Calciferol and its Relatives. Part XII.[1,2] (*S*)-3-Ethynyl-4-methylcyclohex-3-en-1-ol

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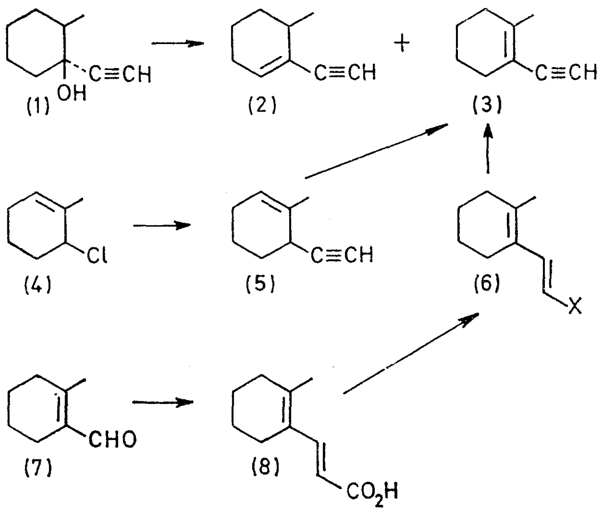
1-Ethynyl-2-methylcyclohex-1-ene, hitherto obtained only as a mixture with one of its double-bond isomers, is obtained pure by dehydrohalogenation of ω-halogenodienes such as 1-(2-chlorovinyl)-2-methylcyclohexene (6; X = Cl). The optically active 5-hydroxy-2-methylcyclohex-1-enecarbaldehyde (10) reacts with chloromethylenetriphenylphosphorane giving mixed *cis*- and *trans*-ω-chloro-dienes [*cf.* (11)], dehydrohalogenation of which gives the title compound (12), required for the synthesis of precalciferol$_3$.

For use in the synthesis[3] of precalciferol$_3$ we required the title compound (12),† which was destined to provide ring A and carbon atoms 6 and 7 of the previtamin. Experiments on its preparation are now reported.

The parent compound 1-ethynyl-2-methylcyclohex-1-ene (3) has been prepared several times in the past,[4] but always in admixture with one of its double-bond isomers. Thus, by dehydration of the appropriate isomer *rac*-(1) † of 1-ethynyl-2-methylcyclohexanol with phosphoryl chloride and pyridine, a mixture is obtained[5] containing *ca.* 75% of the desired compound (3) and 25% of the isomer *rac*-(2). We have separated these two isomers by preparative g.l.c. The isomer (3), $\lambda_{max.}$ 230 nm. (ε 11,500), in its n.m.r. spectrum, showed no vinyl proton signal but singlets corresponding to one ethynyl proton (τ 7·0) and three allylic methyl protons (τ 8·12). In contrast, the isomer *rac*-(2) showed signals for one vinyl proton (τ 3·9 multiplet), one ethynyl proton (τ 7·33, singlet), and three methyl protons (τ 8·85, doublet, J 6·5 Hz).

As this method is not suitable for preparing hydroxy-derivatives of the enyne (3), other routes which might lead to the homogeneous parent compound were explored. The unconjugated isomer *rac*-(5) was obtained by treatment of 6-chloro-1-methylcyclohexene *rac*-(4) with ethynylmagnesium bromide and copper(I) chloride[6] in tetrahydrofuran. Treatment of compound *rac*-(5) with sodamide in liquid ammonia moved the double bond into conjugation with the ethynyl group, and gave in high yield the enyne (3); it was free (g.l.c.; n.m.r. spectrum) from the starting material. In further experiments of this kind, however, formation of conjugated material was incomplete, although extensive, and although we were later able to repeat the original successful experiment, the conditions necessary could not be defined.

A satisfactory method was found instead in the dehydrohalogenation of ω-halogeno-dienes such as (6; X = Br or Cl) with base. In order to obtain the ω-bromo-diene, the aldehyde[7] (7) was converted, by treatment with ethoxycarbonylmethylenetriphenylphosphorane, followed by hydrolysis, into the *trans*-dienoic acid (8), $\lambda_{max.}$ 279·5 nm. (ε 22,500). The dry sodium salt reacted in dimethylformamide[8] with 1 equiv. of bromine, giving the bromo-diene (6; X = Br) in *ca.* 40% yield. Its conjugated nature was apparent from its u.v. spectrum [$\lambda_{max.}$ 253·5 nm. (ε 19,800)], and its *trans*-geometry from the coupling constant (J 13 Hz) of its two vinyl protons.



A more efficient route to halogeno-dienes of type (6) was found in the reaction of the aldehyde (7) with chloromethylenetriphenylphosphorane, generated by use of piperidinolithium[9] as the base. This gave a mixture (*ca.* 3 : 1) of the *trans*-ω-chloro-diene (6; X = Cl) and its *cis*-isomer; the n.m.r. spectrum of the former showed vinyl protons with J 13 Hz and that of the latter showed J 8 Hz. Dehydrohalogenation of the

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† Structural formulae in this paper represent absolute configurations. The prefix *rac* denotes a racemate; thus *rac*-(1) means the racemate corresponding to the structure (1).

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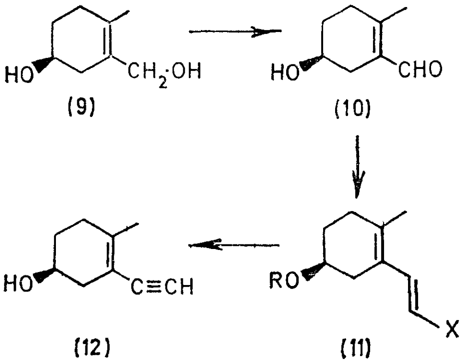
[9] G. Wittig and M. Schlosser, quoted by G. Köbrich, H. Trapp, K. Flory, and W. Drischel, *Chem. Ber.*, 1966, **99**, 689.

mixture with n-butyl-lithium gave the homogeneous enyne (3) in over 40% yield from the aldehyde (7). The enyne (3) was also obtained by dehydrohalogenation of the ω-bromo-diene (6; X = Br) with sodamide in ammonia, but the overall yield was then much lower [*ca.* 10% from the aldehyde (7)].



These methods were applied to the racemic hydroxy-aldehyde *rac*-(10), which was obtained by treatment of the corresponding diol[10] *rac*-(9) with manganese dioxide in acetone. The *trans*-dienoic acid *rac*-(11); R = H, X = CO_2H) was acetylated and converted into the *trans*-ω-bromo-diene *rac*-(11; R = Ac, X = Br). Treatment with sodamide in liquid ammonia, followed by deacetylation, gave the racemic hydroxy-acetylene *rac*-(12). More efficiently, the aldehyde *rac*-(9) was converted, by treatment with a large excess of chloromethylenetriphenylphosphorane, into a mixture of the *trans*-ω-chloro-diene *rac*-(11; R = H; X = Cl) (major product) and its *cis*-isomer. Dehydrochlorination of the mixture with sodamide in ammonia gave the crystalline hydroxy-enyne *rac*-(12), $\lambda_{max.}$ 231 nm. (ε 11,000), in *ca.* 50% yield from the aldehyde *rac*-(10).

Application of similar methods to the optically active diol[1] (9) provided in turn the (—)-aldehyde (10), and then, in over 30% overall yield, the crystalline enyne (12), $[\alpha]_D^{35}$ —65° (in $CHCl_3$).

EXPERIMENTAL

Light absorption data refer to solutions in ethanol unless otherwise stated. N.m.r. data refer to solutions in deuteriochloroform.

Separation of 1-*Ethynyl*-6-*methylcyclohexene* rac-(2) *and* 1-*Ethynyl*-2-*methylcyclohexene* (3).—A Varian Aerograph (series 1525) preparative g.l.c. apparatus was used, with a 20 ft. 18% dilauryl phthalate column at 100° (injector temperature 193°; collector temperature 82°). A mixture[5] of the enynes *rac*-(2) (*ca.* 10%) and (3) (*ca.* 90%) was separated. The major fraction consisting of the *isomer* (3) (Found: M^+ 120·0935. C_9H_{12} requires 120·0938) had $\lambda_{max.}$ 230 (ε 12,000), 225sh, and 245sh nm., $\nu_{max.}$ (film) 3350s, 2100s, and 1640m cm.$^{-1}$. The minor fraction, *isomer rac*-(2) (Found: M^+ 120·0935) had $\lambda_{max.}$ 225 nm. (ε 11,000), $\nu_{max.}$ (film) 3375s, 2100m, and 1630m cm.$^{-1}$.

6-*Ethynyl*-1-*methylcyclohexene* rac-(5).—Thionyl chloride (90 c.c.) was added slowly to 2-methylcyclohex-2-en-1-ol (27 g.) in dry benzene (1 l.); the solution was kept at 20° for 12 hr., and then washed thoroughly with water and with aqueous sodium hydrogen carbonate. Evaporation of the solvent and distillation of the residue gave the allylic chloride (17·4 g.), b.p. 70—72°/65 mm. It was added to N-ethynylmagnesium bromide in tetrahydrofuran (120 c.c.); anhydrous copper(I) chloride (665 mg.) was then added, and the mixture was stirred and heated under reflux for 3 hr. under nitrogen. After most of the solvent had been removed by distillation, saturated aqueous ammonium chloride (300 c.c) was added, the mixture was extracted with ether, and the extract was washed with water, dried, and evaporated. Distillation gave the enyne *rac*-(5) (5 g.) b.p. 66—70°/43 mm., which was purified by preparative g.l.c. over 15% polyethylene glycol adipate at 85° (flow rate 46 c.c./min.). It showed $\nu_{max.}$ (film) 3280m and 2140w cm.$^{-1}$; τ 4·62 (m, =CH–), 7·18 (m, >CH–C≡), and 8·12 (d, *J* 2·8 Hz, ≡CH).

Isomerisation of the Unconjugated Enyne rac-(5).—The enyne (800 mg.) was stirred for 2 hr. at −45° under nitrogen with a suspension of sodamide [from sodium 1·15 g.)] in liquid ammonia (50 c.c.). Ammonium chloride (3·3 g.) was then added in portions, the ammonia was allowed to evaporate, water was added to the residue, and the mixture was extracted with ether. The extract was then washed, dried, and evaporated. The residual oil (743 mg.), dissolved in light petroleum (b.p. 30—40°), was filtered through neutral alumina (grade 2); evaporation gave an oil (700 mg.), $\lambda_{max.}$ (MeOH) 229 nm. (ε 10,000); the n.m.r. spectrum showed no vinyl proton signals, but signals characteristic of the conjugated enyne (3). G.l.c. showed a purity of *ca.* 95% and the absence of the enyne (5).

trans-2-*Methylcyclohex*-1-*eneacrylic Acid* (8).—2-Methylcyclohex-1-ene carbaldehyde (1·38 g.) and ethoxycarbonylmethylenetriphenylphosphorane (4·0 g.) were heated together under reflux in dry benzene (50 c.c.) under nitrogen for 16 hr. The solvent was removed under reduced pressure, and the residue was heated under reflux with aqueous methanolic 7% sodium hydroxide (30 c.c.) under nitrogen for 2 hr. The methanol was then removed under reduced pressure, and neutral materials were extracted with ether. Acidification of the aqueous phase with hydrochloric acid and recrystallisation of the product from acetone gave the *dienoic acid* (1·4 g.), m.p. 191—192° (Found: C, 71·75; H, 8·45. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%).

1-(trans-2-*Bromovinyl*)-2-*methylcyclohexene* (6; X = Br). —The dry sodium salt of the acid (8) (4·02 g.) and dry dimethylformamide (150 c.c.) were stirred together rapidly while bromine (3·4 g.) in dimethylformamide (27·5 c.c.) was added dropwise. The product was isolated by dilution with water and extraction with ether; it was triturated with light petroleum (b.p. 60—80°) which left undissolved material, crystallisation of which gave back the acid (8) (0·75 g.). The soluble material was purified by filtration of the solution through silica gel and evaporation of the solvent. The resultant oil (1·29 g.) was shown by g.l.c. to be over 90% pure, but satisfactory analytical figures could not be obtained. This material, $\lambda_{max.}$ 253·3 nm. (ε 19,800), showed coupled n.m.r. doublets (*J* 13 Hz) centred on τ 3·92 and 2·90 (vinyl protons).

For dehydrobromination, a portion (600 mg.) was added to a stirred suspension of sodamide [from sodium (1 g.)] in liquid ammonia (75 c.c.). After 2 hr. stirring at −40°,

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ammonium chloride (3 g.) was added, the ammonia was allowed to evaporate, and the product was isolated by addition of water and ether. Evaporation of the dried ether extract gave an oil (200 mg.), $\lambda_{\text{max.}}$ 231 nm. (ε 9100). The i.r. spectrum of this sample of the enyne (3) was identical with that of material obtained by isomerisation of the enyne (5).

1-(trans-2-*Chlorovinyl*)-2-*methylcyclohexene* (6; X = Cl) *and its* cis-*Isomer*.—To a stirred suspension of chloromethyltriphenylphosphonium chloride (9·72 g.) in dry ether (50 c.c.) containing piperidine (2·38 g.), 1·21M-butyl-lithium (23·15 c.c.) was added dropwise under nitrogen during 30 min.; stirring was continued for a further 1 hr. A solution of 2-methylcyclohex-1-enecarbaldehyde (2·91 g.) in dry ether (15 c.c.) and benzene (15 c.c.) was then added, and the mixture was stirred and heated under reflux under nitrogen for 12 hr., then cooled and filtered. The filtrate was washed with dilute hydrochloric acid and with water, dried, and evaporated, and the residue was distilled. The product, an oil (2·18 g.), b.p. 88—94°/20 mm. showed two components on g.l.c. (polyethylene glycol adipate at 102°; flow rate 75 c.c./min.); main component (75%) retention time 14·5 min.; minor component (25%) 7 min. The mixture showed $\lambda_{\text{max.}}$ 249 nm. (ε 16,600). The n.m.r. spectrum showed coupled doublets (*J* 13 Hz) near τ 3·10 and 4·0 due to the major, *trans*-isomer (6; X = Cl), and also coupled doublets (*J* 8 Hz) near τ 3·70 and 4·07, due to the *cis*-isomer.

A portion (1·71 g.) in dry ether (30 c.c.) under nitrogen was stirred during the addition (1 hr.) of ethereal 1·2M-butyl-lithium; stirring was continued for a further 2 hr., after which the mixture was cooled in ice, and water (5 c.c.) was added. The ethereal layer was washed with dilute hydrochloric acid, aqueous sodium carbonate, and water, and then dried and evaporated. The 1-ethynyl-2-methylcyclohexene (730 mg.) had b.p. 49—51°/19 mm., $\lambda_{\text{max.}}$ 230 nm. (ε 12,000). It was homogeneous on g.l.c., and showed i.r. absorption identical with that of material obtained by the preparative g.l.c. separation of the isomers *rac*-(2) and (3).

5-*Hydroxy*-2-*methylcyclohex*-1-*enecarbaldehydes* rac-(10) *and* (10).—A solution of the crude racemic diol *rac*-(9)[10] (4 g.) in dry acetone (280 c.c.) was stirred vigorously for 4 hr. with active[11] manganese dioxide (24 g.). The solution was filtered and the residue was washed thoroughly with hot chloroform. The combined filtrate and washings were evaporated and the residue was chromatographed on silica gel (200 g.). Ethyl acetate–benzene (1 : 3) eluted small amounts of less polar material; ethyl acetate–benzene (2 : 3) then eluted the *aldehyde* rac-(10) as an oil (2·56 g.) which was homogeneous on g.l.c. Crystallisation from ether–pentane at −40° gave needles, m.p. *ca.* 20° (Found: M^+ 140·0827. $\mathrm{C_8H_{12}O_2}$ requires 140·0837); $\lambda_{\text{max.}}$ 248·5 nm. (ε 12,400); $\nu_{\text{max.}}$ (film) 3550s, 1670s, and 1640s cm.$^{-1}$; τ −0·16 (1H, s) and 7·84 (3H, s). The *semicarbazone* had m.p. 232° (decomp.) (from 90% ethanol) (Found: C, 54·5; H, 7·85; N, 21·45. $\mathrm{C_9H_{15}N_3O_2}$ requires C, 54·8; H, 7·7; N, 21·3%).

The optically active *aldehyde* (10) was similarly prepared from the diol (9) in 65% yield. It solidified on cooling and had m.p. *ca.* 10°, $[\alpha]_D^{32}$ −64° (in $\mathrm{CHCl_3}$) (Found: M^+ 140·0835. $\mathrm{C_8H_{12}O_2}$ requires 140·0837). The *semicarbazone* formed needles (from 95% ethanol), m.p. 205—207° (decomp.) (Found: C, 55·25; H, 7·6; N, 21·5%).

5-*Hydroxy*-2-*methylcyclohex*-1-*eneacrylic Acid* rac-(11; X = $\mathrm{CO_2H}$).—The aldehyde *rac*-(10) (630 mg.) and ethoxycarbonylmethylenetriphenylphosphorane (1·7 g.) were heated together under reflux in dry benzene (25 c.c.) under nitrogen for 16 hr. The mixture was processed as described for the analogue (7); crystallisation of the product from methanol–benzene gave the racemic *dienoic acid* (410 mg.), m.p. 173° (Found: C, 66·0; H, 7·7. $\mathrm{C_{10}H_{14}O_3}$ requires C, 65·9; H, 7·7%). Treatment with acetic anhydride in pyridine gave the *acetate* as needles (from acetone), m.p. 160—161° (Found: C, 64·3; H, 7·5. $\mathrm{C_{12}H_{16}O_4}$ requires C, 64·3; H, 7·2%); $\lambda_{\text{max.}}$ 276 nm. (ε 22,900); $\nu_{\text{max.}}$ (Nujol) 2400–2800m, 1725s, 1675s, and 1603s cm.$^{-1}$; τ 2·13 (d, *J* 16 Hz) and 4·26 (d, *J* 16 Hz) (vinyl protons) and 4·92 (m, AcO·C*H*<).

4-*Acetoxy*-2-(trans-2-*bromovinyl*)-1-*methylcyclohexene* rac-(11; R = Ac, X = Br).—The anhydrous sodium salt of the acetoxy-dienoic acid [from the acid (6·5 g.)] in dry dimethylformamide (140 c.c.) was stirred during the slow addition of bromine (1·4 c.c.) in dry dimethylformamide (35 c.c.). Aqueous sodium carbonate was added and the solution was extracted with ether. The extract was washed, dried, and evaporated; chromatography of the residual oil on silica gel and elution with light petroleum (b.p. 40—60°) containing ether (5%) gave the bromo-diene (1·85 g.) as an oil, $\lambda_{\text{max.}}$ 251 nm. (ε 18,300); $\nu_{\text{max.}}$ (film) 1735 cm.$^{-1}$; τ 2·89 (d, *J* 13 Hz) and 3·90 (d, *J* 13 Hz) (vinyl protons) and 5·00 (m, AcO·C*H*<).

For dehydrobromination, the bromo-diene (500 mg.) in ether (10 c.c.) was stirred for 2 hr. at −40° with a suspension of sodamide [from sodium (1·5 g.)] in liquid ammonia (75 c.c.). Ammonium chloride (4·5 g.) was then added, the ammonia was allowed to evaporate, and the residue was treated with water and ether. The ether phase was washed, dried, and evaporated, and the residue was heated for 0·5 hr. under nitrogen with methanol (5 c.c.) containing aqueous 2N-sodium hydroxide (1 c.c.). Isolation in the usual manner gave the hydroxy-acetylene *rac*-(12) (198 mg.) as an oil, $\lambda_{\text{max.}}$ 229 nm. (ε 10,400); $\nu_{\text{max.}}$ (film) 3450m, 3350s, 2095w, and 1642w cm.$^{-1}$.

3-(trans-2-*Chlorovinyl*)-4-*methylcyclohex*-3-*enol* rac-(11; R = H, X = Cl) *and its Optically Active Analogue*.—1·1M-Butyl-lithium (58·6 c.c.) was added during 30 min. to a stirred suspension of chloromethyltriphenylphosphonium chloride (22·5 g.) in dry ether (150 c.c.) containing piperidine (5·7 g.) under nitrogen. After stirring had been continued for 1 hr., most of the solid had dissolved. A solution of the aldehyde *rac*-(10) (2·25 g.) in ether (25 c.c.) and benzene (25 c.c.) was added during 15 min., after which the mixture was stirred under reflux for 12 hr. and then cooled. After the addition of water (1 c.c.) the solution was filtered and the filtrate was washed with dilute hydrochloric acid and then with saturated brine. The residue left by removal of the solvents was chromatographed on silica gel (450 g.); the column was eluted first with ether–benzene (1 : 9). Ether–benzene (1 : 7) then eluted an oil (2·1 g.) which g.l.c. (on polyethylene glycol adipate at 148°) showed to contain three components. A portion of this material was separated by preparative g.l.c. on cyclohexanedimethanol succinate; the component (*ca.* 30%) with the lowest retention time was the *cis*-form of the chloro-diene *rac*-(11; R = H, X = Cl); $\lambda_{\text{max.}}$ 243 nm. (ε 8,200); τ 3·68 (d, *J* 8 Hz) and 4·01 (d, *J* 8 Hz) (vinyl protons) and 8·35 (3H, s)

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(Found: M^+ 172·0646 and 174·0624. $C_9H_{13}ClO$ requires 172·0654 and 174·0625). The second component (10%), $\lambda_{max.}$ 248 nm. (ε 4000), $\nu_{max.}$ (film) 3450, 1610, and 880 cm.$^{-1}$, showed only 1 vinyl proton, τ 3·59br (s) [and 8·36 (3H, s, Me)], and is regarded as the ωω-*dichloro-compound* [Found: M^+ 206·0262, 208·0232, 210·0213 (in ratio 9 : 6 : 1). $C_9H_{12}Cl_2O$ requires 206·0265, 208·0236, 210·0206]. The third component (60%) had $\lambda_{max.}$ 249·5 nm. (ε 20,000); τ 3·08 (1H, d, J 13 Hz) and 3·92 (1H, d, J 13 Hz) (vinyl protons) and 8·20 (3H, s) (Found: M^+ 172·061 and 174·0622. $C_9H_{13}ClO$ requires 172·0655 and 174·0625). It was the trans-*chloro-diene* rac-(11; R = H, X = Cl). The p-*nitrobenzoate* formed plates, m.p. 115—116° (from ethanol) (Found: C, 59·95; H, 5·2; Cl, 11·1; N, 4·55. $C_{16}H_{16}ClNO_4$ requires C, 59·7; H, 5·0; Cl, 11·0; N, 4·35%).

The use of the (−)-aldehyde (10) in a similar reaction gave a similar mixture of optically active *cis*- and *trans*-chloro-dienes in similar yield. The *trans*-chlorodiene was characterised as the *p*-nitrobenzoate, which formed pale yellow needles (from ethanol), m.p. 117—118° $[\alpha]_D^{32}$ +32·5° (in $CHCl_3$) (Found: C, 59·8; H, 5·2; Cl, 11·2; N, 4·8%).

3-*Ethynyl*-4-*methylcyclohex*-3-*en*-1-*ol and its Optically Active Form* (12).—To a stirred suspension of sodamide [from sodium (0·93 g.)] in liquid ammonia (750 c.c.), the mixture of racemic chloro-dienes (770 mg.) (prepared as already described) in dry ether (20 c.c.) was added during 15 min.; stirring was continued for 3 hr., and the mixture was then kept for 12 hr., after which solid ammonium chloride was added. The remaining ammonia was evaporated in a current of nitrogen, water was added, and the mixture was extracted with ether. The extract was washed with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, then dried and evaporated. Distillation at 75°/0·6 mm. gave the *hydroxy-acetylene* (446 mg.), which was homogeneous on t.l.c. and g.l.c. Recrystallisation from ether–pentane at −40° gave light- and air-sensitive plates, m.p. 42—43·5° (Found: C, 78·7; H, 8·7%; M^+, 136·0885. $C_9H_{12}O$ requires C, 79·4; H, 8·9%; M 136·0888); $\lambda_{max.}$ 231 (ε 11,000), 224sh, and 242sh nm.; $\nu_{max.}$ (Nujol) 3380s, 2100m, 1640w, and 1040s cm.$^{-1}$; τ 6·95 (1H, s, $\equiv$CH) and 8·08 (3H, s, (=C–CH_3). The p-*nitrobenzoate* formed pale yellow needles (from ethanol), m.p. 104—106·5° (Found: C, 66·7; H, 5·4; N, 4·75. $C_{16}H_{15}NO_4$ requires C, 67·4; H, 5·3; N, 4·9%).

The optically active *hydroxy-enyne*, similarly prepared, formed flakes (from ether–pentane at −40°), m.p. 33·5—34·5°, $[\alpha]_D^{35}$ −65° (in $CHCl_3$) (Found: C, 78·9; H, 8·9. $C_9H_{12}O$ requires C, 79·4; H, 8·9%). It was stored under nitrogen at −40° in the dark.

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