# Chiral Allenes are Racemised by Organocuprates†

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*Summary* The chiral allenes (**1**) and (**2**) are racemised in the presence of various organocuprates, or, in the case of the alcohol (**2**), by methylmagnesium iodide alone; the racemisations probably proceed *via* an anion radical.

THE reactions of chiral prop-2-ynylic derivatives such as acetates,[1] sulphinates,[2,3] carbamates,[4] toluene-*p*-sulphonates,[4] and ethers,[5] with various organocuprates give rise to chiral allenic hydrocarbons[1–4] and alcohols.[5] The influence of various factors on the enantiomeric yield and overall stereochemistry (*syn* or *anti* substitution) is of current interest. It has been claimed that the observed variations in enantiomeric composition may be due to leaving group effects, to structural influences from the acetylene as well as the organocuprate, and to modifications in experimental procedure.[1–4]

We report here that the chiral allenes (**1**) and (**2**) undergo racemisation in the presence of various organocuprates, or, in the case of the alcohol (**2**), in the presence of methylmagnesium iodide alone. Our results make the interpretation of some earlier reported observations[4] more difficult and may have an important bearing on future work with chiral allenes involving organocuprates, or in some cases, Grignard reagents.

The allenes (*R*)- and (*S*)-(**1**), and (*R*)-(**2**)[6] were treated with various reagents and under different conditions as described in the Table. The reaction mixtures were hydrolysed either with water or, in runs 2,3,5,6,9, and 10, with $D_2O$. The allenes were isolated by preparative g.l.c. and the optical rotations measured. No other products were formed from the allenes and in no case was deuterium incorporation observed (n.m.r.). Treatment of the alcohol (*R*)-(**2**) with 1 equiv. of $LiAlH_4$ in tetrahydrofuran (THF) at −30 °C for 17 h did not alter the optical rotation.

The optical rotation values in the Table show that the enantiomeric excess of the allene (**1**) is drastically reduced by

TABLE. Treatment of chiral allenes with organocuprates and Grignard reagents.

| Run | Allene, $[\alpha]_D$[a] | Reagent (equiv.) | Solvent | Time/h | Temp./°C | Final $[\alpha]_D$[a] |
|---|---|---|---|---|---|---|
| 1 | (*S*)-(**1**), +54·9° | $LiCuBu_2$ (2)[b] | $Et_2O$ | 3 | −30 | +11·0° |
| 2 | (*R*)-(**1**), −64·8° | $LiCuBu_2$ (2)[b] | THF | 0·5 | −65 | −20·3° |
| 3 | (*R*)-(**1**), −64·8° | $LiCuBu_2$ (2)[b] | THF | 3 | −30 | −5·3° |
| 4 | (*R*)-(**1**), −64·8° | EtMgBr (2)–CuBr (0·2)[c] | $Et_2O$ | 4 | −30 | −39·1° |
| 5 | (*R*)-(**1**), −64·8° | EtMgBr (2)–CuBr (0·2)[c] | $Et_2O$–THF[d] | 6 | −30 | −0·1° |
| 6 | (*R*)-(**1**), −64·8° | EtMgBr (2) | $Et_2O$–THF[d] | 4 | +20 | −62·9° |
| 7 | (*R*)-(**1**), −64·8° | MeMgI (2) | $Et_2O$–THF[d] | 3 | +20 | −56·0° |
| 8 | (*R*)-(**2**), −27·2° | MeMgI–CuI (4 + 1)[c] | $Et_2O$ | 3 | −30 | −16·6° |
| 9 | (*R*)-(**2**), −42·4° | MeMgI–CuI (4 + 1)[c] | $Et_2O$–THF[d] | 3 | −30 | −3·1° |
| 10 | (*R*)-(**2**), −42·4° | MeMgI (4) | $Et_2O$ | 3 | +20 | −3·6°[e] |

[a] Optical rotations were measured in methanol. [b] Prepared from butyl-lithium and purified CuI. [c] Copper(I) halide was added to the Grignard reagent at −30 °C and the mixture was stirred for 10 min before the allene was added. [d] Solvent was a 1 : 2 mixture. [e] Mean value of two runs giving $[\alpha]_D$ −6·7° and −0·5°, respectively.

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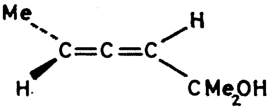
† For Part 18 of the series Allenes and Acetylenes, see A. Claesson, C. Sahlberg, and K. Luthman, *Acta Chem. Scand.*, 1979, **B33**, in the press.

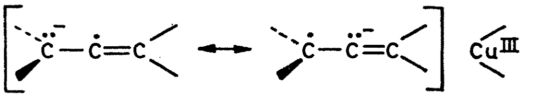
all organocuprate reagents but only slightly affected by alkylmagnesium halides (runs 6 and 7). In contrast, the rotation of the alcohol (**2**) is altered to a similar extent by both organocuprates and methylmagnesium iodide (run 10).

$MeCH{=}C{=}CHC_6H_{13}$

(1)



(*R*)-(2)



(3)

In view of the known electron transfer ability of organocuprates[7] it might be expected that chiral allenes would be affected by these reagents. The reversible formation of an anion radical (**3**) from an allene and an organocuprate is conceivable, and in this species, rotation around the single bond is allowed thus giving equal probability for the formation of the two enantiomeric allenes when the electron is transferred back to the cuprate. This is identical to the mechanism that House proposed for the *cis* to *trans* isomerisation of certain $\alpha\beta$- unsaturated ketones[7] and it was also demonstrated that ketyls are formed reversibly from aromatic ketones and $LiCuMe_2$.[8] It appears that chiral allenes, like certain other types of compounds,[7] could be used as probes of anion radical intermediates.

It is noteworthy that the rate of racemization is increased by THF (*e.g.* run 2). This corresponds to known solvent effects on certain substitution reactions of organocuprates.[9]

Part of the ability of MeMgI to racemise the alcohol (**2**) must be a neighbouring-group effect from the alcoholate since the allene hydrocarbon (**1**) is much less affected by both MeMgI (run 7) and EtMgBr (run 6). It is known that Grignard reagents may exhibit single electron transfer (SET) capabilities with certain substrates and that this effect is strongly augmented by traces of transition metals, notably iron.[10] No precautions were taken to avoid such trace impurities in these Grignard reactions. It is possible that the presence of SET promoting agents in the Grignard reagent may have combined with an activation energy-lowering neighbouring-group effect to make the racemization of (**2**) unusually efficient.

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