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ALKYLCOPPER- AND ALKYLSILVER-INDUCED SUBSTITUTION IN ENYNYL OXIRANES. NOVEL ROUTE TO BUTATRIENYL CARBINOLS

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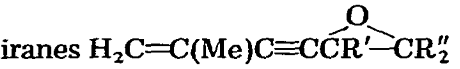
Summary

The enynyl oxiranes  $H_2C{=}C(Me)C{\equiv}C\overset{O}{CR'{-}CR''_2}$ (I) react with alkylsilver compounds to form butatrienyl carbinols $RCH_2C(Me){=}C{=}C{=}C(R')CR''_2OH$ (IV, V). Alkylcopper reagents, on the other hand, preferentially convert I into allenyl carbinols $H_2C{=}C(Me)C(R){=}C{=}C(R')CR''_2OH$ (III).

Introduction

It has recently been found in our laboratory that alkylsilver compounds are useful synthetic reagents. Their behaviour is often complementary to that of their copper analogs. For example, alkylcopper compounds preferentially react with the triple bond of conjugated enynes [1,2], but alkylsilver reagents react with their double bond [3]. A similar difference in regiochemistry has been found for the reaction of alkylcopper and -silver compounds with conjugated enynenitriles [4] and esters derived from enynyl carbinols [5].

This paper describes the reaction of some enynyl oxiranes with alkylcopper and alkylsilver reagents. It is shown that the complementary behaviour of these Group IB metal compounds is also found in reactions with such oxiranes.

Results and discussion

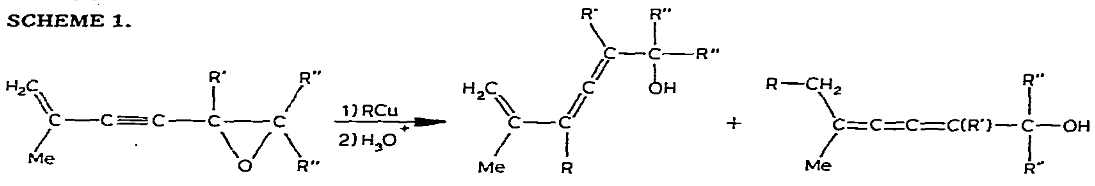
Reaction of enynyl oxiranes with alkylcopper

Oxirane I reacted smoothly with n-BuCu in tetrahydrofuran (THF) to form the allenyl carbinol IIIa (Scheme 1). This 1,3-substitution took place very regioselectively and gave IIIa in 95% yield. The absence of detectable amounts of isomeric products such as IVa was deduced from ^{1}H NMR and GLC analyses.

Thus, although a 1,5-substitution in I is possible in principle, n-BuCu prefers the 1,3-substitution path. We found the same pattern previously for the reaction of  $CH_3C{\equiv}CC(CH_3)(-O-)CH_2$ with organocopper compounds [6]. A similar preference for the 1,3-substitution route has been observed for organocopper-induced substitution in $H_2C{=}C(Me)C{\equiv}CCMe_2OS(O)Me$ [5]. On the other hand, the bulky organocopper compound t-BuCu reacts less selectively with I, and produces a 60 : 40 mixture of allene IIIb and butatriene IVb.

In another study it was shown that, in contrast to n-BuCu, t-BuCu also attacks the double bond in 2-methyl-1-buten-3-yne [3]. In that case no addition of t-BuCu to the triple bond occurs. However, reaction of $H_2C{=}C(Me)$-$C{\equiv}CCMe_2OS(O)Me$ with t-BuCu only gave $H_2C{=}C(Me)C(t\text{-}Bu){=}C{=}CMe_2$, i.e. the product resulting from attack of t-BuCu on the triple bond. The pattern observed for reactions of t-BuCu with enyne substrates thus largely depends on the type of substrate.

SCHEME 1.



(I : R' = H , R'' = Me)

(IIIa : R = n-Bu;
IIIb : R = t-Bu)

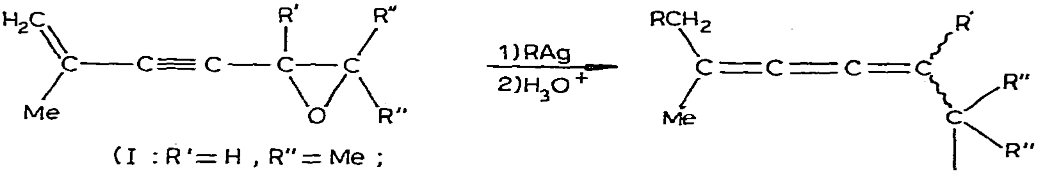
(IVa : R = n-Bu ;
IVb : R = t-Bu)

(Ratio IIIa/IVa>99/1 ;
ratio IIIb/IVb : 60/40)

Reaction of enynyl oxiranes with alkylsilver

In the preceding section the formation of a substantial amount of butatriene IVb was noted. In view of the preference of alkylsilver compounds for attack on the double bond of conjugated enynes [3—5], it seemed likely that alkylsilver compounds convert enynyl oxiranes selectively into butatrienyl carbinols such as IVb. Oxirane I did in fact undergo selective 1,5-substitution when treated with alkylsilver compounds RAg (solvent: THF). Oxirane II (Scheme 2) also gave butatrienyl carbinols (V) upon reaction with RAg. In this case the terminal oxirane C atom is not very hindered as R'' is hydrogen, but even so the RAg compounds react only at the other side of the molecule, which suggests that these Group IB metal compounds strongly prefer to give 1,5-substitution products.

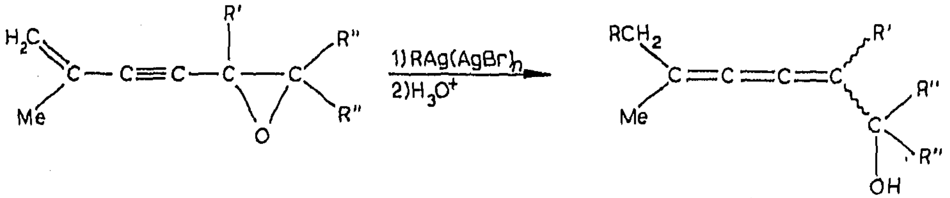
SCHEME 2.



(I : R' = H , R'' = Me ;
II : R' = Me , R'' = H)

(IVa : R = n-Bu , R' = H , R'' = Me ;
IVb : R = t-Bu , R' = H , R'' = Me ;
IVc : R = i-Pr , R' = H , R'' = Me ;
Va : R = n-Bu , R' = Me , R'' = H ;
Vb : R = t-Bu , R' = Me , R'' = H ;
Vc : R = i-Pr , R = Me , R'' = H)

TABLE 1



(I : R' = H , R'' = Me ;
II : R' = Me , R'' = H)

(IV/V)

Compound	R	*n*	Product [a,b]	b.p. (°C/mm Hg)	n_D^{20}	Yield (%)	^{1}H NMR (ppm, CCl$_4$) (R'=H)	^{13}C NMR (ppm, CDCl$_3$)		IR [c] (cm^{-1})
								δ (C_{sp})	δ (C_{sp^2})	
I	n-Bu	1	IVa	138/12	1.5121	90	5.4	157.1, 157.0 156.6	119.7, 119.5 110.6, 110.4	2056
I	t-Bu	0	IVb	65/ 0.1	1.5145	90	5.4	159.6, 156.5 156.3	117.5, 117.4 111.4, 110.9	2050
I	i-Pr	1	IVc	110/12	1.5135	90	5.4	157.7, 157.4 156.8, 156.5	118.2, 110.0 110.7	2062
II	n-Bu	1	Va	143/12	1.5180	85		154.9, 153.3, 153.1	115.5, 110.8, 110.7	2055
II	t-Bu	0	Vb	132/12	1.5242	90		157.5, 153.0, 152.7	113.0, 112.9, 111.4, 111.3	2060
II	i-Pr	1	Vc	122/12	1.5278	85		155.8, 153.0, 152.8	114.4, 111.1, 111.0	2055

[a] Purity: ⩾95% (determined by GLC (Carbowax, 10% on Chromosorb W) and ^{1}H NMR analysis). [b] Based on ^{13}C NMR spectroscopy: *E/Z* ≃ 50/50. [c] Neat; the values indicated refer to ν(C=C=C=C).

The yields of IV and V were high (≃90%) when t-BuAg was used (an excess of t-BuAg was required: see Experimental section). The yields of IV and V fell considerably when n-BuAg and i-PrAg were used (yields ≃50%). Attempts to improve the conversion of I and II in these cases by using a large excess of RAg (2—3 mole equivalents) gave IV and V in 60—70% yield. Homoargentates could not be used because of the formation of hitherto unidentified contaminants in IV and V.

A better means of improving the yield of IV and V is the use of n-BuAg and i-PrAg to which an equimolar amount of AgBr has been added. Table 1 shows that using these complexed silver compounds gave excellent yields of the butatrienes. Nevertheless, excess of the silver reagent (2.0 mole equivalents) was still required.

Butatrienes IV and V were obtained as *E/Z* mixtures. In the ^{13}C NMR spectrum both isomers give (partly) different signals for their *sp*- and sp^2-hybridized carbon atoms (see Table 1). The relative heights of these signals indicate that the two isomers were formed in about equal amounts during the conversion of I and II into IV and V, respectively. In the IR spectrum the characteristic butatriene absorption was present in all cases.

Neither MeAg, PhAg, nor their complexed reagents RAg · AgBr (R = Me or Ph) were able to convert I or II into the corresponding butatrienes. The unreactivity of these reagents is remarkable, but it is known that MeAg and PhAg also do not react with conjugated enynes [3] and enynenitriles [4].

To summarize, this study shows that alkylcopper and alkylsilver compounds behave in a rather complementary way towards enynyl oxiranes. Complementary behaviour can be expected towards other enynyl compounds, and work in the field is being continued.

Experimental

All reactions with RCu and RAg compounds were performed under dry nitrogen. The products were analysed by GLC (Carbowax, 10% on Chromosorb W) and by NMR (Varian EM-390 and CFT-20 spectrometers) and IR spectroscopy. The oxiranes I and II were prepared by reaction of the lithium alkynylide derived from 2-methyl-1-buten-3-yne with 2-bromoisobutyraldehyde or chloroacetone followed by ring closure of the resulting halohydrines [7].

(a) Reaction of I with RCu

To a stirred solution of $LiCuBr_2$ (0.030 mol; prepared by adding LiBr to a CuBr suspension in THF) in THF (60 ml) a solution of RMgCl (0.030 mol, R = n-Bu or t-Bu) in THF (23 ml) was added at —60 to —50°C. The mixture was stirred for 20 min at —60°C. Subsequently, oxirane I (0.030 mol) was added at —60°C, and the temperature of the mixture was then raised during 15 min to 0°C. The mixture was then poured into an aqueous solution of ammonium chloride containing NaCN (2 g). The products were isolated by extraction with diethyl ether (3 × 50 ml). After washing and drying (K_2CO_3) of the combined extracts the solvent was evaporated in vacuo and the residue distilled. Compound IIIa (see Scheme 1): Yield 95%; b.p.: 123—124°C/12 mmHg; n_D^{20} 1.4947; IR (cm^{-1}) 1943 (C=C=C); ^1H NMR (ppm, CCl_4, TMS): δ 5.50 (=CH), 5.00—

4.80 (H_2C=), 1.80 (CH_3), 1.30 (2 CH_3). Compound IIIb was contaminated with butatriene IVb (ratio IIIb/IVb: 60/40).

(b) Reaction of I and II with t-BuAg

To a stirred solution of AgBr · 3 LiBr (0.040 mol) in THF (120 ml) a solution of t-BuMgCl (0.040 mol) in THF (30 ml) was cautiously added at —60 to —50°C. Stirring at —60°C was continued for 20 min and then I or II (0.030 mol) was added at this temperature. The mixture was stirred for 4 h at 0°C. The products IVb and Vb were isolated by pouring the mixture into a saturated aqueous solution of ammonium chloride containing NaCN (2 g), extracting the products with diethyl ether, washing the combined extracts, drying the extracts over K_2CO_3, and evaporating the solvent in vacuo. The residue was purified by chromatography over Al_2O_3 (10 cm column) deactivated with 5% H_2O (eluent: Et_2O), followed by distillation in vacuo (see Table 1 for relevant data). Prepurification by column chromatography was necessary in order to prevent substantial decomposition during distillation.

(c) Reaction of I and II with RAg · AgBr

A solution of RMgCl (0.060 mol) in THF (45 ml) was added at —60 to —50°C to a stirred solution of the complex AgBr · LiBr (0.120 mol) in a mixture of THF (120 ml) and hexamethylphosphoric triamide (HMPT, 60 ml). After stirring for 5 min at —60°C, oxirane I or II (0.030 mol) was added. The temperature of the mixture was raised during 90 min to 0°C, stirring at 0°C was continued for 4 h. The products were isolated and purified as described under (b). Physical constants, yields, and spectroscopic data for IV and V are given in Table 1.

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