STUDIES IN SESQUITERPENES—XXX SYNTHESIS OF *ar*-HIMACHALENE AND HIMACHALANES*

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Abstract—The conversion of β -himachalene into *ar*-himachalene by a "low-temperature"-dehydrogenation-isomerization sequence is described and the unambiguous synthesis of *ar*-himachalene and himachalanes reported.

STRUCTURE determination of himachalenes, the major sesquiterpene constituents of the essential oil of *Cedrus deodar* Loud., has been described.¹ Since, himachalenes constitute a new type in sesquiterpene framework the synthesis of this system is now reported.

ar-Himachalene

Se-dehydrogenation of either α - I or β -himachalene (II) gives, besides cadalene (III) and 2-methyl-6-(*p*-tolyl) heptane (IV), another aromatic derivative which, in view of the structure of himachalenes, has been assigned the structure V.¹ These authors did not attempt to isolate V in a pure state, though, in an independent investigation Bredenberg and Erdtman² mention its isolation. We now describe a two-step conversion of β -himachalene into V and its total synthesis. The compound has been



found[†] to occur in the essential oil of *Cedrus deodara* and has been named arhimachalene.

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† Unpublished results of S. C. Bisarya. The naturally occurring material has $[\alpha]_D + 2.92$ (c, 1.7% in CHCl₃).

'Low temperature' dehydrogenation and isomerization. In the anticipation that ar-himachalene may be the chief product in a hydrogen transfer reaction³ of β -himachalene with a suitable quinone, its reaction with chloranil has been investigated. β -Himachalene readily reacted with a molar equivalent of chloranil in refluxing benzene to give a product in 90% yield, which was shown, by GLC, to consist of at least three components a, b and c in the ratio 45:32:23 and having relative retention times 1, 1.9 and 2.26 respectively. The composition of this product remains unchanged by using either toluene or xylene as the refluxing solvent. By the peak accentuation method, component b was expected to be ar-himachalene. The total product showed λ_{max} 236 mµ (ϵ , 5600) which suggested that the major component (a) may be VI, arising from VII or VIII; lack of significant absorption at higher wavelengths argues against



structures with extended or homo-annular conjugation. In conformity with this component a smoothly underwent alicyclic-aromatic isomerization⁴ to ar-himachalene when the total product was treated with 20% Pd-C in refluxing xylene. The material resulting from this isomerization contained 72% (GLC) ar-himachalene. The product was further purified by treatment with KMnO₄ aq in acetone when GLC-pure material was obtained. This sequence of reactions gives ar-himachalene in a yield of 50-60% from β -himachalene.

Structure V is fully supported by its spectral characteristics. Thus, in the UV it shows λ_{max} 260 (step-out, ε , 311), 266 (ε , 384) and 275 mµ (ε , 275), values which are in order for an alkylated benzene.⁵ Its IR spectrum (Fig. 1) shows a very strong band at 813 cm⁻¹ and another of medium intensity at 878 cm⁻¹ assignable,⁶ respectively, to the CH out-of-plane deformations of the two adjacent and one free hydrogen atom of the aromatic ring. The PMR spectrum (Fig. 2) clearly shows the presence of two quaternary Me's^{*} (3H s[†] at 79, 84 c/s), one CH₃—CH⁸ (3H d centred at 78.5 c/s, J = 7 c/s), one Me on an aromatic nucleus (3H s at 135 c/s), one benzylic CH-CH₃ (1H m centred at 191 c/s) and three aromatic protons between 405–424 c/s, coupled in an ABC fashion.

Synthesis. The above structure V of *ar*-himachalene is fully confirmed by its synthesis. Two syntheses have been achieved; the first followed an unambiguous route while, the second provided a sample of known absolute stereochemistry.

The first route is schematically shown in Fig. 3. *m*-Methylacetophenone on interaction⁷ with ethyl cyanoacetate furnished the required unsaturated ester (IX), $\lambda_{max} 282 \,\mathrm{m\mu}(\epsilon, 10,800)$. The conjugate addition⁸[‡] of MeMgI to IX proved unexpectedly

^{*} The down-field shift of these methyls is ascribed to their being on a benzylic carbon, e.g. the Me signal in ethylbenzene occurs at 75 c/s.

[†] s = singlet; d = doublet; m = multiplet, etc.

¹ After the completion of present work an improved procedure for such condensation was reported.⁹

Studies in sesquiterpenes-XXX



FIG. 1 IR Spectra of *ar*-himachalene. A. From β-himachalene; B. Synthetic (route one); C. Synthetic (route two).



FIG. 2 PMR Spectrum of ar-himachalene.

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FIG. 3. Synthesis of ar-himachalene (first route).

difficult. It has been recommended¹⁰ that such Grignard additions are profitably carried out in presence of Cu₂Cl₂. However, in the present work it was soon realized that under these conditions, reduction* to X rather than conjugate addition to furnish XII, took place. The desired 1,4-addition could be achieved, by carrying out the reaction in the absence of Cu₂Cl₂. The crude product was directly hydrolysed and decarboxylated to give XIII. The chain extension by two C atoms was done by the standard malonic ester synthesis to finally give XVI, which readily underwent intramolecular acylation with polyphosphoric acid to give the required 5,5,7-trimethylbenzosubarone (XVII; $v^{C=0}$ 1686 cm⁻¹; λ_{max} 249 mµ; ε , 8700). MeMgI in ether failed

^{*} Such a reduction has been observed previously.¹⁰

to react appreciably with the ketone XVII and, ultimately the desired conversion could be achieved with MeLi, under forcing conditions. This reaction directly gave the unsaturated hydrocarbon (XVIII), which was separated from unchanged subarone and then hydrogenated to give a material, which was identical (IR, Fig. 1; physical properties, Table 1) with *ar*-himachalene in all respects.

	Source					
	From β-himachalene		Synthetic			
			Route one 105-110° (bath)/1-6		Route two 120-125°(bath)/5	
b.p./mm						
nD ³⁰	1.5268		1-5250		1.5291	
d_{4}^{31}	0-9376		_		_	
[α] ²⁷	_				+ 5-9°(C c, 1-04%	HCl3;).
2 m- testane mu(e)	260 (step-out) (311)		260 (step-out) (320)		260 (step-out) (240)	
	266	(384)	_66	(375)	266	(356)
	275	(275)	375	(258)	275	(309)
2,4-Dinitrophenyl sulphide (m.p.)	138-139°	,,	138-139°	、 /	_	()

TABLE I	PROPERTIES	OF AR-HIMACHALENE
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The second route utilizes Friedel-Crafts intramolecular alkylation of *ar*-turmerone (XIX) to cyclo-*ar*-turmerone (XX), a reaction first investigated by Colonge and Chambion.^{11*} This reaction furnishes XX in good yield and this structure is fully supported by its spectral characteristics: $v^{C=0}$ 1706 cm⁻¹; two quaternary Me's (3H signals at 82 and 87 c/s), one CH₃-CH (3H d centred at 85 c/s, J = 6 c/s), one on an aromatic ring (3H s at 137 c/s), -C-CH₂-C=O (a 2H AB qu centred at 165 c/s with $J_{AB} = 13$ c/s and $J_{AB}/\delta_B - \delta_A = 0.3$), Ar-CH-CH₂-C=O (an 8 line, Me

2H signal located between 125–165 c/s; an one H m centred at 212 c/s) and three aromatic protons coupled in an ABC manner (located between 407–427 c/s, cf. Fig. 2). Wolff-Kishner reduction of XX gave *ar*-himachalene, indistinguishable, except for its $[\alpha]_D$, from the earlier samples (Fig. 1; Table 1). Since, the absolute stereochemistry of (+)-*ar*-turmerone, the starting material for the present work, is well-established¹² as in XIX, the same S-configuration at the asymmetric centre C₇ follows for (+)-*ar*himachalene (XXI; $[\alpha]_D$ + 5.9, CHCl₃) described now. Furthermore, since the



* We are grateful to Dr. G. S. Krishna Rao who drew out attention to this work.

naturally occurring material^{*} is also dextro-rotatory ($[\alpha]_D + 2.92$) S-configuration at C₇ must also be assigned to this product.

Himachalanes

Hydrogenation of synthetic (\pm) -ar-himachalene over Rh-Pt catalyst¹³ yielded the fully saturated hydrocarbon, which was shown by GLC to be a mixture of at least two isomers in the ratio 30: 70. Catalytic hydrogenation of β -himachalene (II) over PtO₂ catalyst yielded a mixture of the same hydrocarbon (20:80). The essential identity of the two preparations is borne out by a comparison of their IR spectra (Fig. 4).



---- synthetic ---- from β-himachalene

EXPERIMENTAL

For general remarks see Part XXIX of this Series.

β-Himachalene

 β -Himachalene used in this investigation had b.p. 113–114°/5 mm, n_D^{30} 1.5088, $[\alpha]_D^{27}$ + 192.4° (neat).

Dehydrogenation of β -himachalene with chloranil

 β -Himachalene (15.15 g, 0.075 mole), chloranil (18.45 g, 0.075 mole) and dry benzene (150 ml) were refluxed (2 hr) in an atm of N₂. The reaction mixture was cooled, tetrachlorohydroquinone (19 g; m.p. 233-235°) filtered off and washed with pet. ether. The filtrate was washed with 20% NaOH aq (75 ml \times 2), water (75 ml \times 2) and dried. Solvent was removed and the residue distilled to give a colourless, mobile liquid: b.p. 111-112°/3.5 mm, n_D^{30} 1.5298, yield 13.6 g (90%); $\lambda_m^{n-heptane}$ 236 mµ (ϵ , 5647).

as-Himachalene

The above product (2 g), 20% Pd-C (0.6 g) and dry xylene (20 ml) were refluxed (N₂ atm) for 12 hr, after

* See the footnote on page 3829.

which the reaction mixture was cooled, catalyst filtered off and washed with xylene. Removal of the solvent and distillation of the residue gave a colourless liquid: b.p. $112^{\circ}/3$ mm, n_0^{20} 1.5298, yield 1.75 g (88%).

This product (2.7 g) was taken in acetone-water mixture (90:10, 100 ml) and treated with powdered KMnO₄ with stirring at 25-30° till no more was consumed (~2.3 g). The MnO₂ was filtered off and the filtrate diluted with water (200 ml) and extracted with pet. ether (100 ml × 3) and dried. Solvent removal and distillation of the residue over Na gave a colourless, mobile liquid: b.p. 109-110°/2.5 mm (122°/5.2 mm), n_D^{30} 1.5268, yield 1.73 g. (Found: C, 88-80; H, 10-60. C₁₅H₂₂ requires: C, 89-10; H, 10-89%).

2,4-Dinitrophenyl-ar-himachalene sulphide. To a soln of 2,4-dinitrophenyl sulphenyl chloride¹⁴ (0.350 g) in dry ethylene chloride (5 ml), anhyd AlCl₃ (0.5 g) was added while keeping the temp below 5° (ice bath). To this *ar*-himachalene (0.5 g) was added and the reaction mixture well mixed and occasionally shaken at that temp for 30 min. Abs EtOH (3 ml) was then added slowly with cooling. The reaction mixture was extracted with HClaq (10 ml \times 2), water (10 ml \times 2) and the organic soln dried. Removal of the solvent gave a residue (1 g) which was purified on a column of Al₂O₃/I, (15 cm \times 2 cm). The required derivative (0.78 g) eluted out with benzene (50 ml) was crystallized first from pet. ether-EtOH and later from EtOH to furnish canary-yellow lustrous needles: m.p. 138-139°, yield 120 mg. (Found: C, 63.43; H, 5.81. C₂₁H₂₄O₄N₂S requires: C, 63.00; H, 6.00%).

m-Methylacetophenone

m-Toluic acid (6.8 g, 0.05 mole), SOCl₂ (8.37 g, 5.7 ml) and dry benzene (10 ml) were refluxed for 2 hr and then worked up to give the acid chloride b.p. $140^{\circ}/32$ mm, yield 7 g (91%).

In a 250 ml 3-necked flask equipped with a slip-sealed stirrer, dropping funnel and a reflux condenser, Mg (1-34 g, 0-055 g atom) EtOH (2 ml), and CCl₄ (0-6 ml) (anhyd conditions) were added. The reaction which started almost immediately was allowed to proceed for a few min and then 20 ml ether added. To the resulting mixture a soln of diethyl malonate (8-8 g, 0-055 mole) in abs EtOH (5 ml) and dry ether (5 ml) was added at such a rate that rapid refluxing was maintained. After the addition, the mixture was refluxed for 3 hr (till all the metal disappeared). To the clear soln the above acid chloride (7 g) in ether (15 ml) was added with stirring (10 min) and the mixture refluxed (1.5 hr). The reaction mixture was cooled, acidified with dil H_2SO_4 and the ether phase, with which an ether extract of the aq phase was combined, was washed with water (100 ml \times 2) and the solvent flashed off.

The above crude product was hydrolysed and decarboxylated by refluxing (5 hr) with conc H₂SO₄ (2 ml) in AcOH (15 ml) and water (10 ml). The reaction mixture was cooled, made alkaline with 20% NaOH aq and extracted with pet. ether (75 ml × 3). The combined pet. ether extracts were washed with water (100 ml) and dried. Solvent removal and distillation of the residue gave the acetophenone as a colourless, mobile liquid: b.p. 94°/8.5 mm, n_0^{28} 1.5256, yield 4.16 g (lit.¹³: b.p. 109°/12 mm, n_0^{15} 1.533).

Ethyl m-tolyl-α-cyano-β-methylacrylate (IX).

Ethyl cyanoacetate (11.3 g, 0.1 mole), *m*-methyl-acetophenone (13.4 g, 0.1 mole), benzylamine⁷ (1.07 g, 0.01 mole), gl. AcOH (5 ml) and benzene (100 ml) were refluxed with continuous removal of water, using a modified Dean-Stark apparatus¹⁶ till no more water separated (16 hr). Usual work up gave, after fractionation, the desired product as a colourless liquid: b.p. 139–140°/10 mm, n_D^{27} 1.5436, yield 15.1 g (65.6%); λ_{max} 282 mµ (s, 10,800). IR spectrum: C=N 2227 cm⁻¹; COOEt 1724 cm⁻¹. (Found: C, 72.9; H, 6.70. C₁₄H₁₅NO₂ requires: C, 73.40; H, 6.55%).

Action of methyl magneisum iodide on ethyl m-tolyl- α -cyano- β -methyl acrylate (IX).

(i) Without catalyst. To MeMgI (from 0-608 g Mg and 3-55 g MeI) in ether (25 ml) a soln of IX (3-43 g, 0-015 mole) in ether (25 ml) was added slowly (20 min) with vigorous stirring. After the addition, the mixture was stirred at room temp (3 hr) and then at reflux (2 hr). The complex was decomposed with dil HCl and the product extracted with ether (75 ml \times 3). The combined ether extracts were washed with water (50 ml \times 2) and dried. Ether removal and distillation of the residue gave a light yellow mobile liquid : b.p. 126-128°/

0-5 mm, n_D^{28} 1-5200, yield 2-84 g (77-3%). IR spectrum : C=N 2222 cm⁻¹; COOC₂H₅ 1724 cm⁻¹; COOC₂H₅ 172

1387, 1359 cm⁻¹. From its e_{282} 3952, the product was estimated to contain, beside the required XII, ~36% of the unreacted IX. This material was used as such in the next step.

(ii) With catalyst. A soln of MeMgI (from 1.21 g Mg and 7.1 g MeI) in dry ether (50 ml) was cooled to 0° (~10 min), after which one molar proportion (0.045 g) of dried Cu₂Cl₂ was added in one lot with stirring.

To the vigorously stirred mixture a soln of IX (6.87 g, 0.03 mole) in dry ether (50 ml) was added dropwise (20 min). After the addition, the reaction mixture was stirred at room temp (3 hr) and then refluxed (2 hr) and, worked up as above to give a colourless, mobile liquid, identified as X: b.p. 135-136°/0.8 mm, n_{3}^{30} 1.5060, yield 4.43 g. IR spectrum: C=N 2242 cm⁻¹; COOEt 1725 cm⁻¹.

m-Tolyl-*β*-methylpropionic acid (XI)

(i) From Cu₂Cl₂ catalysed Grignard product. The above product (4.4 g) was refluxed with gl. AcOH (10 ml), water (5 ml) and conc H₂SO₄ (5 ml) for 24 hr and worked up to yield XI as a colourless liquid: b.p. 125-127°/0.8 mm, n_0^{30} 1.5110, yield 2.2 g. S-Benzylthiuronium salt was obtained as white shining flakes, m.p. 135-136°. (Found: C, 66.64; H, 7.20. C₁₉H₂₃O₂N₂S requires: C, 66.47; H, 6.70%).

(ii) By reduction and hydrolysis of IX. Compound IX, (4.5 g) was hydrogenated, at room temp and press, in alcohol (40 ml) over pre-reduced Adam's PtO₂ catalyst (100 mg). The H₂ uptake came to a close after absorption of one mole equiv of the gas during 7 hr. The catalyst was removed by filtration and the filtrate worked up in the usual fashion to yield a colourless, mobile liquid: b.p. 133-134°/ 1.4 mm, n_D^{30} 1.4973, yield 3.83 g.

The above product (3.83 g) was hydrolysed following the method given earlier and the product worked up in the usual fashion to yield a colourless liquid (1.9 g), b.p. $120-125^{\circ}/0.7$ mm, n_0^{30} 1.5104. The product was shown to be identical with that described under (i) by a comparison of their IR spectra as well as preparation and comparison (mixed m.p.) of the same S-benzylthiuronium salt.

m-Tolyl-β,β-dimethylpropionic acid (XIII)

The crude XII (11·3 g) in 90% MeOH (275 ml) was saturated with dry HCl at room temp and left overnight (20 hr). The mixture was, next, refluxed (5 hr), after which MeOH was distilled off and the residue diluted with water, extracted with ether (100 ml \times 3) and the solvent removed. The residue was further hydrolysed with refluxing 10% KOH in 90% aqueous MeOH (100 ml). After 4 hr, the reaction mixture was cooled, poured into water (100 ml) and extracted with ether (100 ml \times 2) to remove the neutral fraction which was discarded.* The alkaline soln was acidified with conc HCl with cooling and the organic acid extracted with ether (100 ml \times 4) and the combined ether extracts washed with water (100 ml \times 2) and dried. Removal of the solvent and distillation of the residue under vacuum gave a colourless liquid : b.p. 150-153°/2·5 mm, $n_D^{25.5}$ 1.5188, yield 3.5 g (39%); λ_{max} 257 (z, 771), 263 (z, 808) and 271 mµ (z, 705). IR spec-

trum: COOH 2632, 1681 cm⁻¹; $>C < CH_3 CH_3 CH_3 CH_3 CH_3 CM^{-1}$. (Found: C, 75.10; H, 8.50. $C_{12}H_{16}O_2$

requires: C, 75.00; H, 8.33%).

S-Benzylthiuronium salt was crystallized from EtOH: white shining flakes, m.p. 119–120°. (Found: C, 67.54; H, 7.71. C₂₀H₂₆O₂N₂S requires: C, 67.03; H, 7.26%).

m-Tolyl-β,β-dimethyl propanol (XIV)

m-Tolyl- β , β -dimethylpropionic acid (2.3 g) was esterified by refluxing with MeOH (7.5 ml), conc H₂SO₄ (1 ml) and benzene (8 ml) for 6 hr and then worked up to give methyl m-tolyl- β , β -dimethylpropionate as a colourless liquid : b.p. 108–110°/1-6 mm, n_D^{30} 1.4983, yield 2.21 g (90%); λ_{max} 257 (ϵ , 296), 262 (319) and 271 mµ

(223). IR spectrum : COOMe 1739 cm⁻¹; $CC < Me_{Me}^{Me}$ 1389, 1366 cm⁻¹. (Found : C, 76·20; H, 9·00. C₁₃H₁₈O₂

requires: C, 75.72; H, 8.73%).

To a well-stirred ice-cold suspension of LAH (0.722 g) in dry ether (50 ml) a soln of methyl *m*-tolyl- β , β -dimethyl propionate (2.21 g) in dry ether (50 ml) was let in slowly (20 min). After stirring at ice temp (1 hr) the reaction mixture was left aside at room temp (2 hr) and then refluxed (6 hr) with stirring. Excess of the hydride was destroyed at -5 to -10° by EtOAc (5 ml) and the complex decomposed with ice-cold 15% H₂SO₄ (50 ml) and the reaction mixture worked up to give XIV as a colourless liquid: b.p. 106-107°/ 2.6 mm, n_{20}^{20} 1.5154, yield 1.77 g (93.4%). IR spectrum: CH₂OH 3390, 1026 cm⁻¹. (Found: C, 80.26; H, 10.28. C_{1.2}H_{1.8}O requires: C, 80.89; H, 10.11%).

* This consisted essentially of m-methylacetophenone resulting from the acid-catalysed cleavage of the unsaturated cyano ester IX, which was present as an impurity in the product from Grignard addition. Its 3,5-dinitrobenzoate was crystallized from benzene-pet. ether mixture as button-like crystals, m.p. 68-69°. (Found: C, 61.80; H, 5.70. C₁₉H₂₀O₆N₂ requires: C, 61.26; H, 5.36%).

Ethyl m-tolyl-8,8-dimethyl-a-carbethoxyvalerate (XV).

To a cooled (below -10°) soln of *m*-tolyl- β , β -dimethylpropanol (0.85 g) in pyridine (5 ml), *p*-toluene sulphonyl chloride (1.24 g) was added and the mixture kept at ~0° overnight (24 hr). The reaction mixture was diluted with 10% NaHCO₃ aq (50 ml) and extracted with ether-benzene (1:1, 30 ml × 4). The combined extracts were washed with water (50 ml × 2), ice cooled 10% AcOH (50 ml × 3), water (50 ml × 2), NaHCO₃ aq (50 ml × 2) and dried. The solvent was removed in *vacuo* and the crude *p*-toluene sulphonate (1:3 g) used as such for further condensation.

Ethyl sodiomalonate was prepared as usual in THF (25 ml) from malonic ester (1·16 g, 0·0072 mole) and Na (0·161 g, 0·0078 g atom). The above tosylate in THF (10 ml) was then added and the reaction mixture refluxed (anhyd conditions) for 25 hr, when it was cooled, poured into water (50 ml), extracted with benzenepet. ether mixture (1:1, 50 ml \times 3) and dried. Solvent removal and distillation of the residue gave a colourless liquid: b.p. 150–152°/1·0 mm, n_D^{30} 1·4826, yield 0·95 g. (Found: C, 70·80; H, 8·70. C₁₉H₂₉O₄ requires: C, 71·25; H, 8·75%).

m-Tolyl-δ,δ-dimethylvaleric acid (XVI).

Ethyl *m*-tolyl- δ , δ -dimethyl- α -carbethoxy valerate (2.85 g), conc HCl (42 ml), water (10 ml) and gl. AcOH (36 ml) were refluxed for 24 hr and the product poured into water extracted with ether-pet. ether (1:1, 50 ml × 3) and the combined extracts washed with NaHCO₃ aq (50 ml × 6). The combined NaHCO₃ extracts were acidified (dil HCl) and the product extracted with ether-pet. ether (1:1, 50 ml × 4). The combined extracts were washed with water (50 ml × 2) and dried. Solvent removal and distillation of the residue gave a colourless liquid: b.p. 147-148°/1.25 mm, n_{30}^{30} 1.5075, yield 1.65 g (85.2%). IR Spectrum: COOH 2632, 1706 cm⁻¹. (Found: C, 76.00; H, 8.90. C₁₄H₂₀O₂ requires: C, 76.30; H, 9.09%).

S-Benzylthiaronium salt was crystallized from EtOH: white shining flakes, m.p. $132-133^{\circ}$. (Found: C, 68-10; H, 7-70. C₂₂H₃₀O₂N₂S requires: C, 68-29; H, 7-77%).

5,5,7-Trimethylbenzosuberone (XVII)

To polyphosphoric acid prepared from P_2O_3 (15 g) and 85% phosphoric acid (9-0 ml) in widemouth test-tube *m*-tolyl- $\delta_i\delta_j$ -dimethyl valeric acid (1-22 g) in pet. ether (2 ml) was added at room temp and then heated and stirred (glass rod) on a steam-bath to remove pet. ether. The test tube was then stoppered and heated on water-bath till the colour of the reaction mixture changed from yellow to deep red (5 hr). It was cooled and worked up as usual to give the ketone as a colourless liquid: b.p. 120-121°/16 mm, n_{D}^{30} 1:5430, yield 0-91 g (81.8%); λ_{max} 249 mµ (ϵ_i 8704). IR spectrum: C=O 1686 cm⁻¹. (Found: C, 82.5; H, 9-23. C₁₄H₁₈O requires: C, 83.16; H, 8.91%).

2,4-Dinitrophenylhydrazone. The above ketone (20 mg) in EtOH (5 ml) was treated with a soln of 2,4dinitrophenylhydrazine in diglyme¹⁷ (1.5 ml) and two drops of conc. HCl added. Usual work up gave a gum which was purified by passing through a column of $Al_2O_3^*/I$ (15 cm \times 1 cm) and eluting with benzene.

Removal of benzene and crystallization of the residue from MeOH furnished fine light orange needles. m.p. 175-176. (Found: C, $63\cdot10$; H, $5\cdot89$. $C_{20}H_{22}O_4N_4$ requires: C, $62\cdot82$; H, $5\cdot76\%$).

Action of methyl lithium on 5,5,7-trimethylbenzosuberone (XVII)

To a soln of MeLi (from 84 mg Li; 0.4 ml MeI and 15 ml ether), XVII (300 mg) in benzene (10 ml) was added and the mixture distilled to remove ether, which was replenished by adding benzene (20 ml). The reaction mixture was finally refluxed (N₂) with stirring (12 hr), cooled and the complex decomposed with saturated NH₄Claq. Benzene layer was separated and the aqueous layer extracted with ether (25 ml \times 2). The combined organic layers were washed with brine and dried. Solvent removal and distillation of the residue gave a product b.p. 73–75°/1.25 mm, yield 0.22 g. This product, which was shown by its IR spectrum to contain some unchanged ketone, was chromatographed on SiO₂/II (15 cm \times 0.6 cm) and the course of separation followed by IR spectroscopy. Pet. ether (10 ml \times 4) eluted the required hydrocarbon (145 mg), while pet. ether-benzene (1:1, 10 ml \times 3) and ether (10 ml \times 8) together eluted 60 mg of unchanged ketone.

Alumina used in this work was made neutral by the HNO₃ method^{18s} and satandardized according to Brockmann.^{18s} The hydrocarbon fraction on distillation gave a colourless liquid: b.p. $105-110^{\circ}$ (bath)/1.75 mm, n_D^{30} 1.5348, yield 137-6 mg.

3,5,5,9-Tetramethyl benzosubarane (ar-himachalene) (V)

The above hydrocarbon (1376 mg) was hydrogenated at room temp and press over pre-reduced Adam's Pt catalyst (23·1 mg) in gl. AcOH (15 ml). The H₂ uptake came to a close (6·35 hr) when the hydrocarbon had absorbed one mole equiv. The reaction mixture was worked up in the usual fashion to give a colourless liquid having the characteristics recorded in Table 1. (Found : C, 88·80; H, 10-60. $C_{15}H_{22}$ requires : C, 89·10; H, 10-89%).

(+) Cyclo-ar-turmerone (XX)

To ar-turmerone⁴ (432 mg) in CS₂ (15 ml), cooled to -10° , AlCl₃ (500 mg) was added in two lots, while stirring. After the addition stirring was continued at -10° for 1 hr and the reaction mixture finally refluxed for 4 hr. The product was poured onto ice HClaq and the CS₂ layer separated and the aqueous layer extracted with CH₂Cl₂ (25 ml × 2). The solvent extract was washed with water (50 ml × 3) and the solvent flashed off. The crude residue on steam distillation afforded 351 mg of a product which was shown by TLC (solvent system: 5% EtOAc in C₆H₆) and GLC (Aerograph, column: P; temp 150°, flow: 50 ml/min) to consist of cyclized and uncyclized material, which was separated by preparative-layer-chromatography to give, besides unchanged ar-turmerone (148 mg), the required cyclo-ar-turmerone (179 mg): b.p. 190° (bath)/16 mm, n_{3}^{30} 1:5393, $[\alpha]_{25}^{25}$ + 564° (c, 0.76%), TLC: single spot (5% EtOAc in C₆H₆). (Found: C, 83:50; H, 9:78. C₁₅H₂₀O requires: C, 83:30; H, 9:25%).

(+)-ar-Himachalene (XXI)

Cyclo-*ar*-turmerone (40 mg), KOH (0.2 g), 100% hydrazine hydrate (0.2 ml) and diethyleneglycol (2 ml) were heated under reflux for 2 hr. The temp was then raised to 210° and heating continued for 4 hr. The reaction mixture was worked up in the usual manner to give the required hydrocarbon as a colourless liquid: b.p. 120-130° (bath)/50 mm, yield 45.3 mg, n_D^{30} 1.5291, $[\alpha]_D^{27}$ + 5.9° (c, 1.38%). (Found: C, 89.25; H, 11.10. C₁₅H₂₂ requires: C, 89.10; H, 10.80%).

Himachalanes

(i) Hydrogenation of β -himachalene. β -Himachalene (0.585 g) was hydrogenated over a pre-reduced suspension of Adam's Pt catalyst (90 mg) in gl. AcOH (40 ml). The H₂ uptake came to a close after about 8 hr, when 167 ml H₂ was absorbed at 27°/708 mm (calculated for two double bonds: 1576 ml). The catalyst was filtered off and the filtrate worked up as usual. Solvent removal and distillation of the residue gave a colourless liquid: b.p. 110-111°/3 mm, n_{2}^{26-5} 1.4876, $[\alpha]_{2}^{24}$ - 21.05° (c, 4.3%), yield 0.44 g. (Found: C, 86.58; H, 13.59. C_{1.5}H₂₈ requires: C, 86.53; H, 13.46%).

(ii) Hydrogenation of ar-himachalene. ar-Himachalene (175 mg) was hydrogenated at room temp and press in gl. AcOH (20 ml) over pre-reduced Rh-Pt catalyst (50 mg). The H₂ uptake came to a close after absorption of 3 mole equivs during 19 hr. Usual work up gave the product as a colourless liquid: b.p. 100-120° (bath)/2.5 mm, n_D^{30} 1.4820, yield 135.2 mg. (Found: C, 86.50; H, 13.89. C₁₅H₂₈ requires: C, 86.53; H, 13.46%).

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