(R = t-Bu, R^1 = H) with cyanogen bromide. [b] The ^{1}H-NMR spectra were recorded with solutions of II and IV in CCl_4; the ^{13}C-NMR spectra were recorded with solutions of II an IV in $CDCl_3$. [c] The allene was contaminated with 10% of t-$BuCH_2CH(Br)$—C≡CH. [d] The other allenic H absorption was found at 5.27 ppm. [e] The other allenic H absorption was found at 4.59 ppm. [f] The allene was contaminated with 10% of $H_2C=C(Me)—C(CH_2CH=CH_2)=CH$—Bu (for the origin of this product, see ref. 2). The chemical shift of H^a could not be assigned because of overlap with the $H_2C=$ absorption of the allyl group in the spectrum. [g] The carbonyl C atom was found at 172.8 ppm in the ^{13}C-NMR spectrum; in the IR spectrum the C=O absorption was found at 1690 cm^{-1}. [h] $\delta(H^a)$ could not be assigned because of overlap with $\delta(H_2C=)$ of the allyl group in the spectrum. [i] $\delta(C = 0)$ was found at 172.8 ppm; in the IR spectrum $\nu(C=O)$ was found at 1690 cm^{-1}.

Experimental

All reactions 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.

(1) Preparation of the silver(I) compounds, I

To a stirred solution of RAg · 2 LiBr (0.030 mol) * in a mixture of THF (180 ml) and HMPT (18 ml) an appropiate amount of $H_2C{=}C(R^1){-}C{\equiv}CH$ (0.060 mol; R^1 = H or Me) was added at —60°C. The resulting mixture was stirred for 3 h at —20°C (R = t-Bu; R^1 = H or Me), for 3 h at 0°C (R = i-Pr; R^1 = Me), or for 6 h at 0°C (R = Bu; R^1 = Me).

(2) Reaction of I with E—Z

To a stirred solution of adducts I obtained as described in (1) the electrophile E—Z (0.030 mol) was added at —50°C. After stirring of the mixture for 1 h at —50°C, the temperature of the reaction mixture was allowed to rise to 25°C. Stirring at 25°C was continued for 1 h (E—Z = Br—CN, I_2, or MeS—SO_2Me), 2 h (E—Z = allyl—Br, Me—I, NCS, or NBS), or 40 h (E—Z = Me_3Si—Cl, Me_3Ge—Cl, or Me_3Sn—Cl). Subsequently, the mixture was added to a solution of ammonium chloride in water containing NaCN (2 g). The products were isolated by extraction with pentane (3 × 50 ml). After washing the combined extracts with water (5 × 100 ml) and drying with $MgSO_4$ the solvent was distilled off and the products were analysed. Physical constants and spectroscopic data of the distilled compounds II are given in Table 1.

(3) Reaction of I with CO_2

A dry CO_2 stream (50 ml/min) was bubbled through the under (1) obtained THF-HMPT solution of I (~0.03 mol, R = i-Pr or t-Bu; R^1 = Me), initially for 1 h at —50°C and subsequently for 1 h at 25°C. The mixture was then treated with 1 *N* HCl. The produced carboxylic acids IV were extracted with ether (5 × 50 ml); the combined extracts were washed with 1 *N* HCl (3 × 50 ml), dried with $MgSO_4$, and concentrated in vacuo. The residues were distilled. Physical constants and some characteristic spectroscopic data of IV are given in Table 1.

Acknowledgement

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References

1 X. Creary, J. Amer. Chem. Soc., 99 (1977) 7632, and references cited therein.
2 H. Westmijze, H. Kleijn, and P. Vermeer, J. Organometal. Chem., 172 (1979) 377.
3 H. Westmijze, K. Ruitenberg, J. Meijer, and P. Vermeer, Tetrahedron Lett., 21 (1980) 1771.
4 G. Linstrumelle and D. Michelot, J. Chem. Soc., Chem. Commun., (1975) 561.
5 D. Michelot and G. Linstrumelle, Tetrahedron Lett., (1976) 275.
6 R.G. Pearson, J. Chem. Educ., 45 (1968) 581, 643.

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* RAg · 2 LiBr was prepared from RMgX and AgBr · 2 LiBr in THF-HMPT according to our procedure given in ref. 2.