464. *Allenes. Part VI.* The Absolute Configuration of* 3,4,4-*Trimethylpent*-1-*yn*-3-*ol and* 1-*Chloro*-3,4,4-*trimethylpenta*-1,2-*diene*

By R. J. D. Evans and S. R. Landor

The absolute configuration of (—)-3,4,4-trimethylpent-1-yn-3-ol has been determined by oxidation to (*S*)-(+)-butyl-lactic acid which was asymmetrically synthesised from menthyl pyruvate and t-butylmagnesium chloride. Thionyl chloride under S_Ni' conditions gave (—)-1-chloro-3,4,4-trimethylpenta-1,2-diene, which therefore has the (*S*)-configuration.

THE first stereochemical correlation of an allene with a tetrahedral carbon atom was reported in 1959.[1] (+)- and (—)-3,4,4-Trimethylpent-1-yn-3-ol (I) were converted into (+)- and (—)-1-chloro-3,4,4-trimethylpenta-1,2-diene (II), respectively, by an essentially stereospecific method.[2]

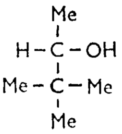
* Part V, P. D. Landor and S. R. Landor, *J.*, **1963**, 2707.

[1] Landor and Taylor-Smith, *Proc. Chem. Soc.*, **1959**, 154.

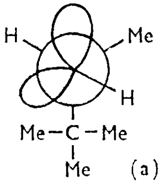
[2] Evans, Landor, and Taylor-Smith, *J.*, **1963**, 1506.

The absolute configuration of the allenic chloride can be deduced if the absolute configuration of the corresponding alcohol is first determined. A simple application of Brewster's theory [3] comparing the polarisabilities of substituents in pinacolyl alcohol and the acetylenic alcohol (I) predicts the (*S*) configuration for the (+)-alcohol.[4] It may be held that optical activity is not due to a second-order difference in polarisability of methyl and t-butyl,* as assumed in the simple interpretation, but to the conformational asymmetry either of the hydroxyl group or the cyclic form resulting from the interaction of hydroxyl and ethynyl groups.† The following arguments show clearly that all such asymmetry factors predict the same, *i.e.*, the (*S*)-configuration for the (+)-alcohol and that such an assignment is therefore sound.

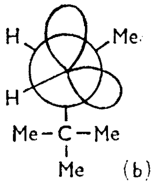
Newman projections (with oxygen in front and the asymmetric carbon atom eclipsed behind) give the following conformations for pinacolyl alcohol, in order of statistical weight (on the assumption that the lone-pair electrons are sterically larger than the hydrogen atom).



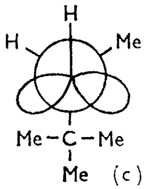
$\mathrm{H{-}C(Me)(OH){-}C(Me)_2{-}Me}$



(a)



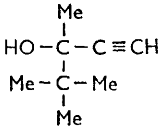
(b)



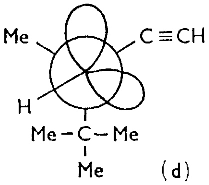
(c)

Clearly, the preferred conformation (a) will make the largest contribution to the rotation. From the order of polarisabilities of substituents (on the oxygen: lone pair > H and on the asymmetric carbon: Me > Bu^t > H) it follows that, numerically, the largest interaction is between lone pair and methyl and as it is positive in (a) the rotation of (*S*)-pinacolyl alcohol is predicted to be positive.

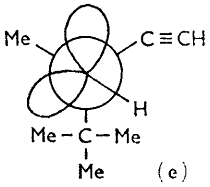
Similarly Newman projections (with oxygen in front and the asymmetric carbon atom eclipsed behind) give the following conformations for (*S*)-3,4,4-trimethylpent-1-yn-3-ol in order of statistical weight.



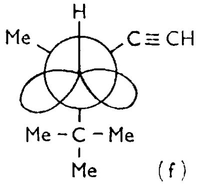
$\mathrm{HO{-}C(Me)(C{\equiv}CH){-}C(Me)_2{-}Me}$



(d)



(e)



(f)

Again the preferred conformation (d) will make the largest contribution. From the order of polarisabilities of substituents (on the oxygen: lone pair > H and on the asymmetric carbon: C≡CH > Me > Bu^t) it follows that, numerically, the largest interaction is between lone pair and the ethynyl, and as it is positive in (d) (*S*)-3,4,4-trimethylpent-1-yn-3-ol is predicted to be dextrorotatory.

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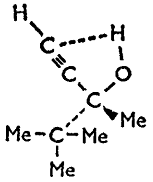
* From the refractivities (Bu > t-Bu) and the slight difference in hybridisation predicted for the carbon–carbon bond formed between either methyl or t-butyl and the asymmetric carbon atom it may be argued that polarisabilities are Me > t-Bu. It then follows that both (*S*)-pinacolyl alcohol and (*S*)-3,4,4-trimethylpent-1-yn-3-ol should be dextrorotatory.

† We thank Professor Eliel for drawing our attention to these points.

[3] Brewster, *J. Amer. Chem. Soc.*, 1959, **81**, 5475.

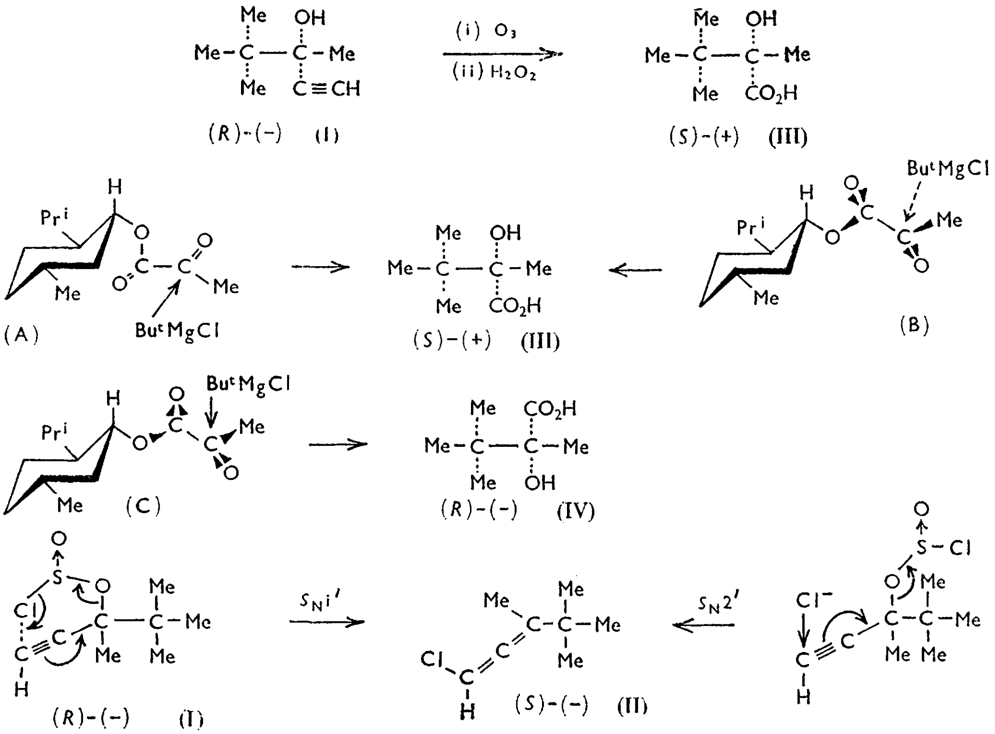
[4] Eliel, *Tetrahedron Letters*, 1960, No. 8, 16. The substituent with the lowest polarisability (H) is replaced by that with the highest polarisability (C≡CH). It has to be assumed that optical activity is due to a second order difference in polarisability of Me and t-Bu.

Lastly intramolecular hydrogen-bonding of the hydroxyl and the linear ethynyl group, although geometrically not favoured, is just possible. Consideration of such a cyclic system



(*S*)

still predicts a positive rotation for the (*S*)-alcohol (but cf.*). Thus, consideration of (*a*) atomic asymmetry based on second-order polarisability differences, (*b*) conformational asymmetry of the acyclic system, and (*c*) conformational asymmetry of the cyclic system all predict that (*S*)-3,4,4-trimethylpent-yn-3-ol will be dextrorotatory. This we have confirmed by the following method.†



The (—)-alcohol (I), $[\alpha]_D^{20}$ —0·73°, was converted by ozonolysis and oxidative hydrolysis with hydrogen peroxide into (+)-2-t-butyl-lactic acid (β-hydroxy-αββ-trimethylbutyric acid) (III) which crystallised as the hemihydrate, m. p. 67—69°, $[\alpha]_D^{20}$ +1·4°. Preliminary work had shown that both ozone [5a] and potassium permanganate [5b] oxidise

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* Considerations of atomic asymmetry predict that (*S*)-but-1-yn-3-ol should be lævorotatory but conformational asymmetry of the hydrogen-bonded cyclic form predict it to be dextrarotatory. As it has been shown (cf. Jones, Loder, and Whiting, *Proc. Chem. Soc.*, 1960, 180) that (*S*)-but-yn-3-ol is lævorotatory the cyclic form can make little contribution.

† See *Proc. Chem. Soc.*, 1962, 182, for a preliminary report of this work.

[5] (*a*) Favorskaya, *J. Gen. Chem. U.S.S.R.*, 1948, **18**, 52; (*b*) Lebedeva and Mishmina, *ibid.*, 1953, **23**, 592.

acemic 3,4,4-trimethylpent-1-yn-3-ol to racemic 2-t-butyl-lactic acid, ozonolysis giving somewhat better yields. The same melting point, 141°, has been reported in the literature[6] for the anhydrous acid and the hemihydrate and this is readily explained by the extraordinary behaviour of this acid when heated as observed under a microscope. The flat, laurel-leaf-shaped crystals of the hemihydrate change crystalline form without melting at 65° to oblong needles, which then " melt " at 99° the three-dimensional crystal pattern being destroyed. However, a two-dimensional pattern (possibly liquid crystals) persists until coalescence takes place at about 140°. The infrared spectra of the (+)- and (—)-acid hemihydrates in Nujol were identical, but differed considerably from that of the (±) acid hemihydrate in Nujol. However, in chloroform solution they were all identical. The configuration of 2-t-butyl-lactic acid was established by asymmetric synthesis (cf. Prelog, and earlier work by McKenzie [7]). Menthyl pyruvate, $[\alpha]_D^{20}$ —91·6° [7] and excess of t-butylmagnesium chloride gave (—)-menthyl 2-t-butyl-lactate, the best yields being obtained with tetrahydrofuran as solvent. The sterically hindered ester was only very slowly hydrolysed, and refluxing it with 35% methanolic potassium hydroxide for 96 hr. gave a 31% yield of t-butyl-lactic acid. The dextrorotatory crude acid was fractionally crystallised, yielding (+)-2-t-butyl-lactic acid as the hemihydrate, $[\alpha]_D^{20}$ +0·90, after most of the racemic acid had been removed. It still contained some racemic acid, and therefore showed two melting points, one at 65—70°, and the other at 99—100°. As all the starting materials are lævorotatory, the dextrorotary nature of the acid fractions must have been due solely to the acid and not any impurities. t-Butylmagnesium chloride attacks (—)-menthyl pyruvate in its various conformations predominantly from the least sterically hindered side. Considering the three staggered conformations (cf. Prelog [7]) as representing energy minima, excess of acid of the (*S*)-configuration (III) would be expected in the product, as this results from two of the rotational isomers including the preferred conformation (B), whereas the (*R*)-acid (IV) is only obtained from one isomer (C), and (+)-t-butyl-lactic acid therefore has the (*S*)-configuration.

The (+)-acid (III) was obtained from the (—)-alcohol (I) without involving the asymmetric centre, and this alcohol therefore has the (*R*)-configuration as predicted. This (—)-alcohol $[\alpha]_D^{20}$ —0·82°, has been converted into the (—)-diene (II), $[\alpha]_D^{20}$ —53·1° with thionyl chloride.[2] It was earlier concluded that the reaction proceeds principally by an S_Ni' mechanism (cf. ref. 2) and the (—)-1-chloro-3,4,4-trimethylpenta-1,2-diene (II) therefore has the (*S*)-configuration and the (+)-diene (II) has the (*R*)-configuration as predicted.

An attempt was made to confirm the absolute configuration of the alcohol (I) by applying Prelog's method, the addition of methylmagnesium bromide to the phenylglyoxalate of the alcohol (I). Great difficulty was experienced in preparing the latter compound from the sterically hindered alcohol (I).

EXPERIMENTAL

(±)-2-*t-Butyl-lactic Acid*.—(*a*) Ozonised oxygen was passed through a solution of (±)-3,4,4-trimethylpent-1-yn-3-ol (2·0 g., 0·016 mole) in chloroform (70 ml.) for 5 hr. at room temperature. The solution was then refluxed with hydrogen peroxide (20 ml.; 100-vol.) and 30% potassium hydroxide solution (60 ml.) for 1 hr. The aqueous layer was separated, acidified with 50% hydrochloric acid and extracted five times with ether. The ether extracts were combined, dried ($MgSO_4$), and evaporated, leaving the crude acid as a solid (1·24 g.). Crystallisation from light petroleum gave the pure (±)-*acid* (1·02 g., 41%) as flat oval crystals of the hemihydrate (Found: C, 53·9; H, 9·7%; Equiv., 156·3. $C_7H_{14}O_3,\frac{1}{2}H_2O$ requires C, 54·2; H, 9·7%; Equiv.,

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[6] Richards (*Ann. Chim. Phys.*, 1910, **21**, 323) obtained anhydrous (±)-2-t-butyl-lactic acid by sublimation and gave m. p. 141—142°; Favorskaya (*J. Gen. Chem. U.S.S.R.*, 1948, **18**, 52) obtained a hemihydrate, m. p. 141°.

[7] Prelog, Furlenmeyer, Dickel, and Keller, *Helv. Chim. Acta*, 1953, **36**, 308; McKenzie, *J.*, 1905, **87**, 1373.

155); $\nu_{max.}$ (in Nujol), 3200s br (OH), 1710s, (acid C=O), and 1390w, 1390w, 1360s, 1250s, and 1210m, cm.$^{-1}$ (all CMe_3). The hemihydrate sublimed at 65—70°, giving cubic crystals of the *anhydrous acid* (also obtained by warming the hemihydrate *in vacuo*) (Found: C, 57·6; H, 9·5%; Equiv., 146·3. $C_7H_{14}O_3$ requires C, 57·6; H, 9·6%; Equiv., 146); $\nu_{max.}$ (in Nujol) 3400sh (OH), 1730s (acid C=O), and 1390w, 1360s, 1250s, and 1210m, cm.$^{-1}$ (all CMe_3). The anhydrous acid melted at 99—100° but maintained a two-dimensional structure (a hexagonal array of honeycomb appearance), which coalesced to give a clear liquid only at 140°.

(*b*) An aqueous solution of potassium permanganate (7·9 g., 0·05 mole; in 250 ml. of water) was added dropwise to (±)-3,4,4-trimethylpent-1-yn-3-ol (3·15 g., 0·025 mole) stirred in water (20 ml.). After 30 min., the manganese dioxide was filtered off, residual alcohol removed with ether, and the aqueous solution evaporated to half its bulk. This was acidified with 50% hydrochloric acid and extracted five times with ether. The ether extracts were combined, dried ($MgSO_4$), and evaporated, giving the crude acid as a solid (0·74 g.). Crystallisation from light petroleum gave the pure (±)-acid hemihydrate (0·60 g., 15%). The flat, oval crystals sublimed, as before, at 65—70° to give the anhydrous form, m. p. 99—100°. The infrared spectrum was identical with that of the hemihydrate of the product of method (*a*).

(−)-2-*t-Butyl-lactic Acid*.—3,4,4-Trimethylpent-1-yn-3-ol (1·3 g., 0·01 mole), $[\alpha]_D^{20}$ +0·80°, was ozonised and then hydrolysed oxidatively with hydrogen peroxide, as described in method (*a*). The crude product was crystallised from light petroleum giving the pure (−)-*acid* (0·35 g., 22%), $[\alpha]_D^{20}$ −1·5° (*c* 9·830 in ethanol; *l* = 1 dm.; α = −0·15°) as needles of the hemihydrate (Found: C, 54·5; H, 9·6%; Equiv., 155·5. $C_7H_{14}O_3,\frac{1}{2}H_2O$ requires C, 54·2; H, 9·7%; Equiv., 155); $\nu_{max.}$ (in Nujol) 3400m (OH), 1970w br (chelation hydrogen-bonding), 1720s (acid C=O), and 1380s, 1360s, 1250m, and 1210m cm.$^{-1}$ (all CMe_3). In 5% chloroform solution, this (−)-acid and the (±)-acid gave identical infrared spectra; $\nu_{max.}$ 3600m, 3500m (both OH), and 1710s cm.$^{-1}$ (acid C=O); $\nu_{max.}$ was absent at 1970 and 1670 cm.$^{-1}$. The crystals melted at 67—69° but maintained a two-dimensional structure, which coalesced to give a clear liquid only at 140°. Drying the *hemihydrate in vacuo* for 15 hr. at 50° failed to remove water completely (Found: C, 56·9; H, 9·7%; Equiv., 147·2. $C_7H_{14}O_3$ requires C, 57·6; H, 9·6%; Equiv., 146). The sample became amorphous, but the m. p. and infrared spectrum were unchanged.

(+)-2-*t-Butyl-lactic Acid*.—(*a*) 3,4,4-Trimethylpent-1-yn-3-ol (1·2 g., 0·01 mole), $[\alpha]_D^{20}$ −0·73°, on ozonolysis and oxidative hydrolysis with hydrogen peroxide gave the crude acid (0·47 g.). Crystallisation from light petroleum gave the pure (+)-acid hemihydrate (0·38 g., 25%), $[\alpha]_D^{20}$ +1·4° (*c* 8·630 in ethanol; *l* = 1 dm.; α = +0·12°). The crystalline form, m. p., and the infrared spectrum were identical with those of the (−)acid hemihydrate.

(*b*) 3,4,4-Trimethylpent-1-yn-3-ol (3·15 g., 0·025 mole), $[\alpha]_D^{20}$ −0·73°, was oxidised with potassium permanganate (8·0 g., 0·05 mole) in aqueous soution, as in method (*b*) for the preparation of the (±)-acid. The product was crystallised, giving the pure (+)-acid hemihydrate (0·16 g., 4·4%), $[\alpha]_D^{20}$ +1·5° (*c* 4·070 in ethanol; *l* = 1 dm.; α = 0·03°). The crystalline form, m. p. and infrared spectrum were identical with those of the (+)-acid hemihydrate from method (*a*).

(±)-2-*t-Butyl-lactic Acid from the* (+)- *and* (−)-*Isomers*.—A mixture of equal quantities of the (+) and (−)-2-t-butyl-lactic acid (0·04 g.), $[\alpha]_D^{20}$ +1·5 and −1·5°, respectively, was crystallised from light petroleum. The crystal form, m. p. (99—100°), and infrared spectrum of the product were identical with those of the samples of (±)-2-t-butyl-lactic acid hemihydrate produced by oxidation of the (±)-alcohol.

(−)-*Menthyl Pyruvate*.—An intermittent stream of dry hydrogen chloride was passed through a solution of pyruvic acid (82 g., 0·93 mole) and (−)-menthol {132 g., 0·83 mole, $[\alpha]_D^{20}$ −50·1° (ethanol)} in dry benzene (400 ml.), refluxed for 8 hr. in a Dean and Stark apparatus.

The products were take up in ether, washed thoroughly with aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). Solvents and residual menthol (b. p. 80—122°/8 mm.) were removed by distillation, and finally two fractions were collected: (i) b. p. 129—131°/8 mm. (3·2 g., 4%), d_4^{20} 0·9473, $[\alpha]_D^{20}$ −70·94°; $\nu_{max.}$ 3550w and 3400w cm.$^{-1}$ (both OH), indicating some residual menthol; (ii) b. p. 132—134°/8 mm. (85·1 g., 40%), d_4^{20} 0·9841, $[\alpha]_D^{20}$ −91·58°; $\nu_{max.}$ 1740vs (α-keto C=O) and 1720vs cm.$^{-1}$ (ester C=O). This fraction was free from menthol, as shown by the absence of $\nu_{max.}$ at 3600—3300 cm.$^{-1}$ (OH).

Other experiments gave menthyl pyruvate, $[\alpha]_D^{20}$ −89·98 and −87·47° (d_4^{20} 0·9851 and 0·9848, respectively), containing traces of menthol, as shown by $\nu_{max.}$ 3550vw and 3400w cm.$^{-1}$ (both OH).

(−)-*Menthyl* 2-*t-Butyl-lactate*.—(*a*) A solution of (−)-menthyl pyruvate (37·5 g., 0·166 mole), $[\alpha]_D^{20}$ −91·58° in dry tetrahydrofuran (200 ml.) was added to a stirred solution of t-butylmagnesium chloride, prepared from magnesium (7·2 g., 0·3 g.-atom), iodine (0·1 g.), and t-butyl chloride (27·8 g., 0·3 mole) in dry tetrahydrofuran (200 ml.). After 1½ hr. at room temperature, the mixture was refluxed for 2 hr. The complex was decomposed with dilute hydrochloric acid and the products extracted with ether, washed with aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). After removal of solvents, distillation gave three fractions: (i) b. p. 76—79°/4·0 × 10^{-2} mm. (3·0 g.), d_4^{20} 0·9646, $[\alpha]_D^{20}$ −74·33°, mainly recovered menthyl pyruvate, as shown by $\nu_{max.}$ 3400m (OH) and 1740vs cm.$^{-1}$ (α-keto C=O), and formation of an orange precipitate with 2,4-dinitrophenylhydrazine; (ii) b. p. 79—92°/4·0 × 10^{-2} mm. (4·0 g., 9%), d_4^{20} 0·9721, $[\alpha]_D^{20}$ −61·40°, mainly the lactate, contaminated with some menthyl pyruvate, as shown by $\nu_{max.}$ 3400s (OH) and 1740m cm.$^{-1}$ (α-keto C=O), and the formation of a slight orange precipitate with 2,4-dinitrophenylhydrazine; (iii) b. p. 94—96°/4·0 × 10^{-2} mm. (22·2 g., 26%), d_4^{20} 0·9746, $[\alpha]_D^{20}$ −53·24°; $\nu_{max.}$ 3400s (OH), 1710vs (ester C=O), and 1375m, 1360s, 1250s, and 1210s cm.$^{-1}$ (all CMe_3). No orange precipitate was obtained with 2,4-dinitrophenylhydrazine and there was no peak at 1740 cm.$^{-1}$ (α-keto C=O). This fraction was therefore free from menthyl pyruvate. A syrupy residue (8·5 g.), $\nu_{max.}$ 1785vs cm.$^{-1}$ (possibly lactone C=O) remained after the distillation.

(*b*) A solution of (−)-menthyl pyruvate (37·5 g., 0·166 mole), $[\alpha]_D^{20}$ −91·58°, in dry ether (200 ml.) was added to a solution of t-butylmagnesium chloride [prepared from magnesium (9·6 g., 0·4 g.-atom), iodine (0·1 g.) and t-butyl chloride (37·0 g., 0·4 mole) in dry ether (300 ml.)]. After 2 hr. at room temperature, the mixture was refluxed for 2 hr., and the products were extracted as before and distilled under high vacuum. The fraction boiling at 103—108°/6 × 10^{-3} mm. was collected (10·3 g., 21%), d_4^{20} 0·9744, $[\alpha]_D^{20}$ −53·81°. This gave no precipitate with 2,4-dinitrophenylhydrazine and its spectrum showed no band at 1740 cm.$^{-1}$ (α-keto C=O) indicating that the lactate was free from menthyl pyruvate.

(+)-2-*t-Butyl-lactic Acid*.—(−)-Menthyl 2-t-butyl-lactate (11·2 g., 0·039 mole), $[\alpha]_D^{20}$ −53·24°, was refluxed with potassium hydroxide (20 g.) and 70% ethanol (60 ml.) for 96 hr. Unsaponified matter was then removed by ether extraction, and the alkaline solution concentrated to half volume and acidified with hydrochloric acid. The 2-t-butyl-lactic acid was isolated by multiple ether extractions, the ethereal solution dried ($MgSO_4$), and the solvent removed by slow evaporation, giving four crops of the crystalline acid (see Table). Each crop was crystallised from light petroleum, the third crop being subdivided further by fractional crystallisation during this process (total weights of acid, 1·78 g.; 31% max. $[\alpha]_0^{20}$ + 0·9°).

The crops were mixtures of the (+)- and (±)-*acid hemihydrates* (Found, for main crop: C, 54·5; H, 9·6%; Equiv., 154·8. $C_7H_{14}O_3,\frac{1}{2}H_2O$ requires C, 54·2; H, 9·7%; Equiv., 155). The infrared spectra were identical with that of the (±)-acid hemihydrate obtained by oxidation of the alcohol except for that of the crop having m. p. 67—70° max $[\alpha]_0^{20}$ + 0·9° which showed characteristics of the optically active acid hemihydrate, *i.e.*, $\nu_{max.}$ 3400m, 3200m (both OH), and 1970 (broad)vw cm.$^{-1}$ (chelation hydrogen-bonding).

Reaction between (+)-3,4,4-*Trimethylpent*-1-*yn*-3-*ol and Phenylglyoxylyl Chloride*.—(*a*) A solution of 3,4,4-trimethylpent-1-yn-3-ol (4·5 g., 0·036 mole) in dry ether (50 ml.) was added slowly at 0° to a stirred solution of ethylmagnesium bromide, prepared from magnesium (0·9 g., 0·036 g.-atom), iodine (0·1 g.), ethyl bromide (3·0 g., 0·036 mole), and dry ether (150 ml.). The mixture was refluxed for 2 hr., then cooled to 0°. A solution of phenylglyoxylyl chloride (6·1 g., 0·036 mole) [8] in dry ether (50 ml.) was added dropwise, with stirring. The suspension was refluxed for 2 hr., the complex decomposed with dilute hydrochloric acid and the products extracted with ether. The ethereal solution was washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). Evaporation of the solvent yielded a solid, which on crystallisation from light petroleum gave benzoic acid (1·8 g.), m. p. 122°. The infrared spectra (in Nujol) of this product and of authentic benzoic acid were identical.

(*b*) A solution of 3,4,4-trimethylpent-1-yn-3-ol (3·8 g., 0·03 mole) in dry tetrahydrofuran (50 ml.) was added to a stirred solution of ethylmagnesium bromide, prepared from magnesium (0·75 g., 0·03 g.-atom), iodine (0·1 g.), ethyl bromide (3·3 g., 0·03 mole) and dry tetrahydrofuran (150 ml.). The mixture was refluxed for 2 hr., then cooled to 0°, and a solution of phenylglyoxylyl chloride (5·0 g., 0·03 mole) in tetrahydrofuran (50 ml.) was added. The solution was

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[8] Kharasch and Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 329) gave b. p. 91°/9·5 mm., yield 75%.

refluxed for 2 hr., then the products worked-up as before and crystallised, giving 3,4,4-trimethylpent-1-yn-3-yl benzoate (2·8 g., 40%) as hexagonal plates, m. p. 91—92°, insoluble in sodium hydroxide solution (Found: C, 78·1; H, 7·6. $C_{15}H_{18}O_2$ requires C, 78·1; H, 7·8%); $\nu_{max.}$ (in Nujol) 3230m (C≡C), 2100w (C≡CH), 1730vs (ester C=O), 1600m, 1580w (aromatic C=C), 1390m, 1360s, 1260s, and 1220m cm.$^{-1}$ (all CMe_3).

(*c*) A solution of phenylglyoxylyl chloride (6·0 g., 0·036 mole) in dry benzene (15 ml.) was added slowly to a stirred solution of 3,4,4-trimethylpent-1-yn-3-ol (4·5 g., 0·036 mole) in a mixture of dry benzene (15 ml.) and dry pyridine (10 ml.). The mixture was stirred for a further 4 hr., and left for 5 days. Water (50 ml.) was then added and the products extracted with ether, washed with dilute acetic acid, then with water, and dried ($MgSO_4$). Evaporation of the ether followed by crystallisation of the crude product gave benzoic acid (2·7 g.), m. p. 122°.

(*d*) A solution of phenylglyoxylyl chloride (6·7 g., 0·04 mole) in dry benzene (20 ml.) was added slowly to a stirred solution of 3,4,4-trimethylpent-1-yn-3-ol (3·8 g., 0·03 mole) in a mixture of dry benzene (15 ml.) and dry pyridine (10 ml.). The mixture was stirred for 2 hr. and left overnight. The products were worked up in the same way as in method (*c*) and crystallised, giving needle-like crystals of a nitrogenous compound (2·2 g.), m. p. 179° (Found: C, 73·8; H, 4·9; N, 8·5%; *M*, 296); $\nu_{max.}$ (in Nujol) 3350m (bonded N–H), 2320w (hydrogen bonding), and 1670s cm.$^{-1}$ (possibly amide).

(*e*) As for (*d*) except that the solution of the reactants was refluxed; the product was a syrupy compound (0·9 g.); $\nu_{max.}$ 1780vs cm.$^{-1}$ (probably lactone C=O).

(*f*) A Schotten–Baumann esterification was attempted by using 3,4,4-trimethylpent-1-yn-3-ol (1·6 g., 0·015 mole) and phenylglyoxylyl chloride (5·0 g., 0·03 mole). Only the unchanged alcohol and benzoic acid, m. p. 122°, were recovered.

Reaction between (±)-3,4,4-*Trimethylpent*-1-*yn*-3-*ol and Benzoyl Chloride.*—A Schotten–Baumann esterification was attempted by using 3,4,4-trimethylpent-1-yn-3-ol (1·6 g., 0·015 mole) and benzoyl chloride (4·2 g., 0·03 mole). Only the unchanged alcohol and benzoic acid, m. p. 122° (identified by its infrared spectrum), were isolated.

(±)-*Phenylglyoxylate of* 3,4,4-*Trimethylpent*-1-*yn*-3-*ol.*—An intermittent stream of dry hydrogen chloride was passed through a solution of 3,4,4-trimethylpent-1-yn-3-ol (8·0 g., 0·063 mole) and phenylglyoxylic acid (14·0 g., 0·083 mole) in dry benzene (150 ml.), refluxed for 12 hr. in a Dean and Stark apparatus (the water being removed). The products were taken up in ether, washed with aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). Removal of solvents by evaporation under reduced pressure gave a solid, which, on recrystallisation from light petroleum yielded needle-like crystals (3·0 g.), m. p. 143°, believed to be the phenylglyoxylate (Found: C, 74·4; H, 7·1%; *M*, 235. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%; *M*, 258); $\nu_{max.}$ (in Nujol) 3400m (C≡C), 2320vw, 1790vs (C=O) and 1620w cm.$^{-1}$.

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