Stereochemistry of Allenes

By T. E. DEVILLE, M. B. HURSTHOUSE, S. W. RUSSELL, and B. C. L. WEEDON*
(*Department of Chemistry, Queen Mary College, Mile End Road, London, E.*1)

WE recently reported the synthesis of a racemate of the allene (4).[1] Later Meinwald and Hendry[2] outlined an alternative route to this structure. These authors assumed that the lithium aluminium hydride reductions of the acetylenic intermediates (1 and 2, respectively) to give the initial allene (3) proceed with the *trans*-stereochemistry suggested by Borden and Corey[3] to account for the 1,3-di-t-butylallenes (8) produced on similar reduction of sulphonates of the alcohols (7). They therefore suggest that in our racemic ketone (m.p. 111°) and theirs (m.p. 95·5°), which may be polymorphs,[2] the allenic proton is *trans* to the C-5 hydroxy-group. However, an X-ray crystallographic analysis of the p-bromobenzoate (6) of our product shows that the C-5 hydroxy-group is *trans* to both other oxygen functions, *i.e.*, *cis* to the allenic hydrogen (Figure). Thus the stereochemistry of the reduction of (1) to (3) is the same as that observed in many S_N2 substitutions,[4] though the reduction may involve an organoaluminium intermediate. An overall *cis*-stereochemistry of the entering and leaving groups is also observed, apparently, in the conversion of (7) into (8), on treatment with lithium aluminium hydride in the presence of aluminium chloride.[3]

Crystals of the p-bromobenzoate (6) are monoclinic, spacegroup $P2_1/c$ with $a = 11{\cdot}84$, $b = 12{\cdot}98$, $c = 13{\cdot}60$ Å, $\beta = 113.0°$. $D_m = 1{\cdot}39$, $Z = 4$, $D_c = 1{\cdot}405$. The structure was determined by conventional techniques using *ca.* 1300 independent reflections collected on a General Electric XRD5 manual diffractometer with Cu-K_α radiation. R is currently 0·16. The structure found is shown in the Figure, which is a view down the c axis.

In $(CD_3)_2CO$, both our racemate (4) and its acetate (5) exhibit n.m.r. bands which are noticeably different from those reported previously for deuteriochloroform solutions.[1] The solvent shifts for the signals due to the allenic hydrogens are significantly larger than those for the C-9 and other methyls. The (optically active) degradation product (5) from fucoxanthin[5] exhibits the same n.m.r. bands and solvent shifts (Table) as our synthetic racemate (5), and cannot be separated from the latter on mixed t.l.c.† Samples of the allene (4) and its derivative (6) prepared from the "natural" acetate (5) also fail to separate from the corresponding racemates. We therefore conclude that the "natural" acetate has the same geometrical configuration as that now established for our racemate (5). This indicates

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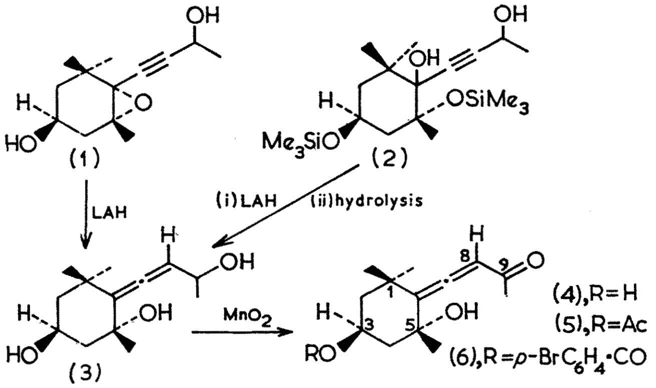
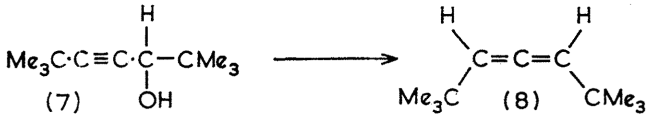
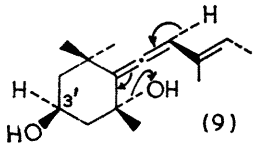
† Kieselgel HF_{254} using ethyl acetate–benzene, acetone–dichloromethane–petrol, ethanol–chloroform, or acetone–petrol as eluent.

that the allenic end groups in fucoxanthin, neoxanthin, and their derivatives, have the absolute stereochemistry shown in (9) since an *S*-configuration seems probable for the 3- and 3′-positions in these compounds.[5–7]

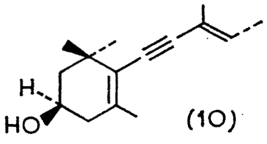




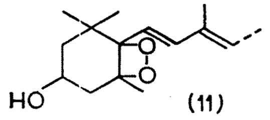
$$\underset{(7)}{\mathrm{Me_3C{\cdot}C{\equiv}C{\cdot}\overset{H}{\underset{OH}{C}}{-}CMe_3}} \longrightarrow \underset{(8)}{\overset{H\qquad\quad H}{\underset{Me_3C\qquad CMe_3}{C{=}C{=}C}}}$$



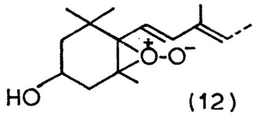
(9)



(10)



(11)



(12)

Natural allenic carotenoids probably result from oxidation of zeaxanthin and related pigments, and intermediates such as (11) or (12) may well be involved. A subsequent elimination of the elements of water from the allenes, as indicated in (9), would then account for the formation of the acetylenic end groups (10) in, for example, alloxanthin which is known to have the same absolute configuration at C-3 and C-3′ as fucoxanthin and neoxanthin.[5,6,8]

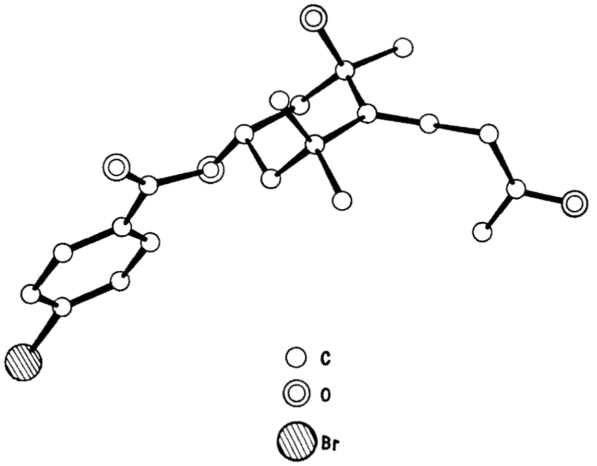


FIGURE. *View down the* c *axis of one enantiomer present in the unit cell of the racemate* (6).

Some allenes formally related to (4) have been reported as minor products from the photosensitised oxidation of simple derivatives of β-ionone. Their formation has been attributed to a concerted attack by singlet oxygen at C-5 and the proton at C-7. A *cis*-arrangement of the oxygen function at C-5 and the allenic hydrogen has therefore been suggested for these compounds.[9]

Solvent shifts in n.m.r. spectra of allenic ketones

	C-8 allenic hydrogen			C-9 methyl group		
	τ^a	τ^b	$\Delta\tau$	τ^a	τ^b	$\Delta\tau$
Racemate (4)	4·33	4·17	0·16	7·87	7·83	0·04
Racemate (5)	4·26	4·18	0·08	7·86	7·82	0·04
"Natural" (5)	4·25	4·15	0·10	7·85	7·83	0·02

[a] In $CD_3{\cdot}CO{\cdot}CD_3$. [b] In $CDCl_3$.

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