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SYNTHESIS OF COMPOUNDS WITH JUVENILE HORMONE ACTIVITY—XI[1]

NEW ROUTES FOR THE STEREO-CONTROLLED CONSTRUCTION OF THE TRISUBSTITUTED *CIS* DOUBLE BOND PORTION OF THE *CECROPIA* JUVENILE HORMONES

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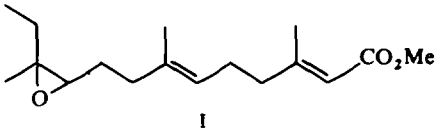
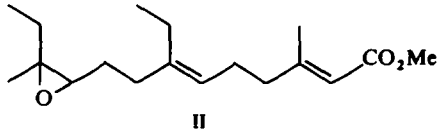
Abstract— 3-Methylpent-2-*cis*-enyl bromide (XI) and 4-methylhex-3-*cis*-enyl bromide (XIX), the key starting materials for the syntheses of the *Cecropia* juvenile hormones, were synthesized stereospecifically or stereoselectively.

TWO APPROACHES are possible for the synthesis of the *Cecropia* juvenile hormones (I and II): one begins with the hydrocarbon end of the molecule and builds towards the ester, and whilst the other begins at the conjugated ester portion.[2] Several groups utilized the former approach in their non-stereoselective syntheses.[3–10] Separation of stereoisomers, however, was found difficult, making a stereo-controlled syntheses far more desirable. Two stereospecific syntheses of the *Cecropia* C_{18}-juvenile hormone



I



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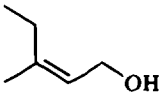

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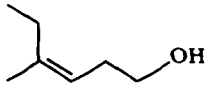

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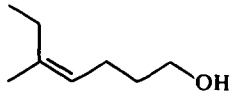

V

(II) were reported by Corey *et al.*[11, 12] They also recorded stereo-controlled syntheses of the C_6-(III), C_7-(IV) and C_8-(V) alcohols, the key starting materials for the head-to-tail syntheses of the *Cecropia* juvenile hormones.[13–15]

This paper describes three novel stereo-controlled syntheses of C_6-(III) and C_7-(IV) alcohols which have enabled us to prepare a considerable amount of these key intermediates in a relatively short period.

A stereospecific synthesis of 3-*methylpent*-2-cis-*en*-1-*ol* (III)

This synthesis is based on a reductive conversion of an α,β-unsaturated δ-lactone

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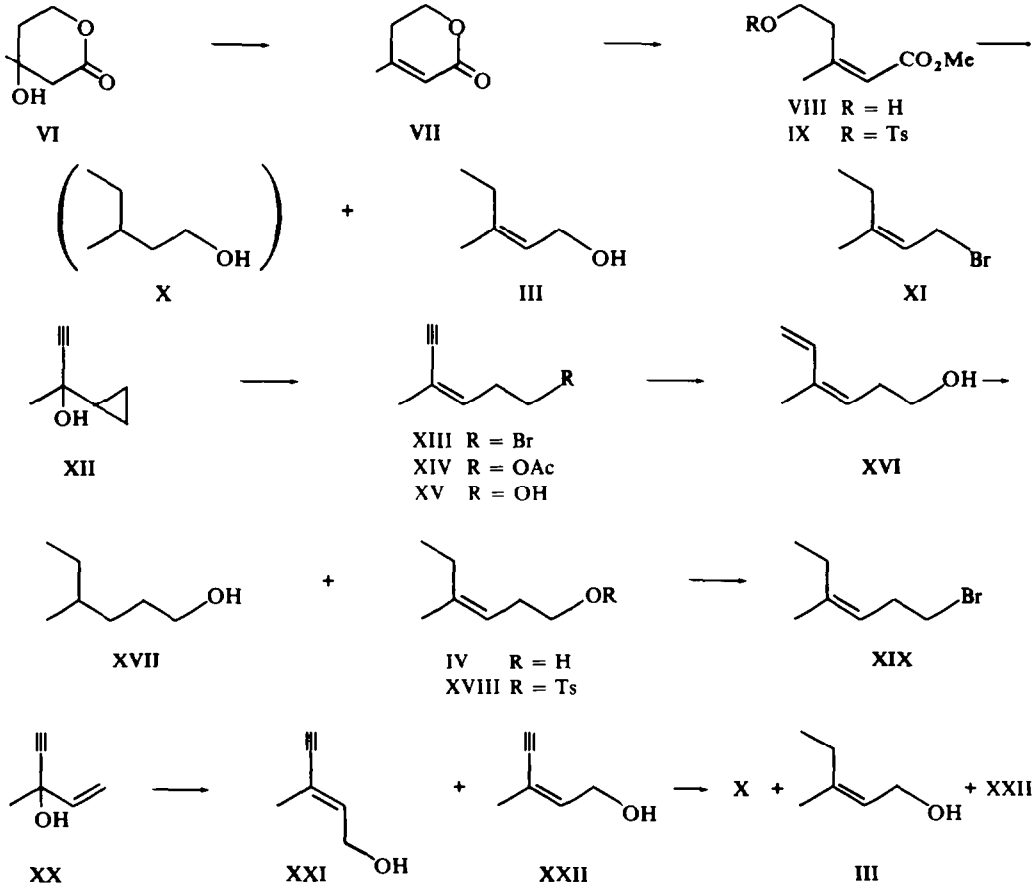
(VII) into the C_6-alcohol (III) with retention of the geometry of the double bond. Fortunately, a synthesis of the required intermediate, methyl 5-hydroxy-3-methylpent-2-*cis*-enoate (VIII) was reported by Cornforth *et al.*[16] According to their method mevalonolactone (VI) was prepared from 3-oxobutan-1-ol acetate. Subsequently it was dehydrated to give a dihydro-α-pyrone (VII), whose hydrolysis and esterification with CH_2N_2 gave the known hydroxy ester (VIII). The corresponding crystalline tosylate (IX), prepared in the usual manner with *p*-TsCl and pyridine, was reduced with LAH to give the C_6-alcohol (III) contaminated with a trace of 3-methylpentan-1-ol (X), an over-reduction product, judged by NMR and GLC. Treatment of this almost pure C_6-alcohol (III) with PBr_3 in ether afforded pure 3-methylpent-2-*cis*-enyl bromide (XI). In the NMR spectrum, the stereochemically pure alcohol (III) exhibits a very sharp 3H triplet signal for the CH_3CH_2- protons and other sharp signals which are in accord with the structure (see experimental). This was also true in the case of pure C_6-*cis*-bromide (XI).



The above synthetic route was disclosed simultaneously by Corey[17] and by ourselves.[18] A non-stereoselective synthesis of this C_6-alcohol (III) had been reported by Dahm *et al.*[3] The NMR spectrum of our product was identical with an authentic

spectrum kindly sent to us by Professor Trost and in good accord with the data kindly supplied by Professors Corey and Dahm.

A highly stereoselective synthesis of 4-*methylhex*-3-cis-*en*-1-*ol* (IV)

The first stereospecific synthesis of this C_7-alcohol (IV) was accomplished by Corey *et al* starting from *p*-cresol methyl ether.[11] However, their route, including Birch reduction and controlled ozonolysis, is not suited to large scale preparation.

Our new procedure is based on Julia's isoprenoid synthesis *via* cyclopropylcarbinol[19] which has been employed in a number of reported syntheses of the juvenile hormones.[4,5,10,20] Among them Johnson's synthesis is highly stereoselective.[20] Julia *et al.* observed that the ring cleavage of 2-cyclopropylbut-3-yn-2-ol (XII) with HBr took place highly stereoselectively to give 1-bromo-4-methylhex-3-*cis*-en-5-yne (XIII) in 95% purity with only 5% of the *trans*-isomer.[21,22] This remarkable stereoselectivity was explained by Julia to be due to the steric effect of the Me group which is bulkier than the ethynyl group.[22a]

Since this bromide (XIII) had been converted by Julia *et al.* into 4-methylhex-3-*cis*-en-5-yn-1-ol (XV) *via* the corresponding acetate (XIV),[21] the remaining task was the selective reduction of the terminal triple bond. For this purpose the acetylenic alcohol (XV) was hydrogenated over Lindlar's catalyst[23] to give a dienol (XVI).[22] Its diimide reduction[24] afforded the C_7-alcohol (IV) in good yield (74% from XVI) with a small amount of over-reduction product, 4-methylhexan-1-ol (XVII).* It was very important to choose appropriate reduction conditions. The best yield was observed when a large excess of hydrazine hydrate and H_2O_2 in EtOH was employed as reducing agent. Presence of cupric ion, as recommended by Corey *et al.*,[12,25] increased the amount of polymeric by-product in our hands. Reduction with hydrazine hydrate and oxygen[24] gave a poor result in this case.

As a large scale hydrogenation of the acetylene (XV) with Lindlar's catalyst was rather troublesome, its direct reduction with diimide was attempted. In this case, too, 4-methylhex-3-*cis*-en-1-ol (IV) was obtained in good yield (71%) by reduction with hydrazine hydrate and H_2O_2 in EtOH. The product contained a considerable amount (17%) of the over-reduction product (XVII).* The NMR spectrum of the C_7-alcohol was as expected and in accord with the published data.[11] The over-all yield of alcohol IV from methyl cyclopropyl ketone was 20–21%. The corresponding tosylate (XVIII) was heated under reflux with LiBr in acetone to give 4-methylhex-3-*cis*-enyl bromide (XIX).[26]

A stereoselective synthesis of 3-*methylpent*-2-cis-*en*-1-*ol* (III)

Although our synthesis of the C_6-alcohol (III) from mevalonolactone (VI) was stereospecific, the over-all yield was very poor (4·8% from 3-oxobutan-1-ol acetate, the starting material). This made us explore a more efficient route.

It is known that 3-methylpent-4-en-1-yn-3-ol (XX), prepared from methyl vinyl

* The structure of the over-reduction product was assumed on the basis of the following observations. GLC analysis of the mixture resulting from the diimide reduction revealed it to be a mixture of two components. The minor one with a shorter retention time was assumed to be XVII, the over-reduction product. When the mixture was hydrogenated over Pd-C it gave a single product identical with the over-reduction product as judged by GLC. Thus the over-reduction product was XVII.

ketone and lithium acetylide,[27] rearranges to a stereoisomeric mixture of *trans*- and *cis*-3-methylpent-2-en-4-yn-1-ols (XXI and XXII),[28] in which the *cis*-isomer (XXII) is predominant (XXI:XXII = 15:85 by GLC).[29] These two isomers can readily be separated by fractional distillation through a spinning band column. The NMR spectra of these stereoisomers are in good accord with the published spectra.[30] The *cis*-isomer (XXII) was reduced with hydrazine hydrate and H_2O_2 in EtOH to give a mixture in 72% yield. It consisted of three components: the desired C_6-alcohol (III), the over-reduction product (X) and starting material (XXII) in a ratio of 82:11:7 as determined by GLC.* Purification by fractional distillation through a spinning band column gave the desired product (III) contaminated with a small amount of the saturated alcohol (X). This was treated with PBr_3 in ether to give 3-methylpent-2-*cis*-enyl bromide (XI).

By this method the C_6-alcohol (III) could be synthesized in three steps from methyl vinyl ketone in 17% over-all yield while the synthesis from acetone *via* mevalonolactone required eight steps for completion.

In conclusion it is now possible to prepare stereoselectively the C_6- and C_7-alcohols (III and IV) in quantity. The diimide reduction, however, is rather difficult to control and inevitably leads to a certain amount (10–20%) of over-reduction products. Syntheses of the racemic *Cecropia* C_{17}-juvenile hormone (I)[31] and the C_{18}-hormone (II)[32] employing these starting materials will be the subjects of our future papers.

EXPERIMENTAL

All m.ps and b.ps were uncorrected. IR spectra refer to Nujol mulls for crystalline samples and films for oils and were determined on a Jasco IRA-1 spectrometer. NMR spectra were recorded on a Jeol NM-4H 100 spectrometer at 100 MHz in CCl_4 with TMS as an internal standard. GLC analyses were performed on a Yanaco G 80 gas chromatograph.

3-Methyl-5-hydroxypent-2-cis-enoic acid δ-lactone (VII). This was prepared by the method of Cornforth[16] from mevalonolactone (VI) in 83% yield, b.p. 120–124°/17 mm; ν_{max} 1710, 1645, 1410, 1320, 1280, 1235, 1165, 1105, 1080, 1010, 870, 810 cm^{-1}; δ 2·00 (3H, s), 2·37 (2H, t, J = 6 Hz), 4·30 (2H, t, J = 6 Hz), 5·66 (1H, br. s) ppm.

Methyl 3-methyl-5-hydroxypent-2-cis-enoate (VIII). This was prepared by the method of Cornforth[16] from VII in 83% yield, b.p. 103–106°/10 mm; ν_{max} ~ 3450, 1700, 1640, 1230, 1150, 1070, 870 cm^{-1}; δ 1·95 (3H, s), 2·80 (2H, t, J = 7 Hz), 2·95 (1H, s, —OH), 3·60–3·67 (5H), 5·70 (1H, s) ppm.

Methyl 3-methyl-5-tosyloxypent-2-cis-enoate (IX). *p*-TsCl (5g) was added during 15 min to a soln of VIII (1·90 g) in dry pyridine (10 ml) with stirring and cooling at 3–5°. The mixture was stirred overnight at 3–5°, poured into ice and dil HCl and ether extracted. The ethereal soln was washed with dil HCl, sat $NaHCO_3$ aq and water, dried ($MgSO_4$) and concentrated *in vacuo* to give 2·34 g (60%) of crystalline IX. Recrystallisation from CCl_4 gave needles, m.p. 76–77°; ν_{max} 1700, 1640, 1600, 1370, 1320, 1260, 1200, 1180, 1160, 1110, 1030, 970, 890, 860, 840, 830, 780 cm^{-1}; δ 1·98 (3H, s), 2·43 (3H, s), 2·93 (2H, t, J = 6 Hz), 3·62 (3H, s), 4·36 (2H, t, J = 6 Hz), 5·71 (1H, s) 7·1–7·4 (2H), 7·65–7·88 (2H) ppm. (Found: C, 55·84; H, 6·05. $C_{14}H_{18}O_5S$ requires: C, 56·30; H, 6·08%).

3-Methylpent-2-cis-en-1-ol (III). To a suspension of LAH (10 g) in dry ether (100 ml), the tosylate IX (20 g) in dry ether (400 ml) was added dropwise under ice-cooling and vigorous stirring during 1 hr. After stirring at room temp for 1·5 hr, excess LAH was destroyed by careful addition of water. The ether layer was separated by decantation and white gelatinous $Al(OH)_3$ was washed twice with ether. The ethereal soln was washed with water until neutral and sat NaCl soln, dried ($MgSO_4$) and concentrated. The residue was distilled to give 4·3 g (64%) of III, b.p. 74–76°/26 mm; ν_{max} ~ 3300, ~1660, 1055, 1010, 980 cm^{-1};

* This ratio varied considerably unless the diimide reduction was carried out very carefully by checking the reaction sequence with IR (disappearance of an absorption at 3250 cm^{-1} due to C≡CH) or GLC. The structure of the over-reduction product (X) was based on similar observations made for XVII.

δ 0·99 (3H, t, J = 7 Hz), 1·70 (3H, s), 2·04 (2H, q, J = 7 Hz), 3·47 (1H, br. s, OH), 3·97 (2H, d, J = 7 Hz), 5·70 (1H, t, J = 7 Hz) ppm. GLC: *Rt* 20·2 min; Column, Carbowax 6000 (30%) on Diasolid, 2 m × 3 mm i.d.; column temp, 120°; carrier gas, He 1·0 kg/cm^2. (Found: C, 71·23; H, 12·95. $C_6H_{12}O$ requires: C, 71·95; H, 12·08%).

3-*Methyl*-2-cis-*enyl bromide* (XI). PBr_3 (80 g) was added dropwise to a stirred soln of the above alcohol III (50g, prepared from XXII) in dry ether (600 ml) under N_2 during 30 min at $-10 \sim -2°$. The mixture was stirred for 3 hr at $-10° \sim 0°$, poured into ice-water and ether extracted. The ethereal soln was washed with water, sat $NaHCO_3$ soln and sat NaCl soln, dried ($MgSO_4$) and concentrated. The residue was distilled to give 59·5 g (73%) of XI, b.p 88–91°/95 mm, 80–83°/75 mm or 49–51°/20 mm; n_D^{20} 1·4892; ν_{max} 1660, 1200, 840 cm^{-1}; δ 1·05 (3H, t, J = 7 Hz), 1·76 (3H, s), 2·10 (2H, q, J = 7 Hz), 3·92 (2H, d, J = 7 Hz), 5·45 (1H, t, J = 7 Hz) ppm. (Found: C, 44·05; H, 6·49. $C_6H_{11}Br$ requires: C, 44·19; H, 6·80%).

4-*Methylhex*-3-cis-*en*-1-*ol* (IV). (a) *From* 4-*methylhexa*-3-cis, 5-*dien*-1-*ol* (XVI). 35% H_2O_2 (110 ml) was added during 1·5 hr to a stirred and ice-cooled soln of XVI[22] (22·4 g) in 99% EtOH (300 ml) and 85% $N_2H_4.H_2O$ (105 g) below 30°. After addition, the mixture was stirred for *ca.* 4 hr at room temp until the IR absorption at 900 cm^{-1} (C=CH_2) disappeared. The mixture was poured into water and ether extracted. The ethereal extract was washed with $FeSO_4$ soln, water and sat NaCl soln, dried ($MgSO_4$) and concentrated. The residue was distilled to give 16·9 g (74%) of IV, b.p. 64–65°/10 mm, n_D^{18} 1·4461; ν_{max} 3300, 1640, 1045 cm^{-1}; δ 0·90 (3H, t, J = 7 Hz), 1·69 (3H, d, J = 1·5 Hz), 2·03 (2H, q, J = 7 Hz), 2·20 (2H, q, J = 7 Hz), 2·98 (1H, br. s, OH), 3·49 (2H, t, J = 7 Hz), 5·04 (1H, t, J = 7 Hz) ppm; GLC: *Rt* 2·3 min (as TMS ether). Column, 5% LAC 2R-446 on Diasolid L (80–100 mesh), 1·5 m × 3 mm i.d., Column temp, 100°, Carrier gas N_2, 1·0 kg/cm^2. (Found: C, 73·40; H, 12·23. $C_7H_{14}O$ requires: C, 73·63; H, 12·36%).

(b) *From* 4-*methylhex*-3-cis-*en*-5-*yn*-1-*ol* (XV). 35% H_2O_2 (1050 ml) was added during 1·5 hr to a stirred and ice-cooled soln of XV (136 g) in 99% EtOH (1300 ml) and 85% $N_2H_4.H_2O$ (1170 g) below 30°. The mixture was stirred for *ca.* 4 hr at room temp until the IR absorptions at 3280 and 2095 cm^{-1} (C≡CH) as well as 900 cm^{-1} (C=CH_2) disappeared. Subsequent work-up gave 99 g (71%) of IV. This contained *ca.* 17% of the over-reduction product XVII judging from the following GLC data. GLC: *Rt* 5·5 min (IV, 83%), 4·2 min (XVII, 17%). Column, 5% LAC 2R-446 on Diasolid L (80–100 mesh), 1·5 m × 3 mm i.d., Column temp, 102°, Carrier gas N_2, 1·1 kg/cm^2. The IR and NMR data of the mixture were essentially identical with those described in (a).

Catalytic hydrogenation of a mixture of IV *and* XVII. The above described product (IV: XVII = 83: 17, 20 mg) in 95% EtOH (5 ml) was shaken under H_2 atmosphere in the presence of 10% Pd-C (15 mg) until hydrogen uptake ceased. The catalyst was removed by filtration and the filtrate submitted to GLC analysis. Before hydrogenation the mixture showed two peaks: *Rt* 2·8 min (XVII), 3·7 min (IV) on LAC 2R-446 at 112° (N_2, 1·2 kg/cm^2) or *Rt* 10·4 min (XVII), 12·8 min (IV) on Carbowax 3000 at 112° (N_2, 1·2 kg/cm^2). After hydrogenation the product showed a single peak: *Rt* 2·8 min (XVII) on LAC or *Rt* 10·4 min on Carbowax.

4-*Methylhex*-3-cis-*enyl* bromide (XIX). *p*-TsCl (57·2 g) was added portionwise during 20 min to a stirred and ice-cooled soln of IV (34·2 g) in dry pyridine (150 ml) at 5–10°. The mixture was stirred for 20 min at 5–10° and then for 20 min at room temp. The precipitated $C_5H_5N.HCl$ was dissolved by careful addition of ice-water. The mixture was poured into ice-cooled 3N-H_2SO_4 (600 ml) and ether extracted. The ethereal layer was washed with water and sat NaCl soln, dried ($MgSO_4$) and concentrated *in vacuo* to give an oily tosylate XVIII (75 g), ν_{max} 1595, 1350, 1170, 950, 910, 810 cm^{-1}. This was dissolved in acetone (G.R., 350 ml), mixed with dry LiBr (60 g) and heated under reflux for 2 hr. The mixture was concentrated, poured into ice-water and extracted with pet. ether. The extract was washed with water and sat NaCl soln, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 38·2 g (72%) of XIX, b.p. 80–82°/35 mm, n_D^{20} 1·4860; ν_{max} 1650, 1265 cm^{-1}; δ 0·95 (3H, t, J = 7 Hz), 1·69 (3H, d, J = 1·5 Hz), 2·02 (2H, q, J = 7 Hz), 2·52 (2H, q, J = 7·5 Hz), 3·25 (2H, t, J = 7·5 Hz), 5·04 (1H, t, J = 7·5 Hz) ppm. (Found: C, 49·62; H, 7·65. $C_7H_{13}Br$ requires: C, 47·45; H, 7·34%). The reason for these incorrect analytical figures is not clear. The alcohol IV gave correct analytical data.

3-*Methylpent*-4-*en*-1-*yn*-3-*ol* (XX). This was prepared by the method of Oroshnik and Mebane[27] in 56–68% yield, b.p. 65–67°/80 mm or 71°/93 mm; n_D^{17} 1·4460; ν_{max} ~3400, 3280, 2980, 2100, 1640, 930 cm^{-1}; δ 1·48 (3H, s), 2·43 (1H, s), 2·99 (1H, s, –OH), 5·00 ~ 6·05 (3H, ABC-type) ppm.

3-*Methylpent*-2-cis-*en*-4-*yn*-1-*ol* (XXII) *and its* trans-*isomer* (XXI). The tertiary alcohol XX (69·5 g) was mixed with dil. H_2SO_4 (100 g of conc. H_2SO_4 in 1l of water) and the mixture stirred under N_2 for 40 hr at room temp, neutralized with solid $NaHCO_3$ and ether extracted. The ether soln was washed with sat NaCl soln, dried (K_2CO_3) and concentrated. During the removal of ether, a Vigreux column was used to

minimize product loss. The residue was distilled to give 53·1 g (76%) of a mixture of XX, XXI and XXII, b.p. 75–80°/20 mm, n_D^{15} 1·4850; GLC: *Rt* 8·2 min (XXII) and 13·6 min (XXI), XXII: XXI = 85: 15, Column, 5% LAC 2R-446 on Diasolid L (80–100 mesh), 1·5 m × 3 mm i.d., Column temp, 102°, Carrier gas, N_2, 1·1 kg/cm². The mixture (130 g) was separated by fractional distillation through a spinning-band column. The separation required *ca.* 30 hr. As a forerun 25 g of XX was recovered. The second fraction boiling at 79–81°/30 mm was the desired *cis*-isomer (XXII, 80 g), n_D^{18} 1·4830 (lit.[29] n_D^{20} 1·4820); ν_{max} ~3300, ~3250, 2180, 1630, 1440, 1375, 1300, 1240, 1160, 1090, 1000, 840 cm^{-1}; δ 1·87 (3H, d, J = 1 Hz), 3·08 (1H, s), 3·46 (1H, s, −OH), 4·21 (2H, d, J = 6 Hz), 5·86 (1H, t, J = 6 Hz) ppm. GLC: *Rt* 6·2 min (single peak), LAC column at 110° with N_2 as the carrier gas, 1·4 kg/cm⁻². (Found: C, 74·51; H, 7·91. C_6H_8O requires: C, 74·97; H, 8·39%). The third fraction boiling at 89–92°/30 mm was the *trans*-isomer (XXI, 9·8 g), n_D^{18} 1·4920 (lit.[29] n_D^{20} 1·4934); IR spectrum was almost identical with that of XXII except that an absorption at 1375 cm^{-1} was stronger than that at 1440 cm^{-1}. δ 1·80 (3H, d, J = 1 Hz), 2·73 (1H, s, CH≡C), 3·77 (1H, s, −OH), 4·10 (2H, d, J = 6 Hz), 5·96 (1H, t, J = 6 Hz) ppm; GLC: *Rt* 10·5 min (single peak) on an LAC column at 110° with N_2 1·4 kg/cm². (Found: C, 74·64; H, 8·25. C_6H_8O requires: C, 74·97; H, 8·39%).

3-*Methylpent*-2-cis-*en*-1-*ol* (III). 35% H_2O_2 (370 ml) was added dropwise during 1·5 hr to a stirred and ice-cooled soln of XXII (40 g) in 95% EtOH (500 ml) and 85% $N_2H_4.H_2O$ (500 g) at 30–40°. After addition the mixture was stirred vigorously for 7 hr at room temp until the IR absorption at 3250 cm^{-1} (—C≡CH) disappeared. The mixture was diluted with sat NaCl soln to 3–3·5 l and ether extracted (x3). The ethereal soln was washed with sat NaCl soln, dil. HCl–$FeSO_4$ soln, sat $NaHCO_3$ soln and sat NaCl soln, dried (K_2CO_3) and concentrated. During removal of ether, a Vigreux column was used to minimize the product loss. The product from 80 g of XXII was distilled *in vacuo* to give 58·0 g (72%) of a mixture, b.p. 66–68°/18 mm; GLC: *Rt* 1·6 min (X, 11%), 2·4 min (III, 82%), 5·9 min (XXII, 7%) on an LAC column at 110° with N_2. This mixture was separated by fractional distillation through a spinning-band column. The separation, which required *ca.* 20 hr, was incomplete and the following five fractions were collected. Fraction 1 (3·5 ml), b.p. 65–67°/29 mm; n_D^{20} 1·4360; GLC: X:III = 41:59. Fraction 2 (25·0 ml), b.p. 67–68°/29 mm; n_D^{20} 1·4390; GLC: X:III = 37:63. Fraction 3 (25·2 ml), b.p. 67°/28 mm; n_D^{20} 1·4455; GLC: X:III:XXII = 11:87:2. Fraction 4 (3·0 ml), b.p. 67–68°/28 mm; n_D^{20} 1·4558; III:XXII = 82:18. Fraction 5 (5·0 ml), b.p. 75°/26 mm; n_D^{20} 1·4758; GLC: III:XXII = 24:76. The purest fraction (3) exhibited the same IR and NMR spectra as those of III prepared from mevalonolactone. (Found: C, 72·02; H, 11·88, $C_6H_{12}O$ requires: C, 71·95; H, 12·08%).

Catalytic hydrogenation of a mixture of III *and* X. The above described fraction 1 (III:X = 59:41, 80 mg) in 95% EtOH (10 ml) was shaken under H_2 in the presence of 10% Pd-C (30 mg) until H_2 uptake ceased. The catalyst was removed by filtration and the filtrate submitted to GLC analysis. Before hydrogenation the mixture showed two peaks: *Rt* 1·7 min (X), 2·5 min (III) on LAC 2R-446 at 112° (N_2, 1·2 kg/cm²) or *Rt* 5·5 min (X), 7·8 min (III) on Carbowax 3000 at 112° (N_2, 1·2 kg/cm²). After hydrogenation the product showed a single peak: *Rt* 1·7 min (X) on LAC or *Rt* 5·5 min (X) on Carbowax.

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