[Contribution from the Central Research Laboratory of the General Aniline and Film Corporation]

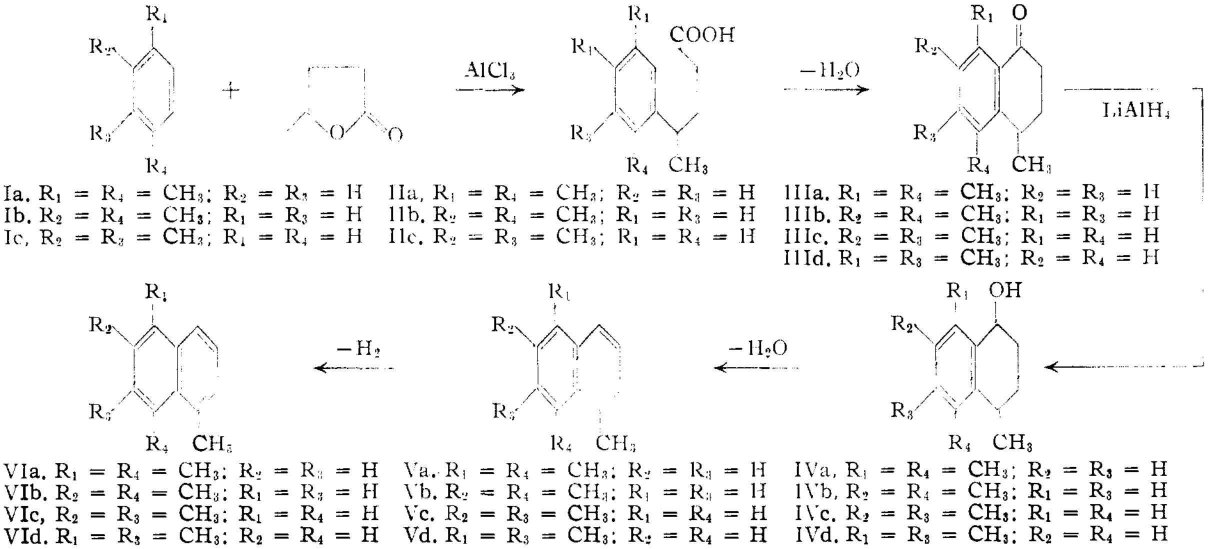
The Friedel–Crafts Reaction with γ-Valerolactone. I. The Synthesis of Various Polymethylnaphthalenes

By William L. Mosby

γ-Valerolactone has been condensed with each of the isomeric xylenes, and the resulting 4-(dimethylphenyl)-pentanoic acids were cyclized to trimethyl-1-tetralones in good yield. Cyclization of 4-(2,4-dimethylphenyl)-pentanoic acid using polyphosphoric acid was accompanied by a rearrangement resulting in 4,6,8-trimethyl-1-tetralone whereas cyclization of the corresponding acid chloride with stannic chloride gave the expected 4,5,7-trimethyl-1-tetralone. The four trimethyl-1-tetralones were converted to four known trimethylnaphthalenes and to three tetramethylnaphthalenes, two of which are new. Durene was condensed with γ-valerolactone and the resulting pentanoic acid was cyclized to 4,5,6,7,8-pentamethyl-1-tetralone. From this tetralone were prepared 1,2,3,4,5-pentamethylnaphthalene and 1,2,3,4,5,8-hexamethylnaphthalene.

Although the reaction of several lactones with benzene and toluene in the presence of aluminum chloride was described by Eijkmann as early as 1904,[1] little application has been made of the reaction in the synthesis of aromatic systems. Arnold, Buckley and Richter[2] have used the reaction to prepare 4,4-dimethyltetralone, and the reaction of δ-dichloro-γ-valerolactone with benzene was studied by Beyer.[3] A brief reference to the preparation of γ-phenylbutyric acid from γ-butyrolactone has also appeared.[4]

As the preceding syntheses afforded satisfactory yields, the following syntheses of trimethylnaphthalenes were attempted (Fig. 1).



Ia. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
Ib. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
Ic. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$

IIa. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
IIb. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
IIc. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$

IIIa. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
IIIb. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
IIIc. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$
IIId. $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

VIa. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
VIb. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
VIc. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$
VId. $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

Va. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
Vb. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
Vc. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$
Vd. $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

IVa. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
IVb. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
IVc. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$
IVd. $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

Fig. 1.

Valerolactone was condensed with the appropriate xylene using an extra mole of xylene as solvent. Other standard Friedel–Crafts solvents such as nitrobenzene, chlorobenzene and carbon bisulfide were distinctly inferior. Good yields of pure xylylvaleric acids could be obtained if the reaction mixture was hydrolyzed immediately after the evolution of hydrogen chloride subsided. If the reaction mixture was heated longer than necessary or allowed to stand, varying amounts of trimethyl-1-tetralone were obtained from partial cyclization of the xylylvaleric acid. This suggests that additional aluminum chloride might effect cyclization at this stage, although this was not tried. In the case of γ-methyl-γ-phenylvaleric acid,[2] where the two γ-methyl groups would favor ring closure, such a cyclization was successful. Cyclization was effected by treating the xylylvaleric acids with "polyphosphoric acid" or "phospholeum."[5] In two instances the xylylvaleric acid was converted to the acid chloride and cyclized in almost quantitative yield with stannic chloride.

Reduction of the tetralones with lithium aluminum hydride gave high yields of the corresponding tetralols. The physical properties of these tetralols suggest that each may well be a pure isomer, but their stereochemical configuration was not investigated. The tetralols were readily converted to the corresponding dihydronaphthalenes by heating with a trace of iodine. Aromatization of the dihydronaphthalenes with sulfur or selenium gave good yields of the corresponding naphthalenes, but considerable purification was required. Therefore, in spite of the loss due to disproportion of the dihydronaphthalene,[6] aromatization was affected with palladium–charcoal. In this fashion 1,4,5-

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(1) J. F. Eijkmann, *Chem. Weekblad*, **1**, 421 (1904); *Chem. Zentr.*, **75**, I, 1416 et seq. (1904).

(2) R. T. Arnold, J. S. Buckley and J. Richter, This Journal, **69**, 2322 (1947).

(3) H. Beyer, *Ber.*, **70**, 1101 (1937).

(4) F.I.A.T. Review of German Science, "Preparative Organic Chemistry," Vol. I, 1948, p. 53.

(5) H. R. Snyder and F. X. Werber, This Journal, **72**, 2965 (1950).

(6) P. A. Plattner, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 52.

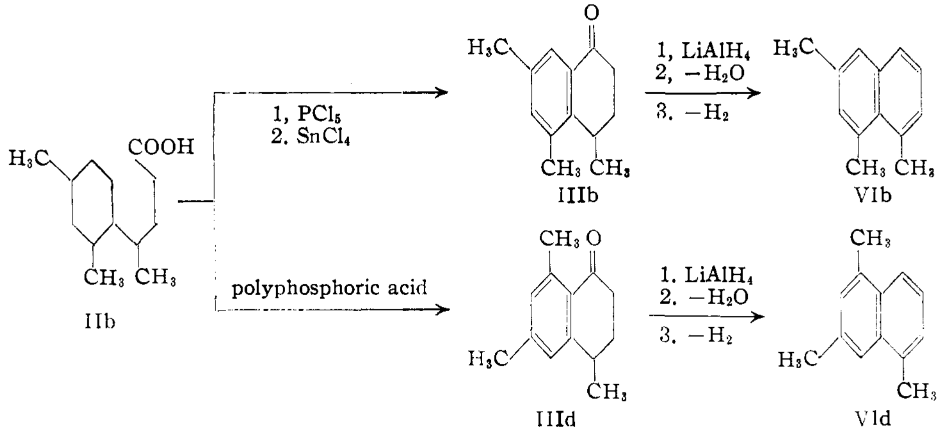

Fig. 2.

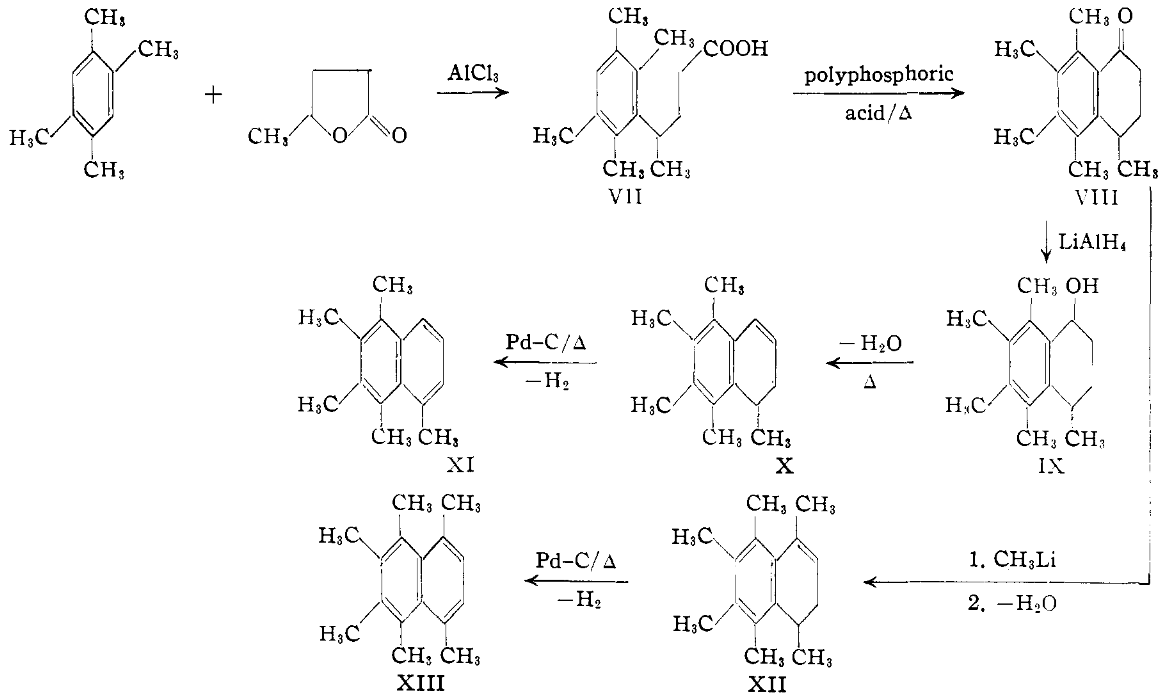

Fig. 3.

(VIa) and 1,6,7-trimethylnaphthalenes (VIc) were obtained pure in about 60% yield.

The trimethylnaphthalene obtained by this method from *m*-xylene was found to be (VId) [the 1,3,5- instead of the expected 1,3,8-isomer (VIb)]. arising from the rearrangement of 4-(2,4-dimethylphenyl)-pentanoic acid (IIb) on treatment with polyphosphoric acid. If, however, (IIb) was converted to the acid chloride, and this cyclized by treatment with stannic chloride, the normal 4,5,7-trimethyl-1-tetralone (IIIb) was obtained (see Fig. 2).

The migration of alkyl groups under the influence of acid catalysts has been studied extensively (refs. 7–10 *inter alia*). The rearrangement of (IIb) on treatment with polyphosphoric acid is of interest in contrast to the observation[10] that 4-(2,4-dimethylphenyl)-butanoic acid apparently does not rearrange on treatment with sulfuric acid, but gives 5,4-dimethyl-1-tetralone. It seems likely that the rearrangement of (IIb) involves the migration of the valeric acid moiety to a position of symmetry in the xylene ring, followed by cyclization. This explanation is supported by the observation that the tetralone (IIIb) is unchanged by heating with polyphosphoric acid. It would seem, however, that under favorable circumstances[8] a methyl group may be displaced by hot polyphosphoric acid. since the cyclization treatment of 4-(2,3,5,6-tetramethylphenyl)-pentanoic acid (VII) afforded a mixture of products containing about 30% of (VIII). This rearrangement and the subsequent reactions are shown in Fig. 3.

To obtain the desired tetramethylnaphthalenes. the trimethyltetralones (IIIa–IIId) were treated with a slight excess of methyl lithium. In each case some of the tetralone was recovered, presumably through enolization. The following table shows the per cent. of product obtained and tetralone recovered in each case.

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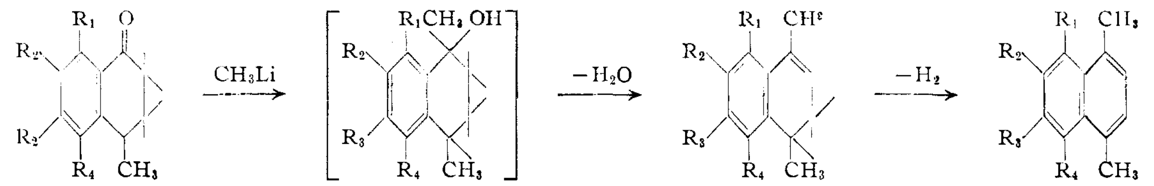
[7] R. T. Arnold and R. A. Barnes, THIS JOURNAL, **66**, 960 (1944).

[8] R. R. Aitkin, G. M. Badger and J. W. Cook, *J. Chem. Soc.*, 331 (1950).

[9] G. Baddeley, *ibid.*, 233 (1944).

[10] F. Krollpfeiffer and W. Schäfer, *Ber.*, **56**, 620 (1923).



IIIa. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
IIIb. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
IIIc. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$
IIId. $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

XVa. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
XVb. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
XVc. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$
XVd. $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

XVIa. $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
XVIb. $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
XVIc. $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$

Fig. 4.

1-Tetralone	Addition product obtained, %	Tetralone recovered, %
4,5,8-Trimethyl-	64.5	32
4,5,7-Trimethyl-	75	21
4,6,8-Trimethyl-	84	12
4,6,7-Trimethyl-	85	10

The tertiary alcohols resulting from this reaction dehydrated spontaneously during isolation so that dihydrotetramethylnaphthalenes were actually the products isolated. Dehydrogenation with palladium–charcoal afforded the tetramethylnaphthalenes.

The infrared spectrograms of the various methylnaphthalenes are shown in the accompanying curves.

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Experimental[11]

The γ-valerolactone was obtained from the Monsanto Chemical Company and redistilled once. The *m*-xylene was from Eastman Kodak and the *o*- and *p*-xylenes were obtained from the Oronite Chemical Company. "Polyphosphoric Acid" of the Victor Chemical Company and Monsanto's "Phospholeum" were used interchangeably in the cyclizations.

General Method for the Synthesis of the 4-(Dimethylphenyl)-pentanoic Acids IIa, IIb and IIc.—A mixture of 212 g. (2.00 moles) of the appropriate xylene and 100 g. (1.00 mole) of γ-valerolactone was placed in a three-necked flask equipped with a reflux condenser and HCl gas trap, a stainless steel Hershberg-type stirrer, and an addition tube for aluminum chloride. To this stirred mixture was added in portions, 140 g. (1.05 moles) of aluminum chloride (C.P. granular), allowing each portion to dissolve before adding the next. The temperature rose and by the end of the aluminum chloride addition the xylene gently refluxed. This refluxing was maintained for a few minutes by external heating, until the evolution of hydrogen chloride largely ceased. If at this point the heating was prolonged, or the mixture allowed to stand, some of the product cyclized to the tetralone under the influence of the strongly acidic medium. To obtain the acids, therefore, it is desirable to hydrolyze the reaction mixture at once by pouring onto ice and dilute hydrochloric acid. The product was extracted with ether, washed with dilute hydrochloric acid, then with water and dried over anhydrous magnesium sulfate. The ether and excess xylene were removed and the product was vacuum distilled. Any tetralone (formed by cyclization of the acid) present distilled first.

According to this procedure, the following acids were prepared:

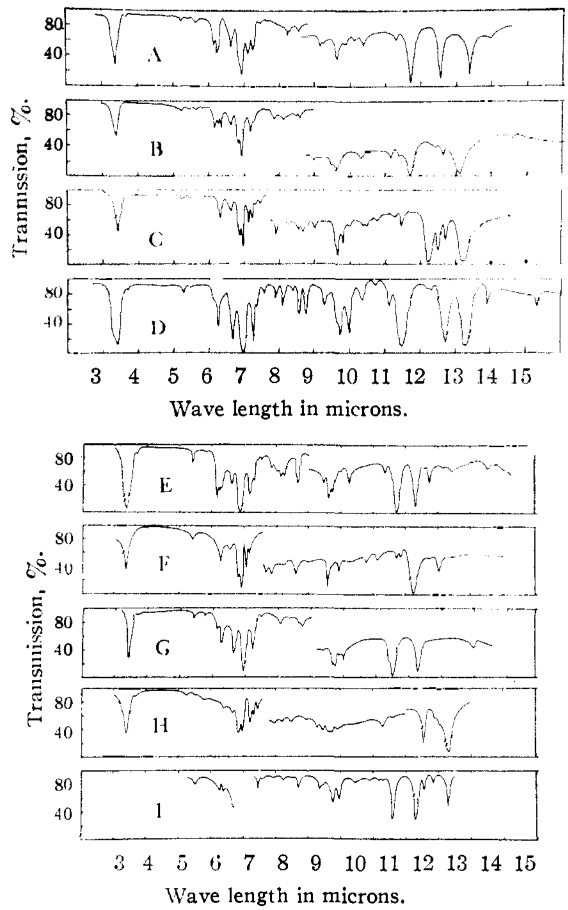

Fig. 5.—Curves A, B, C, E, F, G, H were obtained from a carbon tetrachloride solution of the compound in the 2.0–9.0 μ region, and from a nujol mull in the 9.0–16.0 μ region: (A) 1,3,5-Trimethylnaphthalene; (B) 1,3,8-Trimethylnaphthalene; (C) 1,4,5-Trimethylnaphthalene; (E) 1,4,5,7-Tetramethylnaphthalene; (F) 1,4,5,8-Tetramethylnaphthalene; (G) 1,4,6,7-Tetramethylnaphthalene; (H) 1,2,3,4,5-Pentamethylnaphthalene. Curve (D) is from liquid 1,6,7-trimethylnaphthalene, and Curve (I) from a nujol mull of 1,2,3,4,5,8-hexamethylnaphthalene.

4-(2,5'-Dimethylphenyl-)-pentanoic acid (IIa), yield 96.5 g. (47%), b.p. 126–128° (0.15 mm.) which solidified to white crystals. Had the fore-run and residues from the distillation been worked over, the yield of acid would have been higher. A sample of the acid, recrystallized once from petroleum ether (b.p. 20–40°), had m.p. 109–111° (lit. 113.5°).[12] The acid chloride is described later. The amide, after recrystallization from ethyl ether by the addition of ligroin melted at 94.5–95.5°. The ethyl ester, prepared from the acid chloride in 78% yield, was obtained as a colorless liquid, b.p. 117–118° (0.9 mm.), $n^{25}\text{D}$ 1.4953. Calcd. for $C_{15}H_{22}O_2$: C, 76.9; H, 9.40. Found: C, 76.94; H, 9.54. It is of interest that attempts to prepare this ester in the customary fashion by refluxing the acid with excess

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[11] Melting points were taken in Pyrex capillaries in a Hershberg apparatus using Anschütz thermometers.

[12] L. Ruzicka and L. Ehmann, *Helv. Chim. Acta*, **15**, 140 (1932).

ethanol and a little *p*-toluenesulfonic or sulfuric acid, were unsuccessful.

4-(2,4-Dimethylphenyl)-pentanoic acid (IIb), yield 172 g. (84%) of crude acid, b.p. up to 140° (0.4 mm.) which on redistillation gave 149.3 g. (73%), b.p. 113–114° (0.05 mm.) (lit. 175° (9 mm.)),[13a] $n^{25}\text{D}$ 1.5155; 170–173 (3 mm.).[13b]

4-(3,4-Dimethylphenyl)-pentanoic acid (IIc), yield 108 g. (53%), b.p. 122–127° (0.05 mm.) (lit. b.p. 146–147° (1 mm.)).[14] $n^{25}\text{D}$ 1.5187, accompanied by 28.3 g. (15%) of the corresponding tetralone.

Cyclization with H_3PO_4:P_2O_5 Mixtures (IIIa, IIIc, IIId).—If the tetralone was the desired product, the xylylvaleric acid from hydrolysis of the Friedel–Crafts reaction was not vacuum distilled. The product was simply extracted with ether; the ether extracts were washed with dilute hydrochloric acid, water, then dried and stripped of solvents. The crude acid was added with stirring directly to about three or four times its weight of "Polyphosphoric Acid" or "Phospholeum" which had been pre-heated to about 100°. The organic acid dissolved with the evolution of heat forming a deep brown solution. The temperature rose to about 130–140°, and was kept there (by external heating if necessary) while the mixture was stirred for several minutes. The mixture was then poured into ice-water, the tetralone extracted with ether and the combined ether extracts were washed with dilute sodium carbonate solution, then water, and dried over anhydrous magnesium sulfate. The ether was removed and the residue vacuum distilled to yield the tetralone, which was redistilled for final purification.

As was mentioned earlier, 4-(2,4-dimethylphenyl)-pentanoic acid, when subjected to this treatment gave 4,6,8-trimethyl-1-tetralone instead of the expected 4,5,7-trimethyl-1-tetralone. This latter compound was obtained by the action of stannic chloride on 4-(2,4-dimethylphenyl)-pentanoyl chloride.

4,5,8-Trimethyl-1-tetralone (IIIa) was obtained in 66% yield, b.p. 91–94° (0.16 mm.), $n^{25}\text{D}$ 1.5560. Redistillation gave b.p. 103° (0.2 mm.) (lit. 138° (12 mm.)),[15] $n^{26}\text{D}$ 1.5590. Calcd. for $C_{13}H_{16}O$: C, 83.0; H, 8.51. Found: C, 82.9; H, 8.38.

The oxime melted at 109.2–109.7° after recrystallization twice from methanol. Calcd. for $C_{13}H_{17}NO$: C, 76.9; H, 8.43; N, 6.90. Found: C, 76.9; H, 8.34; N, 7.04.

The semicarbazone, after two recrystallizations from ethanol melted at 227–227.5°.

The 2,4-dinitrophenylhydrazone, recrystallized from ethyl acetate melted at 227–228°. Calcd. for $C_{19}H_{20}N_4O_4$: C, 62.0; H, 5.44; N, 15.21. Found: C, 61.42; H, 5.71; N, 15.29.

4,6,7-Trimethyl-1-tetralone (IIIc) was obtained in 70% yield, b.p. 95–105° (0.15 mm.), $n^{25}\text{D}$ 1.5559. Redistillation gave a 55% yield of a product b.p. 94–96° (0.1 mm.), $n^{25}\text{D}$ 1.5600. Calcd. for $C_{13}H_{16}O$: C, 83.0; H, 8.51. Found: C, 83.0; H, 8.52. In spite of the apparent purity of this tetralone, it probably contains traces of isomeric trimethyltetralones (arising from traces of isomers in the *o*-xylene used) since it is liquid at room temperature and Campbell and Soffer[14] report their product to melt at 30°.

The oxime recrystallized thrice from methanol melted at 103–104°. Calcd. for $C_{13}H_{17}NO$: C, 76.9; H, 8.38; N, 6.90. Found: C, 76.7; H, 8.39; N, 6.79.

The semicarbazone melted at about 234–235° dec. with preliminary darkening. It was probably impure, but recrystallization from ethanol failed to improve the melting point (lit. 238° dec.).[14] Calcd. for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.75; N, 17.13. Found: C, 68.78; H, 7.55; N, 17.04.

The 2,4-dinitrophenylhydrazone after recrystallization from ethyl acetate melted at 240–241°. Calcd. for $C_{19}H_{20}N_4O_4$: C, 62.0; H, 5.44; N, 15.21. Found: C, 61.6; H, 5.63; N, 15.23.

4,6,8-Trimethyl-1-tetralone (IIId) was formed in 77% yield, b.p. 95–100° (0.25 mm.), $n^{25}\text{D}$ 1.5574. Redistillation of this material gave a 70% over-all yield of product, b.p. 92–94° (0.15 mm.), $n^{26}\text{D}$ 1.5576. Calcd. for $C_{13}H_{16}O$: C, 83.0; H, 8.51. Found: C, 82.8; H, 8.62.

The oxime, after two recrystallizations from methanol melted at 132.5–133.5°. Calcd. for $C_{13}H_{17}NO$: C, 76.9; H, 8.38; N, 6.90. Found: C, 77.10; H, 8.21; N, 6.80.

The semicarbazone melted at 219–221° after two recrystallizations from methanol. Calcd. for $C_{14}H_{19}ON_3$: C, 68.5; H, 7.75; N, 17.13. Found: C, 68.1; H, 8.2; N, 17.10.

The 2,4-dinitrophenylhydrazone was recrystallized twice from ethyl acetate, when it melted at 230.8–231.5°. Calcd. for $C_{19}H_{20}O_4N_4$: C, 62.0; H, 5.44; N, 15.21. Found: C, 61.9; H, 5.43; N, 15.3.

Cyclization with Stannic Chloride (IIIa and IIIb). **4,5,8-Trimethyl-1-tetralone** (IIIa).—The acid chloride was prepared from (IIa) by means of phosphorus pentachloride or thionyl chloride in chloroform. When pure, 4-(2,5-dimethylphenyl)-pentanoyl chloride is a colorless liquid, b.p. 124–125° (4 mm.), (lit. 144–145° (12 mm.)),[13] $n^{26}\text{D}$ 1.5178. To a cooled (5°) solution of 300 g. (1.33 moles) of pure acid chloride dissolved in 100 ml. of dry thiophene-free benzene, was added slowly with shaking, a cold (5°) solution of 315 ml. (about 2.75 moles) of stannic chloride in 300 ml. of dry thiophene-free benzene. Considerable heat and hydrogen chloride were evolved, and a thick pale yellow crystalline slurry resulted. The reaction was left in the ice-bath for ten minutes, then poured onto ice and hydrochloric acid and let stand one hour with occasional stirring. At the end of this time the benzene layer was separated, washed with water and 5% sodium hydroxide solution, dried over anhydrous magnesium sulfate, and vacuum stripped of solvent. Vacuum distillation of the residue gave 240 g. (95.6% yield) of colorless 4,5,8-trimethyl-1-tetralone, b.p. 103–105° (0.25 mm.).

4,5,7-Trimethyl-1-tetralone (IIIb).—A mixture of 115 g. (0.55 mole) of phosphorus pentachloride and 200 ml. of dry chloroform was placed in a 1-liter three-necked flask having an all-glass paddle stirrer, an addition funnel and condenser with a trap for hydrogen chloride. To this stirred suspension was added slowly a solution of 103 g. (0.50 mole) of 4-(2,4-dimethylphenyl)-pentanoic acid in 175 ml. of chloroform. The phosphorus pentachloride dissolved, and the mixture needed little external heating to maintain reflux. When all the acid had been added, the solution was stirred and warmed 1/2 hour, then vacuum stripped of chloroform and phosphorus oxychloride. The residue was dissolved in 200 ml. of thiophene-free benzene and cooled to 0° in an ice-bath. To this was added a chilled solution of 260 g. (1.0 mole) of stannic chloride in 200 ml. of thiophene-free benzene. Considerable heat and hydrogen chloride were evolved. After the mixture had stood for about 15 minutes in an ice-bath it was hydrolyzed by the addition of ice. The benzene layer was washed well with dilute hydrochloric acid, dilute sodium carbonate solution and dried over anhydrous magnesium sulfate. Vacuum distillation gave 86.3 g. (92% yield from the acid) of product, b.p. 78–79° (0.005 mm.), (lit. b.p. 174–176° (20 mm.)),[13a] 155–159° (9 mm.)[13b]; $n^{25}\text{D}$ 1.5575. Calcd. for $C_{13}H_{16}O$: C, 83.0; H, 8.51. Found: C, 82.9; H, 8.40.

The oxime, after two recrystallizations from methanol melted at 131.8–132.8°. Calcd. for $C_{13}H_{17}ON$: C, 76.9; H, 8.38; N, 6.90. Found: C, 76.7; H, 8.45; N, 6.71.

The semicarbazone melted at 221.6–222.4°, (lit. m.p. 220–222°)[13] after one recrystallization from ethanol. Calcd. for $C_{14}H_{19}ON_3$: C, 68.5; H, 7.75; N, 17.23. Found: C, 68.6; H, 7.94; N, 17.23.

The 2,4-dinitrophenylhydrazone after recrystallization once from ethyl acetate and once from xylene melted at 232.5–233.5° (lit. m.p. 231–232°[13b]). Calcd. for $C_{19}H_{20}O_4N_4$: C, 62.0; H, 5.44; N, 15.21. Found: C, 61.71; H, 5.53; N, 14.9.

The $LiAlH_4$ Reduction of the Trimethyl-1-tetralones.—A three-necked flask with stirrer, addition funnel (pressure-equilizing type) and condenser, was heated while passing through it a stream of dry nitrogen, and in it, when cool, a slurry of 3.5 g. (0.092 mole) of lithium aluminum hydride and 100 ml. of dry ether was prepared. To this stirred suspension was added dropwise, cooling of the flask in ice, a solution of 37.6 g. (0.20 mole) of the trimethyl-1-tetralone in 100 ml. of dry ether. When all of the tetralone had been added, the mixture was stirred at room temperature a few minutes then hydrolyzed (first with ether containing ethanol, then with about 2% hydrochloric acid). The water layer was separated and extracted with ether. The ether extract was combined with the ether layer and washed with 2% hydrochloric acid, then dilute sodium bicarbonate solu-

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(13) (a) I. Heilbron, L. Morris and D. G. Wilkinson, *J. Chem. Soc.*, 2537 (1930). (b) Dev, *Current Sci.*, **16**, 377 (1947); *J. Soc. Chem. Ind.*, **25**, 69 (1948).

(14) W. P. Campbell and M. D. Soffer, THIS JOURNAL, **64**, 417 (1942).

(15) L. Ruzicka and L. Ehmann, *Helv. Chim. Acta*, **15**, 140 (1932).

tion and dried over anhydrous magnesium sulfate. The ether was removed *in vacuo* and the residue vacuum distilled.

4,5,8-Trimethyl-1-tetralol (IVa) was obtained in 93.5% yield as a colorless liquid, b.p. 106–107° (0.1 mm.), (lit. b.p. 128° (12 mm.)),[15] $n^{25}\text{D}$ 1.5590. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.48. Found: C, 82.1; H, 9.6.

4,6,7-Trimethyl-1-tetralol (IVc), on distillation gave 68% yield of a colorless liquid, b.p. 112–113° (0.25 mm.), $n^{25}\text{D}$ 1.5527. On cooling in Dry Ice and trituration with ligroin it crystallized. Recrystallization from 20–40° petroleum ether gave material melting at 80–81°. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.48. Found: C, 82.2; H, 9.7.

4,6,8-Trimethyl-1-tetralol (IVd) formed in 91% yield, b.p. 106–107° (0.16 mm.), $n^{24}\text{D}$ 1.5506. On standing the product crystallized, m.p. 72–74°. Recrystallization from 20–40° petroleum ether gave material melting at 77.5–78.5°. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.48. Found: C, 82.2; H, 9.51.

4,5,7-Trimethyl-1-tetralol (IVb) was prepared in 84% yield, b.p. 106–107° (0.18 mm.), $n^{25}\text{D}$ 1.5520, and on trituration with ligroin it solidified. Two recrystallizations from cyclohexane gave a product melting at 108–109°. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.48. Found: C, 82.1; H, 9.30.

Dehydration of the Trimethyltetralols.—The trimethyl-1-tetralol (0.1–0.2 mole) was heated in a small Claisen flask with a very small crystal of iodine until the evolution of water ceased, then 0.5 g. of zinc dust was added and the product vacuum distilled.

1,4,5-Trimethyl-7,8-dihydronaphthalene (Va) was obtained in 91% yield from 4,5,8-trimethyl-1-tetralol (IVa). It is a colorless liquid, b.p. 82–84° (0.5 mm.), $n^{23}\text{D}$ 1.5660. Calcd. for $C_{13}H_{16}$: C, 90.8; H, 9.3. Found: C, 90.6; H, 9.3.

2,3,5-Trimethyl-7,8-dihydronaphthalene (Vc), was obtained in 93% yield from 4,6,7-trimethyl-1-tetralol (IVc) as a colorless liquid, b.p. 66–67° (0.15 mm.), $n^{20}\text{D}$ 1.5610. Calcd. for $C_{13}H_{16}$: C, 90.8; H, 9.3. Found: C, 90.6; H, 9.42.

1,3,5-Trimethyl-7,8-dihydronaphthalene (Vd), was prepared in 95% yield from 4,6,8-trimethyl-1-tetralol (IVd) as a colorless liquid, b.p. 77.5–80° (0.15 mm.), $n^{24}\text{D}$ 1.5606. Calcd. for $C_{13}H_{16}$: C, 90.8; H, 9.25. Found: C, 90.8; H, 9.10.

2,4,5-Trimethyl-7,8-dihydronaphthalene (Vb) was obtained in 90% yield from 4,5,7-trimethyl-1-tetralol (IVb) as a colorless liquid, b.p. 64–66° (0.15 mm.), $n^{24}\text{D}$ 1.5616. Calcd. for $C_{13}H_{16}$: C, 90.8; H, 9.3. Found: C, 90.8; H, 9.32.

Aromatization of the Dihydronaphthalenes.—A mixture of 19 g. of the dihydronaphthalene and 1.0 g. of 10% palladium-charcoal was placed in a long-necked flask and heated in a salt-bath at 260–280° until the evolution of hydrogen largely had ceased (1–4 hr.). The mixture was cooled, extracted with benzene, filtered from the charcoal, the benzene removed and the residue vacuum distilled. After a fore-run, presumably the tetrahydronaphthalene formed by disproportionation of the dihydro-compound, the product fraction was obtained in about 60% yield. In three of the four cases it was a solid and was purified by recrystallization two or three times from methanol.

1,4,5-Trimethylnaphthalene (VIa), b.p. 85–89° (0.15 mm.), on recrystallization from methanol melted at 59.6–60.6° (lit. 63°).[15,16] The **picrate** (one recrystallization from methanol) melted at 145–146° (lit. 144–145°[15], 146[16]), and the **styphnate** (recrystallized once from methanol) at 130–130.5° (lit. 129–130°).[15] The **trinitrofluorenone** derivative (TNF) crystallized in scarlet needles, m.p. 160.8–161.2° after one recrystallization from benzene.

2,3,5-Trimethylnaphthalene (VIc) was obtained as a liquid at room temperature (lit. liquid,[15,17] m.p. 25.3°[18]; 28°[16]) b.p. 84–86° (0.15 mm.) (lit. b.p. 138° (2 mm.)[15] and 285° (762 mm.)[16]). It yielded a **picrate** (one recrystallization from methanol), m.p. 124.5–125.2° (lit. 122°,[17] 122.5°,[15] 124°,[18] 125°[16]) and a **styphnate** (recrystallized once from methanol) m.p. 146.5–147° (lit. 146°,[15] 148°,[18] 148–149°,[17] 149°[16]) as well as a **trinitrofluorenone** derivative, m.p. 155–155.5° (recrystallized once from benzene).

1,3,5-Trimethylnaphthalene (VId) was obtained as white crystals, m.p. 46–47° after several recrystallizations from methanol (lit. 43°,[15] 47°[13]). It gave a **picrate** (recrystallized once from methanol) m.p. 141–141.6° (lit. 140°,[15] 141–142°[13]), a **styphnate**, m.p. 137.5–138° (recrystallized once from methanol) (lit. 136.5,[15] 138°[13]) and a **trinitrofluorenone** derivative, which, after recrystallization from benzene, melted at 160.4–161°.

2,4,5-Trimethylnaphthalene (VIb), b.p. 77–79° (0.005 mm.) crystallized from methanol in flat opaque white plates, m.p. 47.6–48.2° (lit. 48°[13]). As described by Heilbron and Wilkinson[13] this material liquefies when triturated with the isomeric 1,3,5-trimethylnaphthalene. Compound (VIb) formed a **picrate**, m.p. 125–125.5° (one recrystallization from methanol) (lit. 125°[13]); a **styphnate**, m.p. 139.5–140° (recrystallized once from methanol) (lit. 140.5°[13]) and a **trinitrofluorenone** derivative, m.p. 142.5–143° after one recrystallization from benzene.

Reaction of the Trimethyltetralones with Methyllithium.—A three-necked flask having a Hershberg stainless steel stirrer, reflux condenser and addition funnel (pressure equalizing type) was swept out well with dry nitrogen. In the flask were then placed 5.54 g. (0.785 mole) clean lithium metal wire and 250 ml. of anhydrous ether. The mixture was stirred and cooled to −10 to 0° and a solution of 57 g. (0.40 mole) of methyl iodide in 100 ml. of anhydrous ether was added dropwise over about a 1/2-hour period. The mixture was stirred until only traces of lithium remained undissolved (about an hour). To this cold solution of methyl lithium was then added directly, dropwise, a solution of 37.6 g. (0.20 mole) of the trimethyl-1-tetralone in 100 ml. of anhydrous ether. When all of the tetralone had been added the mixture was stirred about 1/2–3/4 hour at room temperature, then hydrolyzed by the addition of very dilute hydrochloric acid. The aqueous layer was extracted once with ether, this extract combined with the ether layer and washed with dilute hydrochloric acid, dilute sodium bicarbonate solution, dried over anhydrous magnesium sulfate and vacuum stripped of ether. In one experiment at this point crystals of the tertiary alcohol were obtained (*v.i.*) but the rest of the time the product was found to have dehydrated spontaneously to the dihydrotetramethylnaphthalene. The product was vacuum fractionated in a small Claisen flask to separate unreacted tetralone (from enolization) then redistilled from a small pellet of sodium metal.

1,4,5,8-Tetramethyl-1-tetralol.—In one experiment this material crystallized (about 30% yield) in the crude reaction product before vacuum distillation. Recrystallization twice from 20–40° petroleum ether gave large prisms, m.p. 93–95°. Calcd. for $C_{14}H_{20}O$: C, 82.4; H, 9.8. Found: C, 82.3; H, 9.8.

1,4,5,8-Tetramethyl-1,2-dihydronaphthalene (XVa) was obtained in 64.5% yield (based on tetralone added) together with 32% unreacted tetralone. Redistillation gave a product, b.p. 85–90° (0.05 mm.), $n^{25}\text{D}$ 1.5600. Calcd. for $C_{14}H_{18}$: C, 90.3; H, 9.68. Found: C, 90.13; H, 9.68.

1,4,5,7-Tetramethyl-1,2-dihydronaphthalene (XVd) formed in 84% yield, accompanied by 13% unreacted tetralone. It is a colorless liquid, b.p. 76–77° (0.10 mm.), $n^{25}\text{D}$ 1.5600. Calcd. for $C_{14}H_{18}$: C, 90.3; H, 9.68. Found: C, 90.1; H, 9.75.

1,4,6,7-Tetramethyl-1,2-dihydronaphthalene (XVc) was obtained in 75% yield (based on tetralone added) together with 21% unreacted tetralone. Compound (XVc) is a colorless liquid, b.p. 76–78° (0.15 mm.), $n^{24}\text{D}$ 1.5581. Calcd. for $C_{14}H_{18}$: C, 90.3; H, 9.68. Found: C, 90.4; H, 9.73.

1,4,6,8-Tetramethyl-1,2-dihydronaphthalene (XVb) was obtained in 85% yield (based on tetralone added) accompanied by 10% unreacted tetralone. It had b.p. 80–82° (0.08 mm.), $n^{25}\text{D}$ 1.5602. Calcd. for $C_{14}H_{18}$: C, 90.3; H, 9.68. Found: C, 90.4; H, 9.64.

Aromatization of the Dihydrotetramethylnaphthalenes.—A mixture of 10–25 g. of the dihydrotetramethylnaphthalene and 10% of its weight of 10% palladium–charcoal in a long-necked flask was heated in a salt-bath at 275–290° for 3–10 hours while bubbling through the mixture a stream of carbon dioxide. On cooling the product was extracted with benzene, filtered, stripped of solvent and vacuum distilled.

1,4,5,8-Tetramethylnaphthalene (XVIa).—From 17.5 g. of the dihydro-compound was obtained 9.3 g. of material, b.p. 95–100° (0.15 mm.), which solidified on cooling. Recrystallization from methanol and treatment with norite

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(16) E. deB. Barnett and F. G. Sanders, *J. Chem. Soc.*, 437 (1933).

(17) D. G. Wilkinson, *ibid.*, 1333 (1931).

(18) O. Kruber, *Ber.*, 73, 1174 (1940).

gave 8.7 g. (50% yield) of white crystals, m.p. 129–130°. Recrystallization from ethanol gave long white needles. m.p. 132–133° (lit. 131°[19]). It formed a **picrate** (orange needles), m.p. 154.6–155.4° (lit. 154°[19]), and a **styphnate**, m.p. 143.4–144.2° which appeared to decompose on recrystallization. The **trinitrofluorenone complex** (TNF) was more stable, and after two recrystallizations from benzene formed purple needles, m.p. 158–159°. Calcd. for $C_{27}H_{21}N_3O_7$: C, 64.9; H, 4.20; N, 8.40. Found: C. 64.99; H. 4.39: N, 8.30.

1,4,5.7-Tetramethylnaphthalene (**XVIb**) was obtained both from 1,4,5.7- and 1,4.6,8-tetramethyl-1.2-dihydronaphthalenes on dehydrogenation in 80–82% yield of material b.p. 90–93° (0.08 mm.). Recrystallization from methanol and treatment with norite gave 65–70% yield of white crystals, m.p. 56–57°. Calcd. for $C_{14}H_{18}$: C, 91.3; H. 8.7. Found: C. 91.3; H. 8.73. **The picrate**. after three recrystallizations from methanol gave long orange-red needles, m.p. 152.4–153.4°. Calcd. for $C_{20}H_{19}N_3O_7$: C. 58.1: H, 4.60; N. 10.18. Found: C, 58.06; H, 4.72: N. 10.16. The dark red **trinitrofluorenone complex** (TNF) melted at 152.8–153.4° after recrystallization from benzene. Calcd. for $C_{27}H_{21}N_3O_7$: C. 64.9; H, 4.20: N, 8.40. Found: C, 65.0: H. 4.18: N, 8.23.

1,4,6,7-Tetramethylnaphthalene (**XVIc**). was obtained in 96% crude yield (25.1 g. b.p. 91–97° (0.10 mm.), from 26.6 g. of the dihydro-compound). Recrystallization from methanol and treatment with norite gave 15 g. (57% yield) of white needles, m.p. 63–64°. Calcd. for $C_{14}H_{16}$: C, 91.3; H, 8.7. Found: C, 91.3: H, 8.7. **The picrate**, after two recrystallizations from methanol formed orange needles. m.p. 148–148.8°. Calcd. for $C_{20}H_{19}O_7N_3$: C, 58.1: H, 4.60: N. 10.18. Found: C, 58.08; H. 4.68; N, 10.10. **The trinitrofluorenone complex** (TNF) recrystallized from benzene in scarlet micro-prisms, m.p. 172.4–173.4°. Calcd. for $C_{27}H_{21}O_7N_3$: C, 64.9: H. 4.20; N, 8.40. Found: C. 65.12; H. 4.42; N, 8.23.

Reaction of Durene with γ-Valerolactone. 4,5,6,7.8-Pentamethyl-1-tetralone (**VIII**).—A mixture of 268 g. (2.0 moles) of durene (Standard Oil Development Corp.) and 100 g. (1.0 mole) of γ-valerolactone was heated and stirred in a three-necked 1-liter flask equipped with a reflux condenser and HCl gas trap and a solid-addition tube. To it was added portionwise 140 g. (1.05 moles) of anhydrous aluminum chloride. When all the aluminum chloride had been added the mixture was stirred and heated at 150° for a few minutes until the evolution of hydrogen chloride had almost stopped, then it was poured slowly, with stirring, into cold water containing a little hydrochloric acid. The green oil was extracted with ether. the combined extracts washed with a solution of sodium chloride in water containing a little hydrochloric acid, then with sodium chloride solution, and dried over anhydrous magnesium sulfate. The ether and excess durene were removed *in vacuo* (b.p. up to 110° (20–25 mm.)), leaving 211 g. of brown oil. To this was added 750 g. of "Phospholeum" and the mixture heated to 180° with constant stirring. when a brown homogeneous solution resulted. This was poured into water and the product extracted with ether. The combined ether extracts were washed with 5% sodium carbonate solution and dried with anhydrous magnesium sulfate. Vacuum distillation, after removal of the solvent. gave a small fore-run of durene, then 148 g. of pale yellow oil. b.p. 105–125° (0.10–0.15 mm.) which solidified on standing. Two recrystallizations from 100 ml. (each) of ethanol gave 77 g. of white crystals. m.p. 85–87°. A sample recrystallized twice more from methanol melted at 90–90.6°. Calcd. for $C_{15}H_{20}O$: C, 83.34; H. 9.25. Found: C, 83.31: H, 9.15. **The oxime**, after recrystallization from methanol, melted at 187.5–188.6°. Calcd. for $C_{15}H_{21}ON$: C, 77.88: H. 9.08; N. 6.06. Found: C. 78.79; H, 9.26; N. 5.88. **The 2.4-dinitrophenylhydrazone** was recrystallized first from xylene then from ethyl acetate. when it melted at 237.4–238.2°. Calcd. for $C_{21}H_{24}O_4N_4$: C. 63.6; H, 6.06; N. 14.13. Found: C, 63.63; H, 5.98; N. 13.97.

4,5,6.7,8-Pentamethyl-1-tetralol (**IX**).—To a cooled (ice) slurry of 1.75 g. (0.046 mole) of lithium aluminum hydride and 100 ml. of anhydrous ether under nitrogen in a 3-neck 500-ml. flask with stirrer. reflux condenser and addition funnel (pressure equalizing type). was added dropwise a solution of 21.6 g. of (XVIII) in 150 ml. of anhydrous ether. After stirring overnight. the mixture was hydrolyzed by the addition of a little ethanol followed by dilute (3%) hydrochloric acid. The aqueous phase was separated and extracted with ether. The combined ether extracts and ether phase were washed with dilute (3%) hydrochloric acid, sodium chloride solution, dilute sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo*. gave a residue of 22.0 g. of white solid (quantitative yield). A sample charcoaled and recrystallized twice from hexane formed clusters of white blades. m.p. 99.8–101°. Calcd. for $C_{15}H_{22}O$: C, 82.53; H, 10.16. Found: C, 82.62; H. 10.34.

1,2,3,4,5-Pentamethyl-5,6-dihydronaphthalene (**X**).—To 20 g. (0.0925 mole) of crude (IX) was added a small crystal of iodine and the mixture heated in a small Claisen flask until the evolution of water ceased. About 0.5 g. of zinc dust was then added and the material vacuum distilled giving 16.7 g. (92% yield) of product, b.p. 94–96° (0.07 mm.). which solidified in the receiver. A sample recrystallized from methanol melted at 71.6–72.6°. Calcd. for $C_{15}H_{20}$: C, 90.0: H, 10.0. Found: C, 90.1: H, 10.2.

1,2,3,4,5-Pentamethylnaphthalene (**XI**).—A mixture of 14.4 g. of (X) and 1.5 g. of 10% palladium–charcoal was placed in a long-necked flask and heated for 4 hours at 305° while bubbling through the mixture a stream of carbon dioxide. On cooling the product was extracted with benzene. filtered and vacuum distilled giving 11.7 g., b.p. 115–120° (0.1 mm.). which solidified on cooling. Two recrystallizations from methanol gave 10 g. of very pale yellow crystals. m.p. 69–72°. A sample was dissolved in petroleum ether and chromatographed on an alumina column, then recrystallized again from methanol, then ethanol. when it formed white laminae. melting at 75.2-76.2°. Calcd. for $C_{15}H_{18}$: C. 90.9; H, 9.09. Found: C. 91.18; H. 9.27. **The picrate** was recrystallized once from methanol when it formed long red needles, m.p. 168.6–169.4°. Calcd. for $C_{21}H_{21}O_7N_3$: C, 59.0; H. 4.92; N, 9.84. Found: C. 59.12; H. 5.06; N. 9.67. **The trinitrofluorenone complex** (TNF) recrystallized from benzene in maroon micro-needles, m.p. 180.0–180.8°. Calcd. for $C_{28}H_{23}O_7N_3$: C, 65.5; H, 4.48; N, 8.19. Found: C. 65.49; H, 4.55; N, 8.05.

1.2.3,4,5,8-Hexamethyl-5.6-dihydronaphthalene (**XII**).—The pentamethyltetralone (VIII) (21.6 g., 0.10 *M*) reacted in the manner previously described with methyl lithium prepared from 2.77 g. (0.383 *M*) of clean lithium wire and 27.5 g. (0.20 *M*) of methyl iodide. After working up as before, the material was vacuum distilled, giving 13.9 g., b.p. 102–104° (0.07 mm.). $n^{25}D$ 1.5688. Since it showed a very slightly positive test with 2,4-dinitrophenylhydrazine reagent it was treated with Girard Reagent "P" and redistilled. The product. 11.06 g. (54% yield). b.p. 110–112° (0.10 mm.), solidified on standing. After two recrystallizations from methanol a sample melted at 26–28°. Calcd. for $C_{16}H_{22}$: C, 89.7; H, 10.28. Found: C, 89.51; H. 10.42.

1,2,3,4.5.8-Hexamethylnaphthalene (**XIII**).—A mixture of 10.8 g. of (XII) and 1.1 g. of 10% palladium–charcoal was heated at 325° for seven hours with a slow stream of carbon dioxide bubbling through the reaction mixture. The mixture was extracted with benzene. filtered and vacuum distilled giving 4.6 g., b.p. 110–120° (0.03 mm.) which solidified on standing. This was converted to the picrate which was recrystallized from methanol twice. then dissolved in benzene and the hydrocarbon regenerated by passage over a column of alumina. The hydrocarbon after two recrystallizations from ethanol formed white leaves, melting at 62–63.5°. Calcd. for $C_{18}H_{20}$: C. 90.56; H. 9.44. Found: C. 90.75; H. 9.27. **The picrate** recrystallized from methanol in scarlet needles. *m*.p. 161.4–162.2°. Calcd. for $C_{22}H_{23}O_7N_3$: C. 59.85; H, 5.22; N, 9.52. Found: C, 59.6; H, 5.26; N. 9.59. **The trinitrofluorenone complex** formed maroon micro-needles, after two recrystallizations from benzene, melting at 170.4–171°. Calcd. for $C_{29}H_{25}O_7N_3$: C, 66.0; H. 4.74; N, 7.96. Found: C. 66.06; H, 4.90; N, 8.03.

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