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Allenes and Acetylenes. XXI. Leaving-group Effects on the Stereochemistry of Allene-forming Organocuprate Reactions*

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The reactions of four chiral 1-methyl-2-propynyl derivatives (*4a–d*) with a combination of hexylmagnesium bromide and copper(I) bromide (10:1) in diethyl ether resulted in the formation of chiral 2,3-decadiene in varying enantiomeric yield. The acetate (*4b*) and the mesylate (*4c*) resulted in the highest enantiomeric yields, 79 and 66 %, respectively, when the reaction time was less than 15 min. The longer reaction times used for the derivatives *4a* and *4d* probably resulted in a decrease in yield due to racemization of the allene. The preferred mode of substitution was found to be *anti* in all cases. The chiral allenic alcohols *2* and *3* were prepared by reacting the acetylenic derivatives *1a* and *1b* with methylmagnesium iodide–copper(I) iodide (4:1) and butyllithium, respectively. The enantiomeric yields were low.

There has been recent interest in the formation of chiral allenic hydrocarbons from the reaction of chiral propargylic derivatives, such as acetates,[2] sulfinates,[3] sulfonates,[4] and carbamates,[4] with various organocuprates. The observed variations in enantiomeric yield have been variously ascribed to structural influences from the acetylene as well as the organocuprate,[3,4] leaving group effects,[4] modifications in experimental procedure,[4] and to the reaction temperature.[2,4] A few deviations from the predominant *anti* mode of substitution usually observed may be explained by the biased structures of the acetylenes (17α-ethynyl derivatives of steroids).[5] The observed variations in the enantiomeric yield of allenes, however, are large and disparate, *e.g.* two enantiomeric carbamates in reactions with the same cuprate resulted in allenes in 34 and 61 % enantiomeric yield, respectively.[4] Most of these discrepancies can be explained by the recent finding that chiral allenes are racemized by various organocuprates.[6] We can anticipate, however, that some of the factors mentioned influence the enantiomeric yield. This is of interest not only in synthesis but also regarding the mechanism of this organometallic substitution reaction; it has been shown that the corresponding reaction in allylic systems, with very few exceptions,[7] proceeds with a very high degree of *anti* displacement.[7–9] Furthermore, since the first step in these 1,3-substitution reactions is thought to be a nucleophilic displacement with the formation of a copper(III) intermediate (oxidative addition),[10,11] the mode of substitution might also be of some interest for the current discussion of the stereochemistry of S_N2' reactions.[12]

In this work we have studied leaving group effects on the enantiomeric yield of the allenes *2* and *5* in the organocuprate reactions shown in Schemes 1–3. The mode of substitution in the reaction of *1a* with butyllithium was also determined.

RESULTS

The preparation of the chiral acetylenes *1a* and *4a* has been described.[13] The compounds *1b*, *4b* and *4c* were prepared from resolved (*S*)-(−)-3-butyn-2-ol[14] using standard procedures. The ammonium salt *4d* was obtained in good yield from the mesylate *4c* by reaction with diethylamine followed by quaternization with benzyl bromide.

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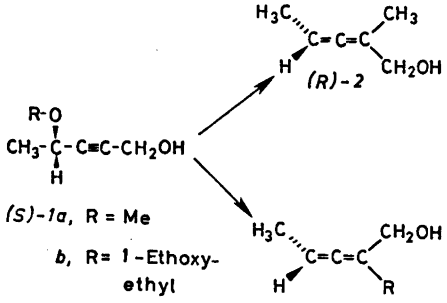
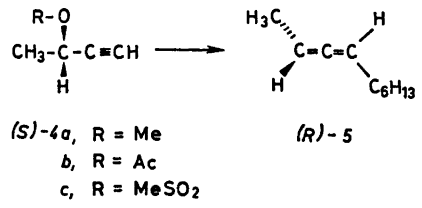
Table 1. Reactions of compounds (S)-*1a* and (S)-*1b* with MeMgI-CuI (4 + 1 mol) and of (*S*)-*1a* with butyllithium (run 7). The temperature was − 20 °C → room temperature in runs 1 − 6 and − 50 °C → room temperature in run 7.

Run	Substrate	Solvent	Reaction time/h	Product	$[\alpha]_D^{22}$(*c*,MeOH)	Yield GLC/%
1	*1a*	Et_2O	4	(*R*)-*2*	− 6.5° (6.6)	80
2	*1a*	Et_2O-THF	4	(±)-*2*	± 0° (5.6)	85
3	*1a*	$(i\text{-}C_3H_7)_2O$	10	(*R*)-*2*	− 1.8° (5.8)	45
4	*1b*	Et_2O	6	(*S*)-*2*	+ 1.9° (7.9)	50
5	*1b*	Et_2O-THF	6	(*R*)-*2*	− 0.3° (4.1)	45
6	*1b*	$(i\text{-}C_3H_7)_2O$	6	(*R*)-*2*	− 0.2° (6.4)	70
7	*1a*	Et_2O	10	(*S*)-*3*	− 1.9° (4.9)	70



Scheme 1.

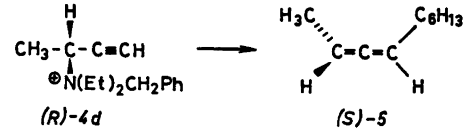


Scheme 2.

The alcohols *1a* and *1b* were allowed to react with an excess of methylmagnesium iodide − copper(I)iodide (4:1) [15] as described in Table 1. The α-allenic alcohol thus obtained was purified by preparative GLC and the optical rotation measured. In all cases except one (run 2) the allene had optical rotation; in two cases (runs 5 and 6) the rotation was very weak. Unsuccessful attempts were made to determine the enantiomeric purity of allene *2* using the chiral shift reagent Eu(hfbc)$_3$ and NMR as have been described for other allenes.[16]

The acetylene *1a* was also treated [17] with butyllithium and the allene *3* (Sheme 1) was formed in moderate yield (run 7).

The (*S*)- or (*R*)-2,3-decadienes (*5*) were obtained from reactions of compounds *4a*−*d* with a two-fold excess of hexylmagnesium bromide in the presence of 10 % copper(I) bromide [18] (Schemes 2 and 3, and Table 2). In this case it was possible to calculate the enantiomeric purity of the allene (*cf.* Discussion). Only small amounts (< 5 %) of the isomeric acetylene, 3-methyl-1-nonyne, from direct substitution, were observed in these reactions.



Scheme 3.

Table 2. Reactions of compounds *4a*−*c* with $C_6H_{13}MgBr$-CuBr (2 + 0.2 mol) in diethyl ether.

Substrate	Reaction time/h	Temp./°C	Product	$[\alpha]_D^{22}$(*c*,MeOH)	% ee	Yield GLC/%
(*S*)-*4a*	1	− 30	(*R*)-*5*	− 11.5° (5.8)	16	70
(*S*)-*4b*	0.2	− 30	(*R*)-*5*	− 57.4° (8.1)	79	70
(*S*)-*4c*	0.2	− 50	(*R*)-*5*	− 48.0° (5.4)	66	80
(*R*)-*4d*	2	− 30	(*S*)-*5*	+ 11.4° (7.5)	16	80

DISCUSSION

There can be no doubt the (*R*) configuration assigned to the allenic hydrocarbon (−)-*5* is correct.[19,20] Determination of absolute configurations of tri- and tetrasubstituted allenes is, however, more problematic. One approach is to use the chirality functions for allenes which were developed by Runge and Kresze.[21] By using this method it was calculated that the pure allene (*R*)-*2* would have a rotation of $[\alpha]_D^{25} - 14.1°$. We therefore tentatively assign the (*R*) configuration to the levo-rotatory allene *2*. Similar calculations on the allene (−)-*3* result in the assignment of the (*S*) configuration to this compound, since butyl is more polarizable than hydroxymethyl.[21]

The determination of enantiomeric purity of 2,3-decadiene (*5*) is based on a value of ±100° for the maximum molecular rotation, $[\phi]_D^{25}$, of any 1,3-di-*n*-alkyl substituted allene. This value was experimentally determined for 3,4-heptadiene by Pirkle and Boeder.[20] Runge, using chirality functions, has calculated a maximum $[\phi]_D^{25}$ value of ±97° for this type of allene.[21] The $[\phi]_D$ value of ±100° for 2,3-decadiene, therefore, cannot be too far from the true one.

Since (−)-*2*, according to the above assumption, has the (*R*) configuration and the starting acetylenes *1a* and *1b* have the (*S*) configuration, we can conclude that *2* is formed in a predominant *syn* displacement (*syn*:*anti* ratio about 73:27) in run 1, a slightly predominant *syn* displacement (*syn*:*anti* about 56:44) in run 3 and without selectivity in runs 2, 5 and 6. In run 4 the opposite stereochemistry is observed (*anti*:*syn* about 57:43).

These results suggest that there are both considerable solvent effects (*cf.* runs 1 and 2) and a leaving group effect (*cf.* runs 1 and 4) on the stereochemical course of the reactions of the acetylenes *1* with the cuprate from MeMgI-CuI (4:1). Any conclusions about solvent effects are, however, premature, since the facile racemization of chiral allenes by organocuprates must be taken into account.[6] The alcohol *2* was not tested for racemization rate but there is no reason to assume that it would not be affected by this cuprate; the zero value for the optical rotation in run 2 is significant since rates of racemization are accelerated in THF.[6] The true enantiomeric yields are, therefore, unknown and we will not discuss further the quantitative aspects of leaving-group and solvent influences.

The opposite and predominant *syn* and *anti* displacements in runs 1 and 4 are, however, real. In the analogous reaction of another methyl ether (*4a*) there is, in contrast to run 1, a predominant *anti* displacement (Table 2). It, therefore, appears that the *syn* displacement observed for the alcohol-ether *1a* is induced by the presence of the hydroxyl group (as an alkoxide). Similar neighbouring-group effects on the *syn*:*anti* displacement ratios have been observed in lithium aluminium hydride reductions of propargylic derivatives.[22]

The overall *anti* displacement of methoxy with butyl in the reaction of *1a* with butyllithium proceeds to (*S*)-*3* *via* a mechanism which is different from the organocuprate reactions. It most likely involves a *trans* addition over the triple bond[17] followed by a slightly preferred *syn* 1,2-elimination of lithium methoxide. It is interesting to note that compound *1a* also reacts with lithium aluminium hydride in a *trans* addition but this, in contrast, is followed by a preferred *anti* elimination reaction.[13]

The reactions of compounds *4a*–*d* with the cuprate from hexylmagnesium bromide and copper(I) bromide give a better indication than the preceding reactions of the preferred stereochemistry in organocuprate reactions in unbiased propargylic systems. In all cases the preferred mode of displacement is *anti* (Table 2) but, again, since the allene product undergoes racemization under the reaction conditions,[6] it is impossible to estimate the exact magnitude of the leaving group influence on the *anti*:*syn* displacement ratio. Earlier work,[6] however, suggests that it is unlikely that chiral allene *5*, formed from the methyl ether *4a*, initially would have had a similar large enantiomeric excess as when formed from the acetate *4b* or the mesylate *4c*. The assumed lower *anti*:*syn* ratio for displacement of methoxy is also in part corroborated by the preferred *syn* substitution observed for *1a* (run 1, Table 1), which is in contrast to the *anti* substitution of *1b* (run 4).

The organocuprate reaction of compound *4d* is the first application of this type of reaction to a propargylic quaternary ammonium compound and is probably the first reported

on any substrate of the quaternary ammonium type.

If one accepts the two-step mechanism for these substitution reactions, *i.e.* nucleophilic substitution of the leaving group to form a copper(III) intermediate followed by reductive elimination[10] (no equally attractive alternative has been forwarded), there are two possibilities for low stereodifferentiation (as presumedly observed in the reaction of *4a*). One is low *syn:anti* selectivity in the displacement step so as to directly produce both enantiomeric copper(III) intermediates and the other possibility is racemization of such a chiral intermediate (the subsequent reductive elimination is probably completely stereospecific[23]). There is at present no way to differentiate between these possibilities. However, it might be mentioned that there is an indication that a postulated copper(III) intermediate derived from an allylic methyl ether is different (possibly more long-lived) than one from the corresponding acetate.[11]

Yet another reaction mechanism can be considered, especially with regards to poor leaving groups, *i.e.* a *cis* addition of alkylcopper over the triple bond followed by a 1,2-elimination of a copper(I) compound, *e.g.* copper methoxide. This mechanism was shown by Normant and co-workers[24] to be operative when allenes are formed from propargylic ether and alkylcopper (from equimolar amounts of a Grignard reagent and a copper(I) salt). If this, in our opinion, less likely mechanism is involved in the present reactions, the stereodifferentiation results from varying degrees of *syn* and *anti* 1,2-eliminations of copper(I) species from the vinylcopper intermediate.

The *anti* stereochemistry observed in the present study has also been reported for the reaction of propargylic acetates,[2,4] sulfonates,[4] and carbamates[4] with lithium dialkylcuprates and for propargylic sulfinates with cuprate reagents prepared from alkylmagnesium halides.[3] Furthermore, chiral 3-phenyl-3-chloro-1-propyne undergoes an S_N2' type reaction with dichlorocuprate(I) to give chiral 1-chloro-3-phenyl-1,2-propadiene in an assumed *anti* displacement.[25] It might also be relevant to mention that a preferred *anti* relationship between the migrating alkyl group and the departing acetate in the allene-forming rearrangement of a trialkyl(3-acetoxy-1-alkynyl) borate has been demonstrated.[26]

The preferred *anti* displacement in all compounds *4a–d* is noteworthy in relation to the current interest in the stereochemistry of S_N2' reactions in allylic[12] and propargylic[22] systems. These reactions, of which some may be termed S_Ni', exhibit variable *syn-anti* selectivity. In contrast, the reaction of chiral allylic derivatives with organocuprates proceeds with an exceptionally high degree of *anti* displacement which approaches the S_N2 reaction in inversion specificity.[7–9]

Results from MO-calculations[27] on the preferred mode of the true S_N2' reaction in allylic systems, when applied to the present propargylic systems, suggest that the ammonium compound *4d* would be a certain candidate for *syn* displacement. A preferred *anti* displacement is observed instead (to an unknown extent but the *anti:syn* ratio 58:42 is a minimum value). It would therefore be of considerable interest to investigate the stereochemistry of the reaction of an allylic quaternary ammonium compound with organocuprates. The result also indicates that the reactions of organocuprates, which have a strong one-electron transfer ability,[28,6] may not be readily compared with the reactions of ordinary nucleophiles.

In conclusion, the stereochemistry of the organocuprate reactions of propargylic derivatives appears more complex than for alkyl and allyl compounds since a greater number of possible mechanistic pathways can be discerned and, furthermore, the experimental studies are impeded by the racemization of the allenic products under the reaction conditions.[6]

EXPERIMENTAL

General. The general IR and NMR instrumentation has been described.[29] These spectra were routinely recorded and are in full agreement with the proposed structures. 100 MHz ^1H NMR spectra were taken with a JEOL JNM-FX instrument. Unless otherwise stated optical rotations were measured in methanol with a Perkin-Elmer 141 spectropolarimeter. The GLC apparatus and columns have been described.[17] The preparative columns were of steel, 600 × 0.96 cm and packed with 20 % Carbowax 20 M or 300 × 0.96 cm and packed with 20 % SE-30, both on Chromosorb W

(60 – 80 mesh). Microanalyses were carried out at the Microanalytical Laboratory, Royal Agricultural College, Uppsala. All reactions with butyllithium, Grignard or organocuprate reagents were performed under argon or nitrogen.

(S)-(–)-4-(1-Ethoxyethoxy)-2-pentyn-1-ol (1b). (*S*)-(–)-3-(1-Ethoxyethoxy)-1-butyne was prepared as described [30] for similar compounds from (*S*)-(–)-3-butyn-2-ol (5.0 g; 71 mmol) and ethyl vinyl ether (10.3 g; 143 mmol). Yield 83 %, b.p. 82 °C/13.3 kPa. $[\alpha]_D^{22} - 146.1°$ (10.1). Anal. $C_8H_{14}O_2$: C, H. This propargylic ether was converted to its Grignard derivative and reaction with gaseous formaldehyde [31] resulted in the title compound (*1b*) in 71 % yield. B.p. 90 °C/20 Pa. $[\alpha]_D^{22} - 144.7°$ (10.4). Anal. $C_9H_{16}O_3$; C, H.

Organocuprate reactions of acetylenes 1a *and* 1b. To a solution of CH_3MgI (48 mmol) in the indicated solvent (Table 1, runs 1 – 6) at – 20 °C was added the acetylene *1a* or *1b* (12 mmol). After stirring for 5 min at the same temperature Cu(I)I (12 mmol) was added. The mixture was brought to room temperature and stirred for the time indicated. Saturated NH_4Cl solution was added and the product was taken up in ether. The organic extract was dried over $MgSO_4$ and the solvent was removed under vacuum. Preparative GLC on SE-30 yielded 2-methyl-2,3-pentadien-1-ol (*2*) and the optical rotation was measured (yields and $[\alpha]_D^{22}$ values are given in Table 1). 2-Methyl-2,3-pentadien-1-ol, ^1H NMR ($CDCl_3$): δ 5.27 (1H,m), 4.02 (2H,d), 2.10 (1H,s), 1.73 (3H,s), 1.65 (3H,d).

(S)-(–)-2-Butyl-2,3-pentadien-1-ol (3) was prepared as described [17] by treating the acetylene *1a* with 2.5 equiv. of butyllithium in diethyl ether. Work up and isolation as above gave the title compound (*3*; run 7, Table 1). ^1H NMR ($CDCl_3$): δ 5.28 (1H,m), 3.99 (2H,d), 1.97 (2H,m), 1.72 (3H,d), 1.41 (4H,m), 0.90 (3H,t).

(S)-(–)-1-Methyl-2-propynyl acetate (4b) [32] was prepared according to standard procedures,[33] *i.e.* to a mixture of 3.0 g (43 mmol) of (*S*)-(–)-3-butyn-2-ol and 4.1 g (52 mmol) of pyridine was added 6.6 g (64 mmol) of acetic anhydride. Yield 85 %. B.p. 127 °C/101.3 kPa. $[\alpha]_D^{22} - 140.4°$ (6.8).

(S)-(–)-1-Methyl-2-propynyl methane sulfonate (4c) [34] was prepared according to a published procedure [35] from 3.0 g (19.5 mmol) of (*S*)-(–)-3-butyn-2-ol and 2.5 g (21.5 mmol) of methanesulfonyl chloride. The product was purified on silica gel 60, using ether – light petroleum (2:3) as the eluent. Yield 94 %. $[\alpha]_D^{22} - 79.8°$ (10.9, dioxane).

(R)-N,N-Diethyl-N-(1-methyl-2-propynyl)-benzyl ammonium bromide (4d). *N,N*-Diethyl-3-amino-1-butyne [36] was prepared by reaction of 7.0 g (47 mmol) of the methanesulfonate *4c* with 6.9 g (95 mmol) of diethylamine in CH_2Cl_2 for 3 days at room temperature. The reaction mixture was diluted with ether and washed with 10 % K_2CO_3. The organic phase was dried over K_2CO_3 and the solvent was removed under vacuum. The tetriary amine was obtained in 90 % yield by purification on silica gel 60 with ether – light petroleum (1:1), $[\alpha]_D^{22} + 8.9°$ (1.4). Treatment of this amine with a two-fold excess of benzyl bromide in acetone for 24 h at room temperature gave the quaternary ammonium compound *4d* in 70 % yield. M.p. 171 °C. Anal. $C_{15}H_{22}BrN$; C, H, N.

Organocuprate reactions of acetylenes 4a – d. Copper(I) bromide (2.5 mmol) was added to an ether solution of hexylmagnesium bromide (25 mmol) at the indicated temperature (Table 2) and the mixture was stirred for 15 min. One of the acetylenes *4a – d* (12 mmol), dissolved in ether, was added and the mixture was stirred at the same temperature for the time indicated. After hydrolysis with NH_4Cl solution and extraction with light petroleum, the solvent was removed under vacuum. 2,3-Decadiene was isolated by preparative GLC on a Carbowax 20 M column and the optical rotation was measured. 2,3-Decadiene, ^1H NMR ($CDCl_3$): δ 5.02 (2H,m), 1.97 (2H,m), 1.63 (3H, double d), 1.31 (8H,m), 0.89 (3H,t).

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