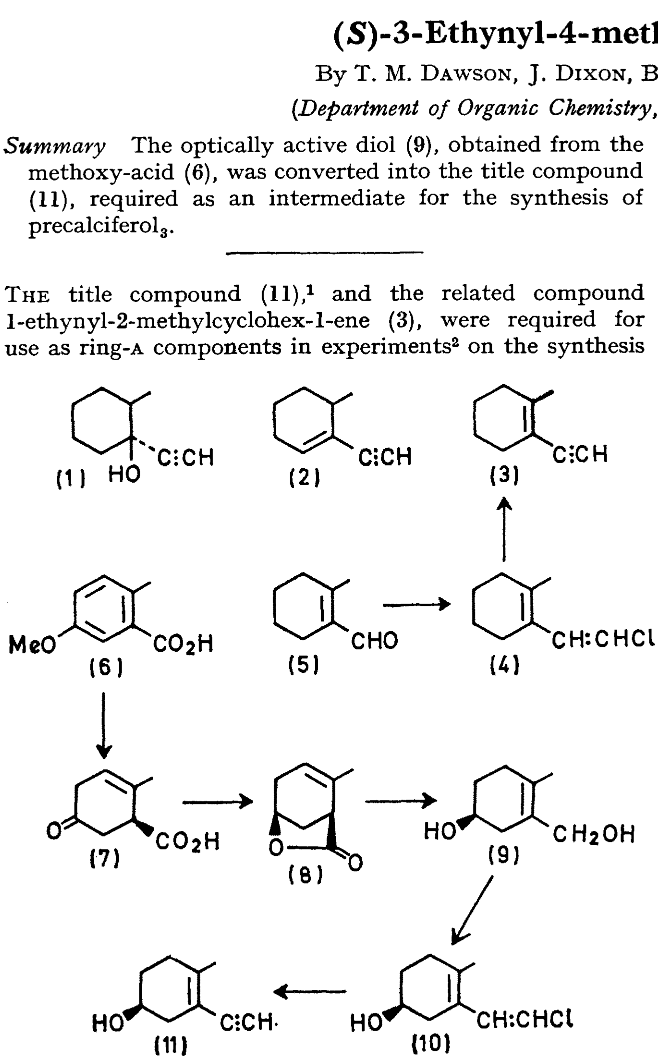
(*S*)-3-Ethynyl-4-methylcyclohex-3-en-1-ol

By T. M. DAWSON, J. DIXON, B. LYTHGOE,* and I. A. SIDDIQUI

(*Department of Organic Chemistry, The University, Leeds* LS2 9JT)

Summary The optically active diol (9), obtained from the methoxy-acid (6), was converted into the title compound (11), required as an intermediate for the synthesis of precalciferol$_3$.

THE title compound (11),[1] and the related compound 1-ethynyl-2-methylcyclohex-1-ene (3), were required for use as ring-A components in experiments[2] on the synthesis of precalciferol$_3$. Hitherto, the en-yne (3) has been available[3] only as a mixture with one of its double bond isomers; for example, a mixture of the en-ynes (3) and *r*-(2)[1] is obtained by dehydration of the tertiary alcohol *r*-(1). For our purposes, homogeneous en-yne (3) was necessary; we have now obtained it from the aldehyde[4] (5). Reaction with chloromethylenetriphenylphosphorane[5] gave a mixture of the *cis*- and *trans*-isomers of the ω-chlorodiene (4), which was dehydrochlorinated with butyl-lithium. The en-yne (3) showed no vinyl proton signal and had λ_{max} 230 nm (ε 11,500 in ethanol).



For the preparation of the optically active en-yne (11) the optically active diol[6] (9) was required. Existing methods were not efficient enough to provide it on the required scale, so an improved route was developed. Careful acidic hydrolysis of the product of reduction of the methoxy-acid (6) with lithium and ammonia gave the keto-acid *r*-(7), which was resolved with quinine. The enantiomer (7), m.p. 101°, $[\alpha]_D^{25}$ −385° (chloroform), was reduced with sodium borohydride to give the (−)-lactone (8), which was converted, by methods[6] previously applied to the racemate, into the optically active diol (9). The corresponding aldehyde, obtained by oxidation with manganese dioxide in acetone, $[\alpha]_D^{25}$ −64° (chloroform) (semicarbazone, m.p. 205—207°, decomp.) was converted into a mixture of the *cis*-form and *trans*-form (major product; *p*-nitrobenzoate, m.p. 117—118°) of the ω-chloro-diene (10). Dehydrochlorination of the mixture with sodamide in ammonia gave the conjugated en-yne (11), m.p. 34·5°, $[\alpha]_D^{25}$ −65° (chloroform), λ_{max} 230·5 nm (ε 11,400 in ethanol). The overall yield was 4·2% from the readily available methoxy-acid (6).

We thank J. Tideswell for technical assistance, and the S.R.C. for Studentships (T.M.D. and J.D.).

(*Received, June* 26*th*, 1970; *Com.* 1014.)

---

[1] Structures capable of optical activity represent absolute configurations; racemates are denoted by the prefix *r*-, so that, *e.g.*, *r*-(2) means the racemate corresponding to structure (2).

[2] J. Dixon, P. S. Littlewood, B. Lythgoe, and A. K. Saksena, following Communication.

[3] Sir I. Heilbron, E. R. H. Jones, D. G. Lewis, and B. C. L. Weedon, *J. Chem. Soc.*, 1949, 2023; H. H. Inhoffen, K. Weissermel, G. Quinkert, and D. Bartling, *Chem. Ber.*, 1956, **89**, 853; J. L. M. A. Schlatmann and E. Havinga, *Rec. Trav. chim.*, 1969, **80**, 1101.

[4] A. S. Dreiding and S. N. Nickel, *J. Amer. Chem. Soc.*, 1954, **76**, 3965.

[5] G. Wittig and M. Schlosser, *Chem. Ber.*, 1961, **94**, 1373; G. Köbrich, H. Trapp, K. Flory, and W. Drischel, *ibid.*, 1966, **99**, 689.

[6] P. R. Bruck, R. D. Clark, R. S. Davidson, W. H. H. Günther, P. S. Littlewood, and B. Lythgoe, *J. Chem. Soc.* (*C*), 1967, 2529.