Tetrahedron. Vol. 26, pp. 631 to 640 Pergamon Press 1970. Printed in Great Britain

STUDIES IN SESQUITERPENES—XLI
ISOLONGIFOLENE (PART 2): DEHYDROGENATION*†‡

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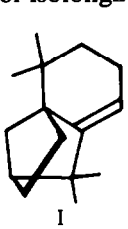
(*Received in the UK* 15 *March* 1969; *Accepted for publication* 2 *October* 1969)

Abstract—Dehydrogenation of isolongifolene over 10% Pd-C, in the vapour phase, at 450-± 5° gave in ~23% yield a mixture of naphthalenes, consisting essentially of 1-methylnaphthalene (7·5%), 1-methyl-7-isopropylnaphthalene (eudalene, 67·5%), 1-methyl-6-isopropylnaphthalene (2·8%) and 1,6-dimethyl-7-ethylnaphthalene (7·0%). The formation of these products is in complete accord with the structure I advanced earlier for isolongifolene.

IN THE preceding communication[1] structure I has been advanced for isolongifolene, on the basis of spectroscopic data of isolongifolene and some of its key derivatives.



I

Dehydrogenation of isolongifolene has now been investigated in an effort to collect further support for the proposed structure. The results of these experiments, which form the subject matter of the present communication, fully substantiate structure I.

Dehydrogenation of isolongifolene over 10% Pd-C at 350° or 400° resulted in little aromatization. However, at 450° considerable dehydrogenation occurred as indicated by the UV absorption of the total product, which showed UV maxima at 320, 312, 280, 274 and 229 mμ suggesting formation of naphthalene[2] derivatives. The total product was segregated into trinitrobenzene (TNB) complexing and non-complexing components; the latter were not investigated further. The different crops of TNB complexes were combined and the complex decomposed by passage through a column of Al_2O_3, to furnish a mixture of aromatic compounds (23% based on I). GLC of this product showed it to consist of at least nine constituents. By preparative GLC and complexing with TNB, four of these components (accounting for over 90% of the product) could be obtained pure and suitably identified. Table 1 summarizes some pertinent data concerning these components.

GLC component 4 was possibly a monoalkylnaphthalene[2] from its UV absorption: $\lambda_{max}^{heptane}$ 312 mμ and, was readily identified as 1-methylnaphthalene by comparison (IR, m.p. of TNB complex) with an authentic sample.

GLC component 6, accounting for over 67% of the total aromatics, was considered

* Communication No. 1328, National Chemical Laboratory, Poona.

† Abstracted from the Ph.D. thesis (Poona Univ. 1967) of J. R. Prahlad.

‡ A repliminary communication appeared in *Tetrahedron Letters* 417 (1964).

TABLE 1. DEHYDROGENATION PRODUCTS FROM ISOLONGIFOLENE

GLC component	RRT*	Identified as	Relative %†
1	0·21	—	1·4
2	0·42	—	1·7
3	0·78	—	3·8
4	1·00	1-methylnaphthalene	7·5
5	1·38	—	6·3
6	1·41	eudalene (XX)	67·6
7	2·10	1-methyl-6-isopropylnaphthalene	2·8
8	2·52	—	1·7
9	2·76	1,6-dimethyl-7-ethylnaphthalene	7·0

* Retention time relative to that of 1-methylnaphthalene; column: 2 meters × 6 mm, packed with 20% diethyleneglycol polysuccinate on Chromosorb W; temp: 160°; gas: H_2, 15 lb. psi.

† In terms of relative areas.

from its UV absorption[2] ($\lambda_{max}^{heptane}$ 318 mμ) to be a dialkyl-naphthalene and was easily recognised (m.p. of its TNB complex and PMR spectrum) as eudalene (1-methyl-7-isopropylnaphthalene). This was confirmed by its comparison[3] (IR, PMR and mixed m.p. of TNB complex) with an authentic sample.[13]

GLC component 7 (*1-methyl-6-isopropylnaphthalene*)

This constituent, also possibly ($\lambda_{max}^{heptane}$ 318 mμ) a dialkylnaphthalene, shows in its PMR spectrum signals assignable to: Ar-C$\underline{H}_3$, 3H singlet at 156 c/s; C$\underline{H}_3$-C$\underline{H}$-CH$_3$, 6H doublet centred at 79·5 c/s, J = 7 c/s; Me_2-C$\underline{H}$-Ar[4], 1H septet centred at 180 c/s, J = 7 c/s; Ar protons, complex 6H multiplet located between 425–472 c/s and hence, is a methyl-isopropylnaphthalene. A consideration of the possible reaction mechanism discussed below, suggested that this component could conceivably be 1-methyl-6-isopropylnaphthalene*. This was confirmed by a comparison (UV, IR, PMR and m.p. of TNB complex) with a synthetic sample.

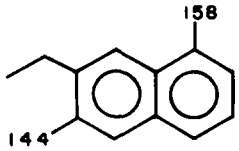
Synthesis. 1-Methyl-6-isopropylnaphthalene (IX) has been described,[6] but since an authentic sample could not be obtained, it was decided to repeat this synthesis. Cumene was condensed with ethyl allylacetate, according to the directions.[6] However, in view of the rather unpredictable nature[7] of this alkylation reaction with regard to orientation, it appeared doubtful if the product of alkylation was solely *para*-oriented (II) as claimed by these workers. This appeared to be supported by the fact that the IR spectrum of the product showed bands assignable[8] to a 1,3-disubstituted (708, 796 cm^{-1}) and 1,4-disubstituted benzene (832 cm^{-1}). GLC of the methyl ester showed two peaks in the ratio 1:1·7. HNO_3 oxidation of the product gave both isophthalic acid and terephthalic acid, the former in almost double the yield. Thus, in contrast to the reportings of Mukherji *et al.*,[6] alkylation of cumene with ethyl allylacetate yields both *meta*-(III) and *para*-substituted (II) products, in which the *meta* isomer predominates by a factor of almost 2. In view of these results this route to

* When this work was carried out, the empirical PMR rules,[5] so useful for the identification of methyl-alkyl-naphthalenes, had not become available.

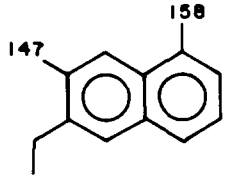
1-methyl-6-isopropylnaphthalene was abandoned and a new unambiguous route (Fig. 1) to this naphthalene worked out. It must be mentioned that the 4-(*p*-cumyl) valeric acid (and its methyl ester) obtained by this route did not show the 708 and 796 cm^{-1} bands in their IR spectra and the methyl ester showed a single peak in GLC, the retention time corresponding to the less-abundant ester of the mixture discussed earlier.

GLC components 9 (*1,6-dimethyl-7-ethylnaphthalene*)

This component showed in the UV, $\lambda_{max}^{heptane}$ 322 mμ and hence was suspected to be a trialkyl-naphthalene.[2] Its PMR spectrum displayed signals for: two Ar-C$\underline{H}_3$, 3H singlets at 146 and 158 c/s; —CH_2.C$\underline{H}_3$, one 3H triplet centred at 78 c/s, J = 7 c/s; Ar-C$\underline{H}_2$-CH_3, 2H quartet centred at 166·5 c/s, J = 7 c/s; Ar protons, 5H complex multiplet located between 425–458 c/s. A consideration of the PMR rules[5] for the identification of methyl- alkyl-naphthalenes suggested two possible structures (X and XI) for this dimethyl-ethyl-naphthalene. Structure X was considered more likely in terms of the structure I for isolongifolene (Fig. 3). This was fully confirmed by a comparison (UV, IR, PMR and m.p. of TNB complex) of GLC component 9 with a synthetic sample of X.



X



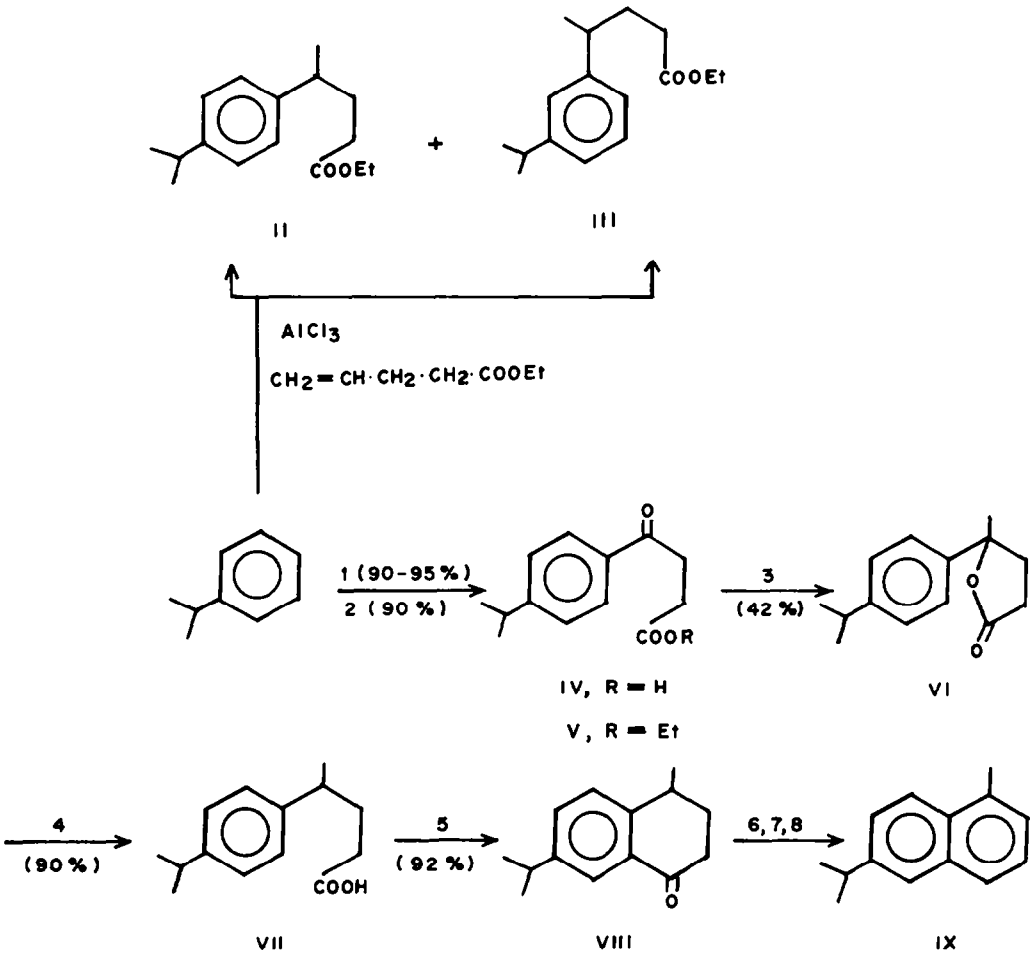
XI

Values on the Me groups are the calculated[5] chemical shifts in c/s.

Synthesis. The synthesis of 1,6-dimethyl-7-ethylnaphthalene was achieved according to the scheme briefly outlined in Fig. 2. GLC of the olefinic ester (XIV) revealed the presence of at least three components in the ratio 0·8:1:4 with RRT of 1, 1·18 and 1·44 respectively. Though, identification of these isomers in the mixture (XIV) is irrelevant to the purpose on hand, it was thought of interest to collect this information, if readily forthcoming from its PMR spectrum. The PMR spectrum of the total product (XIV) shows three sets of signals in the olefinic region: one quartet centred at 287·5 c/s, J_1 = 7 c/s, J_2 = 1–2 c/s; another quartet centred at 339 c/s, J_1 = 7 c/s, J_2 = 1–2 c/s; two overlapping singlets at 378 and 380 c/s.

Since the total area under these signals is approx ¼ the area of signals due to aromatic protons (singlets at 423, 424 and 426 c/s), it is clear that the isomer of XIV with a tetrasubstituted olefinic linkage is not present to any significant extent. The olefinic signals observed are assignable as: 287·5 quartet (XIVc), 339 quartet (XIVb, deshielding by the ethoxy-carbonyl, ?) and 378, 380 singlets (two isomers of XIVa). The area of these signals are in the relative ratio of 2·4:1:1·2 respectively, which thus, indicates the approx composition of XIV.

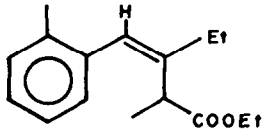
The olefinic ester (XIV) was hydrogenated and the saturated ester (XV) directly cyclized to the tetralone (XVI) with polyphosphoric acid (PPA). The tetralone was next sequentially reduced (LAH), dehydrated (I_2) and dehydrogenated (sulphur) to give the desired 1,6-dimethyl-7-ethylnaphthalene (X).



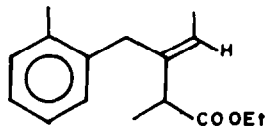
Reagents:

1. Succinic anhydride	3. MeMgI	6. LAH
$AlCl_3$, $NO_2C_6H_5$	4. Pd-C, AcOH, $HClO_4$	7. $KHSO_4$
2. EtOH, H_2SO_4	5. PCl_5, $SnCl_4$	8. S

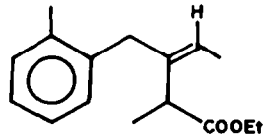
FIG. 1 Synthesis of 1-methyl-6-isopropylnaphthalene.



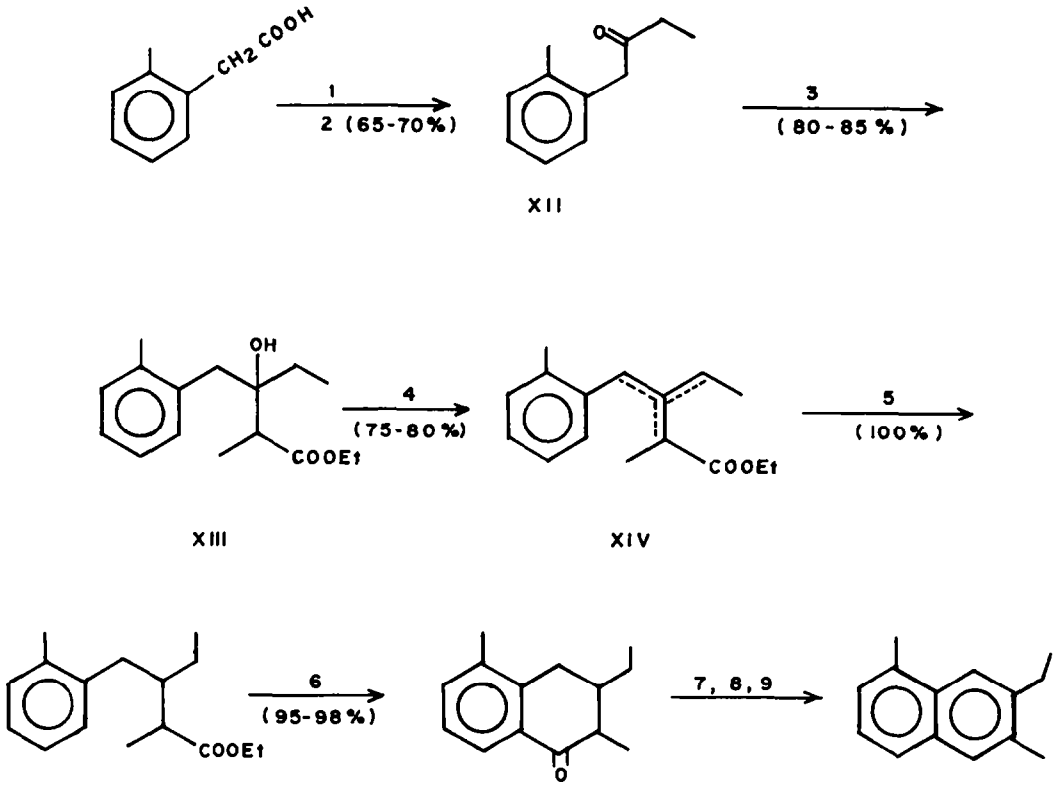
XIVa



XIVb



XIVc



Reagents:

1. PCl_5 C_6H_6	4. 98% HCOOH	7. LAH
2. Et_2Cd	5. Pd-C, EtOH, AcOH	8. I_2
3. Zn, MeCHBr COOEt	6. PPA	9. S

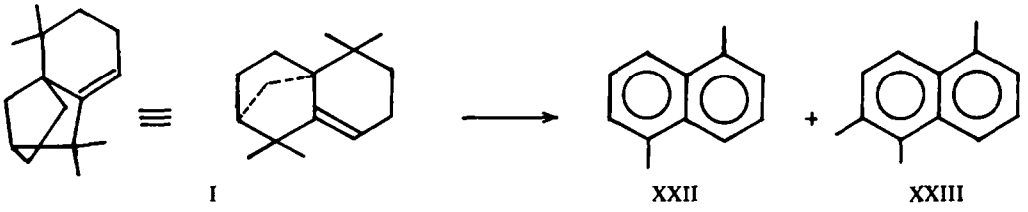
FIG. 2 Synthesis of 1,6-dimethyl-7-ethylnaphthalene.

DISCUSSION

The products of dehydrogenation of isolongifolene are easily explained in terms of structure I for this hydrocarbon. During these relatively high temp vapour phase reactions it is only reasonable to expect both thermal cleavages (possibly aided by catalyst) and catalytic dehydrogenation. It is conceivable[9] that isolongifolene, first, rapidly equilibrates with its double bond isomer (XVII). Allylic cleavage of these isomers can give precursors, which can lead to the observed products (Fig. 3). Conversion of indanes[10] and spiro (5,4) decanes[11] to naphthalenes is well-documented.

Eudalene (XX) is by far the major product. Does it imply that cleavage to XIX is the preferred route or has the final balance of naphthalenes been upset by resistance to complete aromatization of the indane XXI? This aspect is being probed at present.

Another question which remains unanswered is why the alternate possible route (I → XXII, XXIII) to aromatization does not contribute significantly (if at all) to the product development?



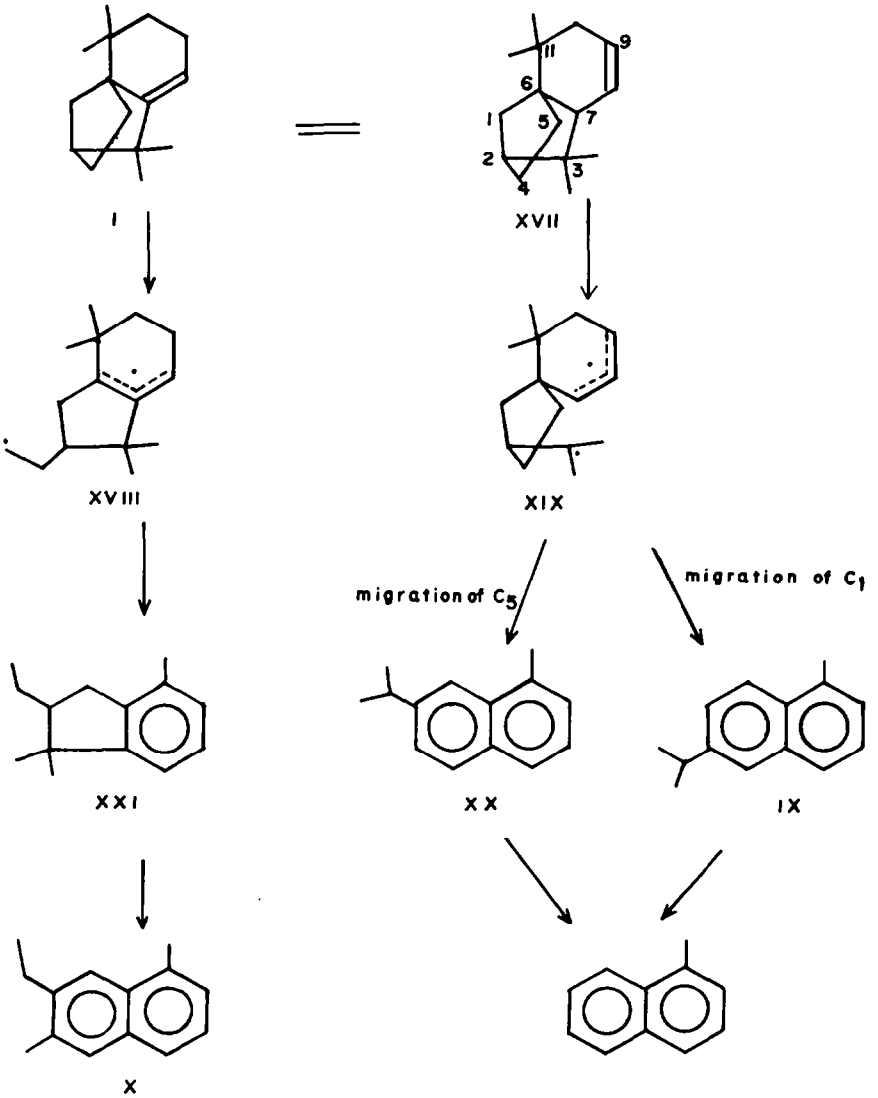


FIG. 3 Possible pathway for the formation of dehydrogenation products of isolongifolene.

EXPERIMENTAL

For general remarks, see Part XL.[1] GLC was carried out on a Perkin–Elmer Vapour Fractometer, model 154-D, using 20% diethyleneglycol polysuccinate on Chromosorb W (mesh: 60–80) as the stationary phase.

Dehydrogenation of isolongifolene

Dehydrogenation was carried out in the vapour phase over a 10–12 cm × 1·0 cm bed of 10% Pd-C (1 g), supported on freshly ignited asbestos (long fibre, 2 g), maintained at 450 ± 5°, under reduced press (35–40 mm) and using the equipment and procedure already described.[1a] Isolongifolene (5 g) was passed over this bed during 2 hr and the faintly blue product collected in a well-cooled receiver.

The above process was repeated 6 times, using a fresh catalyst bed each time. The total dehydrogenate (25–28 g) was taken up in alcohol and successively treated with 5·0 g lots of TNB, filtering off the yellow complex each time, till no more complex separated. In this way 14 g of a bright yellow complex (m.p. 94–99°) could be collected. This was triturated with light petroleum and the suspension poured over a column of Al_2O_3 (basic/grade I; 25 times), which was eluted with light petroleum. The combined eluates were freed of solvent and the residue distilled to give a mixture of naphthalenes as a colourless liquid, b.p. 130–145°/8 mm, yield 6·4 g.

The above product (1·8 g) was separated by preparative GLC (column: 9′ × 1″; temp: 200°; gas: N_2, 15 lb psi; each injection: ~0·2 ml) and 5 fractions, in all, were collected:

Fraction	GLC component(s) (Table 1)	Wt. (mg)
1	1, 2, 3	46
2	chiefly 4	43
3	chiefly 6	600
4	mostly 7	60
5	mostly 9	100

Fraction 1, failed to give any TNB complex.

Fraction 2, in EtOH, gave a yellow complex with TNB, m.p. 148–151° (26 mg); recrystallization from EtOH gave crystals (12 mg), m.p. 150–151°. Mixed m.p. with an authentic sample of TNB complex of 1-methylnahthalene (m.p. 150–151°) was undepressed. The complex was decomposed on Al_2O_3 to get the pure hydrocarbon for UV and IR spectra. UV spectrum, $\lambda_{max}^{heptane}$ mμ (ε): 224·5 (6200), 271·5 (4275), 280 (4360), 290 (2750) and 312 (400).

Fraction 3, readily yielded a TNB complex (EtOH), m.p. 108–109°, mixed m.p. with the TNB adduct of eudalene[3] (m.p. 112–113°) was 109–111° (an authentic sample of eudalene was available as the dehydrogenation product of β-selinene from another study[13]). Spectral data was collected for the pure hydrocarbon after regeneration (Al_2O_3) from the complex; UV spectrum, $\lambda_{max}^{heptane}$ mμ, shoulders being indicated with an asterisk (ε × 10^{-2}): 224* (560), 228 (816), 273* (48), 279 (51), 290* (38), 305* (8), 312* (2.4) and 318 (2.5); PMR spectrum: Ar-C$\underline{H}_3$, 3H singlet at 158 c/s; (C$\underline{H}_3$)$_2$CH, 6H doublet centred at 80·5 c/s, J = 7 c/s; Ar-C$\underline{H}$-Me$_2$, 1H septet centred at 182 c/s, J = 7 c/s.

Fraction 4, in EtOH, yielded a TNB complex (40 mg, m.p. 90–97°), which was recrystallized (EtOH) four times to furnish silky golden yellow needles, m.p. 122–123°; mixed m.p. with the TNB complex (m.p. 123–124°) of 1-methyl-6-isopropylnaphthalene (*vide infra*) was 122·5–124°. The complex was decomposed on Al_2O_3 to get the pure hydrocarbon for spectral data. UV spectrum, $\lambda_{max}^{heptane}$ mμ, shoulders being indicated with an asterisk (ε × 10^{-2}): 222·5* (670), 227 (843), 273* (50), 278 (52·5), 288* (40), 304 (6), 311 (3.8) and 318 (4.4).

Fraction 5, in EtOH, gave a complex with TNB (75 mg, m.p. 109–116°) which was thrice recrystallized from EtOH to yield yellow needles (11 mg), m.p. 124–125°; mixed m.p. with the TNB complex of 1,6-dimethyl-7-ethyl naphthalene (m.p. 124–125°, *vide infra*) was unchanged. Regeneration from the complex over Al_2O_3 gave the pure hydrocarbon for spectral measurements; UV spectrum, $\lambda_{max}^{heptane}$ mμ, shoulders being indicated with an asterisk (ε × 10^{-2}): 225* (670), 230·5 (880), 273* (47), 282 (51), 293* (35), 317 (2·6), 322 (1·8).

Synthesis of 1-*methyl*-6-*isopropylnaphthalene*

β-(p-*Cumoyl*)-*propionic acid* (IV). Cumene (52·8 g, 0·4 mole; purified by washing with conc H_2SO_4) and succinic anhydride (44 g, 0·44 mole) in dry nitrobenzene (200 ml) were condensed in presence of anhyd $AlCl_3$ (117·5 g, 0·88 mole) by exactly following a procedure, described earlier[14] for a similar condensation, to yield crude IV (86 g, m.p. 134–135°). Recrystallization from C_6H_6 furnished pure IV (81 g), m.p. 140–141°. IR spectrum: COOH 2705, 1712 cm^{-1}; C=O 1690 cm^{-1}; 1,4-disubstituted benzene[8] 1618, 1575, 1175, 1110, 1058, 860 and 832 cm^{-1}. (Found: C, 71·14; H, 7·83. $C_{13}H_{16}O_3$ requires: C, 70·80; H, 7·32%).

Ethyl β-(p-*cumoyl*)-*propionate* (V). The above keto acid (67 g), abs EtOH (112 ml), C_6H_6 (130 ml) and conc H_2SO_4 (1 ml) were refluxed with continuous removal of water. Usual work up gave, after distillation, the required ester as a colourless liquid (67·2 g), b.p. 168°/1 mm, n_D^{30} 1·5065; IR spectrum: C=O 1740, 1698 cm^{-1}; 1,4-disubstituted benzene 1608, 1572, 1170, 1110, 1058 and 830 cm^{-1}. (Found: C, 72·66; H, 8·38. $C_{15}H_{20}O_3$ requires: C, 72·55; H, 8·12%).

γ-(p-*Cumyl*)-γ-*valerolactone* (VI). A soln of the above keto ester (24·8 g, 0·1 mole) in dry ether (150 ml) was chilled in an ice-salt bath and an ether soln of MeMgI (from 4·13 g Mg, 25·6 g MeI and 150 ml ether) was added dropwise with stirring during 45 min (N_2). Two layers were formed. The reaction mixture was stirred for another 2 hr at the same temp and then left aside at room temp (20–25°) overnight (12 hr). Finally, the reaction mixture was gently refluxed (4 hr) and then worked up in the usual manner with HCl aq (1:1; 120 ml). The ether soln was washed with $Na_2S_2O_3$ aq (15%, 100 ml × 4), water (50 ml × 2), satd $NaHCO_3$ aq (50 ml × 2), brine and dried (Na_2SO_4). The solvent was flashed off and the residue (16 g), consisting of VI and the unchanged ester (V) refluxed (6 hr) with ethanolic KOH (12 g KOH in 120 ml 95% EtOH). Most of the EtOH was removed from a steam-bath, the residue cooled, diluted with water (50 ml) and extracted with ether (50 ml × 4) to remove any neutral product. The aqueous alkaline soln was acidified (pH 2; HCl aq, 1:1) and the whole mixture heated on a steam bath for 2 hr to complete lactonization. The product was next taken up in ether (100 ml × 4), which was extracted with satd $NaHCO_3$ aq (50 ml × 3) to remove acidic material (4·6 g, essentially IV). The ether soln was next washed with brine, dried and freed of solvent to give crude VI, which was distilled: b.p. 147–148°/1·75 mm, n_D^{30} 1·5200, yield 9·2 g; IR spectrum: C=O 1775 cm^{-1}; 1,4-disubstituted benzene 1515, 1217, 1170, 1081, 1055, 1020 and 840 cm^{-1}. (Found: C, 76·90; H, 8·35. $C_{14}H_{18}O_2$ requires: C, 77·03; H, 8·31%).

γ-(p-*Cumyl*)-*n-valeric acid* (VII). The above lactone (2·12 g), gl AcOH (20 ml), 10% Pd-C (0·5 g) and aqueous perchloric acid (60%, 0·2 ml) were mixed and shaken, at room temp (27°) and press (712 mm), in an atmosphere of H_2 till one mole equiv of H_2 had been consumed (2 hr). The reaction mixture was worked up with ether in the usual manner and the ether soln. separated by satd $NaHCO_3$ aq into a neutral (less than 0·2 g) and acid fraction (2 g); the latter was distilled to give pure VII (1·92 g) as a viscous liquid, b.p. 147°/1 mm, n_D^{30} 1·5048; IR spectrum: COOH 2935, 1695 cm^{-1}.

4-*Methyl*-7-*isopropyltetralone* (VIII).[15] The above acid (1 g) in dry thiophene-free C_6H_6 (5 ml) was converted into the acid chloride by PCl_5 (1 g, covered with 5 ml of C_6H_6) in the usual manner. The benzene soln containing the acid chloride was chilled (~ −5°) and anhyd $SnCl_4$ (2 ml in 2 ml of C_6H_6) added in one lot and the mixture swirled for 5 min. The reaction mixture was left aside as such for 1 hr and then poured onto crushed ice and HCl aq (conc 20 ml) and worked up with ether to give the desired tetralone, b.p. 113°/1 mm, n_D^{30} 1·5390, yield 0·78 g; IR spectrum: C=O 1695 cm^{-1}; benzene ring 1618, 1570, 1497, 1193, 1170, 1020, 918, 840 and 812 cm^{-1}. 2,4-*Dinitrophenylhydrazone*, m.p. 188–189° (Found: N, 14·4. $C_{20}H_{24}O_4N_4$ requires: N, 14·58%).

1-*Methyl*-6-*isopropylnaphthalene* (IX). The above tetralone (0·872 g) in dry ether (40 ml) was reduced with LAH (0·2 g) in ether (50 ml) at 0° during 12 hr and then worked up with ice water (10 ml) followed by sodium potassium tartrate aq (10%, 15 ml) to yield ultimately 0·85 g of crude carbinol. This was dehydrated by mixing with freshly fused and powdered $KHSO_4$ (100 mg) and distilling at 190–200°/2·5 mm to furnish 0·67 g of dialin, which was used as such in the next step.

The above dialin (662 mg) was mixed with finely powdered S (120 mg) and heated at 200 ± 5° for 2 hr under slightly reduced press (500 mm). The product was directly distilled off and then redistilled over freshly precipitated Cu powder (200 mg). The distillate was dissolved in EtOH and treated with TNB to give, after recrystallization (EtOH), silky, golden yellow needles (537 mg) of the TNB complex, m.p. 123–124°. (Found: N, 10·65. $C_{20}H_{19}O_6N_3$ requires: N, 10·58%).

1-Methyl-6-isopropylnaphthalene (IX) was obtained by regeneration from its TNB complex over Al_2O_3 (basic/grade I), in nearly quantitative yield, as an oil, b.p. 138°/4 mm, n_D^{30} 1.578; IR spectrum (strong bands): 1460, 1385, 877, 820, 787 and 758 cm^{-1}. (Found: C, 91·49; H, 8·59. $C_{14}H_{16}$ requires: C, 91·25; H, 8·75%).

Synthesis of 1,6-*dimethyl*-7-*ethylnaphthalene* (X)

O-*Tolylacetic acid.* O-Methylbenzyl bromide[16] (66·5 g) on being refluxed (24 hr) with KCN (82 g, dissolved in minimum amount of H_2O) in EtOH (1800 ml) and usual work up, yielded 34 g of *o*-tolylacetonitrile, which when hydrolysed (15 hr) with KOH (22 g in 22 ml of H_2O) ethyleneglycol (220 ml) gave *o*-tolylacetic acid (38 g), m.p. 88–89°. (Lit.[17], m.p. 88–89°); PMR spectrum: Ar-C$\underline{H}_3$, 3H singlet at 140 c/s; Ar-C$\underline{H}_2$-COOH, 2H singlet at 256 c/s; aromatic protons, 4H singlet at 429 c/s; COO$\underline{H}$ singlet at 730 c/s.

O-*Methylbenzlethyl ketone* (XII). The above acid (16 g) was converted into its chloride by treatment with PCl_5 (22 g) in C_6H_6 (100 ml) in the usual fashion and purified by distillation, b.p. 126°/28 mm.

A soln of Et_2Cd in 200 ml of C_6H_6 was prepared from Mg (1·98 g), EtBr (8·9 g) and anhydrous $CdCl_2$ (8 g) in the usual manner.[18] To this a soln of the above acid chloride (10·8 g) in C_6H_6 (75 ml) was introduced with stirring during 0·5 hr and the mixture heated under reflux for 1 hr. The reaction mixture was cooled (0°) and treated first with ice-water (20 ml) and then H_2SO_4 aq (20%, 150 ml). The C_6H_6 phase was removed, aq. phase extracted with benzene (50 ml × 3) and, the combined C_6H_6 extracts washed with water, brine and dried (Na_2SO_4). The solvent was flashed off and the residue (9·8 g) distilled to furnish pure XII (6·4 g), b.p. 95°/3·5 mm; IR spectrum: C=O 1724 cm^{-1}; PMR spectrum: Ar-C$\underline{H}_3$, 3H singlet at 133 c/s; COC$\underline{H}_2$CH$_3$, 2H quartet centred at 141 cps, J = 7 c/s; Ar-C$\underline{H}_2$-CO-, 2H singlet at 216 c/s. 2,4-*Dinitrophenylhydrazone*, m.p. 137–138°. (Found: N, 16·7. $C_{17}H_{18}O_4N_4$ requires: N, 16·37%).

Ethyl α-*methyl*-β-*hydroxy*-β-(*o*-*methylbenzyl*)-*n*-*valerate* (XIII). This condensation was patterned after the general procedure of Bachmann and Wendler.[19] A mixture of the above ketone (15 g), activated Zn wool (6·45 g), dry C_6H_6 (50 ml), dry ether (50 ml) and a part (one fifth) of ethyl α-bromopropionate (25·2 g) was heated just to boiling and the reaction initiated by adding a crystal of iodine. When the reaction began, the heat source was removed and the rest of bromoester introduced at such a rate (1 hr) the reaction mixture refluxed gently. When the reaction was subsiding, another addition of Zn wool (1 g) was made and the mixture, heated on a steam-bath for 2 hr. The product was cooled, treated with gl AcOH (15 ml) and then diluted with water (50 ml). The organic phase was removed, aqueous portion extracted with ether (25 ml × 3), and the combined organic extracts washed with water, aqueous ammonia (2%; 25 ml × 3) and dried. Solvent was removed and the residue fractionated to give the required XIII as a thick liquid (19·8 g), b.p. 148°/2·5 mm; IR spectrum: OH 3450 cm^{-1}; C=O 1730 cm^{-1}. (Found: C, 72·35. H, 8·77. $C_{16}H_{24}O_3$ requires: C, 72·69; H, 9·15%).

Ethyl α-*methyl*-β-(*o*-*methylbenzyl*)-*n*-valerate (XV). The ester XIII (7·43 g) and formic acid (98%, 25 ml) were mixed and heated under anhydrous conditions on a steam-bath, with occasional swirling for 90 min. The reaction mixture was worked up with ether in the usual manner and the crude product fractionated to give after a forerun (0·5 g) of ketone XII (retrogression), a mixture of unsaturated esters (XIV; 5·4 g), b.p. 113–114°/1 mm.

The above product (3·8 g) was hydrogenated in EtOH (50 ml) containing AcOH (1 ml) over 10% Pd-C (0·5 g) at 25° and 710 mm press till one mole equiv of H_2 had been consumed. Usual work up gave a product which was distilled to give XV (3·8 g), b.p. 118–119°/1·5 mm; IR spectrum: C=O 1730 cm^{-1}.

2,5-*Dimethyl*-3-*ethyltetralone* (XVI). The above saturated ester (1 g) was mixed with PPA (from 5 g of P_2O_5 and 3 ml of 85% H_3PO_4) and heated for 1 hr on a steam-bath under anhyd conditions. The reaction mixture was worked up in the usual manner to give after distillation the required tetralone (755 mg), b.p. 116°/1·5 mm; IR spectrum: C=O. (Found: C, 82·84; H, 9·15. $C_{14}H_{18}O$ requires: C, 83·12; H, 8·97%).

1,6-*Dimethyl*-7-*ethylnaphthalene* (X). The above tetralone (750 mg) was reduced with LAH (150 mg), as described earlier for VIII. The crude carbinol was heated with I_2 (25 mg) on a waterbath at 95° for 1 hr. The product was worked up in the usual manner[20] to give dialin (440 mg), which was mixed with finely divided S (70 mg) and heated at 200 ± 5° for 2 hr under slightly reduced press (500 mm). The reaction mixture was worked up as described for IX and the naphthalene complexed with TNB to furnish yellow needles (430 mg), m.p. 124–125°. (Found: N, 10·80. $C_{20}H_{19}O_6N_3$ requires: N, 10·58%). The hydrocarbon was regenerated from the TNB complex over Al_2O_3; IR spectrum (strong bands): 1445, 882, 871, 790 and 755 cm^{-1}. (Found: C, 90·97; H, 8·56. $C_{14}H_{16}$ requires: C, 91·25; H, 8·75%).

Condensation of cumene with ethyl allylacetate

Condensation of cumene with ethyl allylacetate was carried out according to the directions of Mukherji *et al.*[6] and the product hydrolysed, as described by these authors, to give the alleged 'γ-(*p*-cumyl)-n-valeric acid'. This acid (100 mg) was mixed with conc HNO_3 (1 ml) and water (2 ml) and heated in a sealed tube at 190–200° for 15 hr. The product was evaporated to dryness (steambath) and the residue freed of HNO_3 by repeated evaporations with water. The residue (40 mg), thus obtained, was washed with $CHCl_3$ and the insoluble part (10·7 mg) identified as terephthalic acid[21] (m.p. > 295°; Me ester, m.p. 139–140°). The

chloroform soluble part was converted into its Me ester (CH_2N_2), m.p. 65–66°, which was identified as methyl isophthalate[21] by comparison (m.p., mixed m.p.) with an authentic sample.

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