These were recrystallized from hot benzene and then had the following properties: insoluble in water, petroleum ether and carbon tetrachloride: slightly soluble in ethyl ether, benzene, and ethyl acetate; and soluble in alcohol, acetone, and sodium bicarbonate solution: m. p. 229°, neutral equivalent 153, molecular weight 294. C 60.8%, and H 7.42%. This indicated an empirical formula of $C_{15}H_{22}O_6$. Methoxl groups were absent.

The compound formed a mono methyl ester with methanol in the presence of concentrated sulfuric acid that had the following properties: m. p. 136–137°, neutral equivalent 290, saponification equivalent 164. The ester was soluble in sodium bicarbonate solution and after saponification the original compound was recovered. These properties indicated a dibasic acid.

The compound was obtained in only small yield from one specimen of Sierra juniper wood containing dry rot.

Inasmuch as it was not isolated from sound wood it is questionable whether it is a normal constituent of wood with no decay.

Summary

1. The ethyl ether soluble content of Sierra juniper wood was found to range between 2.96 to 6.5%. Approximately an additional one per cent. of material is soluble in acetone which is chiefly a catechol phlobaphene. A part of the ethyl ether extractive is soluble in petroleum ether. This amounted to 2.53% on the weight of sapwood and 3.01% on the weight of the whole wood from a cross section of the trunk. A detailed analysis of the petroleum ether solubles is tabulated.

2. The constituents of the petroleum ether extract were resin acids, oleic acid and high molecular weight lactonic acids, a mixture of alpha and beta sitosterol and a hydroxy resene, $C_{18}H_{31}O$. The resin acids occurred only in the free state.

3. The volatile oil from the trunk of the tree ranged from 0.9 to 1.25% and was apparently entirely cedrol. That from the rootwood was a mixture of cedrene and cedrol.

CORVALLIS, OREGON RECEIVED MARCH 16, 1948

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

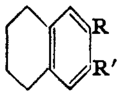
The Jacobsen Reaction. IX.[1] 6,7-Dialkyltetralins

BY LEE IRVIN SMITH AND CHIEN-PEN LO[2]

The only tetraalkylbenzenes so far studied with reference to their behavior under the conditions of the Jacobsen rearrangement are those in which the alkyl groups are methyl and ethyl. Tetraalkylbenzenes of known structure, having alkyl groups above ethyl, and with straight or branched chains, are practically unknown, and the variety and number of such compounds necessary for an extended study of the Jacobsen reaction make the preparation of the starting materials and reference compounds a very formidable task. In the previous paper[1] it was shown that a cyclic chain attached at two ortho-positions to a benzene ring could take the place of two alkyl groups in a tetraalkylbenzene, and it was shown that 6,7-diethyltetralin (a 1,2,4,5-tetraalkylbenzene) underwent the Jacobsen reaction in the normal fashion to produce 5,6-diethyltetralin (a 1,2,3,4-tetraalkylbenzene). Indeed, Schroeter and Gotzky[3] had already shown that two cyclic chains, involving the 1,2,4,5-positions of a benzene ring could replace four alkyl groups, for these authors observed that octahydroanthracene, subjected to the conditions of the Jacobsen reaction, underwent rearrangement to octahydrophrenanthrene, a 1,2,3,4-tetrasubstituted benzene. 6,7-Dialkyltetralins are quite readily prepared in some variety; moreover, these substances, as well as their rearrangement products, are readily dehydrogenated to the corresponding naphthalenes, so that the problems of identification can be solved without much difficulty.

Arnold and Barnes[1] have recently proposed a theory for the mechanism of the Jacobsen reaction. According to this theory, the migrating alkyl group is detached from the sulfonic acid molecule as a cation; this cation then replaces the more hindered sulfonic acid group of the (di)-sulfonic acid, leading to the rearranged sulfonic acid. As a necessary consequence of this theory, migration of a *n*-propyl group in a polyalkylbenzene would involve simultaneous isomerization of the group to iso-propyl, since the latter is the more stable of the two propyl cations under the conditions of the rearrangement.

With the objectives of testing this corollary of the suggested mechanism, and of extending the data on the Jacobsen reaction to groups other than methyl and ethyl, five (four of them new compounds) 6,7-dialkyltetralins have been prepared and subjected to the conditions of the Jacobsen rearrangement. Each tetralin was dehydrogenated to the corresponding naphthalene and the latter identified—hence, incidental to this work, a number of new 2,3- and 1,2-dialkylnaphthalenes have been prepared and characterized.



I. R = R′ = CH_3
II, R = CH_3. R′ = *n*-C_3H_7
III. R = CH_3. R′ = iso-C_3H_7
IV. R = C_2H_5. R′ = iso-C_3H_7
V. R = R′ = *n*-C_3H_7

When 6,7-dimethyltetralin (I) was subjected to the conditions of the Jacobsen reaction, it was converted into 5,6-dimethyltetralin, in analogy

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(1) No. VIII, Arnold and Barens, THIS JOURNAL, 66, 960 (1944).

(2) Abstracted from a thesis by Chien-Pen Lo, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, September, 1947.

(3) Schroeter and Gotzky, *Ber.*, 60, 2035 (1927).

with the previously studied conversion of 6,7-diethyltetralin into the 5,6-isomer.[1] However, when the two alkyl groups are identical, the rearrangement of 6,7-dialkyltetralins to the 5,6-compounds gives no clue as to whether an alkyl group, or the cyclic chain has migrated, for in either case the product would be the same 5,6-dialkyltetralin. Hence it became necessary to study some 6,7-dialkyltetralins in which the substituents were different; for this purpose tetralins II, III, and IV were prepared and characterized; compound V, with two *n*-propyl groups, was also included for comparison.

6-*n*-Propyl-7-methyltetralin II, under the conditions of the Jacobsen rearrangement, was converted into a liquid hydrocarbon which yielded benzene-1,2,3,4-tetracarboxylic acid upon oxidation and 1-*n*-propyl-2-methylnaphthalene upon dehydrogenation. The liquid product was therefore 5-*n*-propyl-6-methyltetralin. There are, *a priori*, four routes for a rearrangement: (a) the propyl group may migrate from the 6- to the 8- (=5) position; (b) the methyl group may migrate to the 5- (=8) position; (c) the tetramethylene ring may open and then close in the *o*-position to the methyl group; and (d) the ring may open and then close in the *o*-position to the propyl group. The product resulting from (a) would, in accordance with the theory of Arnold and Barnes, be 5-isopropyl-6-methyltetralin, and not the *n*-propyl isomer; from (b) and (c) there would result 5-methyl-6-*n*-propyltetralin; route (d) is the only one which would lead to the product actually obtained, namely, 5-*n*-propyl-6-methyltetralin. Hence, the rearrangement proceeded *via* route (d) unless the very improbable assumption is made that a *n*-propyl cation does not rearrange to isopropyl but is stable in the presence of a great excess of sulfuric acid.

6-Isopropyl-7-methyltetralin III, under the conditions of the Jacobsen rearrangement, was converted into 6-methyltetralin, identified by dehydrogenation to 2-methylnaphthalene. In this rearrangement, the *iso*-propyl group became detached and did not re-enter the molecule, a behavior of isopropyl groups for which there is much precedent.[4]

6-Isopropyl-7-ethyltetralin IV, and 6,7-di-*n*-propyltetralin V, when subjected to the conditions of the Jacobsen rearrangement, gave only small amounts of oily products which could not be identified. The bulk of the material was destroyed or else converted into sulfonic acids which were hydrolyzed to hydrocarbons with difficulty—a fact which excluded sulfonic acids of 1,2,3,4-tetraalkylbenzenes.

The results of these experiments, together with those of Arnold and Barnes, show that 6,7-dialkyltetralins undergo the Jacobsen rearrangement to 5,6-dialkyltetralins when one or both of the alkyl groups are methyl or ethyl, or when one group is methyl and the other is *n*-propyl. In the last case, however, it is the tetramethylene ring which migrates rather than either alkyl group. When one of the alkyl groups is methyl and the other is isopropyl, the isopropyl group is lost and the product is a 6-monoalkyltetralin. Moreover, there are certain 6,7-dialkyltetralins which give as products only small amounts of complex mixtures —a behavior paralleling that of 5,6,7,8-tetrahydrobenz(f)-indan and of *s*-hydrindacene, studied by Arnold and Barnes.[1]

Experimental Part[5]

The Jacobsen Reactions.—The general procedure was as follows: a mixture of the 6,7-dialkyltetralin (18 g.) and sulfuric acid was stirred and slowly heated. The color became red, then dark. Complete solution usually occurred at a temperature of about 80°. The mixture was kept at 95° for fifteen minutes, and then allowed to cool to room temperature and stand overnight. The mixture was diluted somewhat with water, and was then distilled with superheated steam (temperature of the reaction mixture, 150°). The distillate was extracted with ether, the extract was washed with aqueous sodium hydroxide, the solvent was evaporated and the residual material was distilled.

6,7-Dimethyltetralin (18 g.) yielded a light yellow oil (5 g.) which, on redistillation, gave colorless 5,6-dimethyltetralin (4.3 g.) boiling at 110–115° (7 mm.) and having $n^{20}\text{D}$ 1.5530. This material (8 drops) was heated with aqueous nitric acid (3 cc. 1:2) to 199–200° for three and one-half hours. The solution was evaporated to dryness, the residue was dissolved in ether, and to this solution was added an ethereal solution of diazomethane (from 2 g. of nitrosomethylurea). The ether was evaporated and the residue, crystallized twice from methanol, melted at 130–131° alone or when mixed with an authentic specimen of tetramethyl benzene-1,2,3,4-tetracarboxylate. Dehydrogenation of the 5,6-dimethyltetralin (1 cc.) led to 1,2-dimethylnaphthalene, identified as the picrate, m. p. and mixed m. p., 129–130°.

6-*n*-Propyl-7-methyltetralin (18 g.) yielded 5-*n*-propyl-6-methyltetralin (4.8 g., 25%), b. p. 140–145° (13.5 mm.). The product was converted to tetramethyl benzene-1,2,3,4-tetracarboxylate, m. p. and mixed m. p. 130–131°, as described above, and was dehydrogenated to 1-*n*-propyl-2-methylnaphthalene, identified as the picrate, m. p. and mixed m. p. 118–119°.

6-Isopropyl-7-methyltetralin (18 g.) yielded a yellow oil (7 g.), separated into three fractions by distillation: I. b. p., 95–105° (4.5 mm.) (2.1 g.), II. b. p. 122–130° (4.5 mm.) (3.0 g.), III. residue (0.8 g.). Fraction II gave no benzene tetracarboxylic acid upon oxidation, and was identified as 6-methyltetralin by dehydrogenation to 2-methylnaphthalene, m. p. and mixed m. p. of the picrate 115–117°.

6-Isopropyl-7-ethyltetralin (8 g.) (oleum, 10% sulfur trioxide, 40 cc. used instead of sulfuric acid) yielded an oil (1.2 g.) which gave no benzene tetracarboxylic acid on oxidation and which gave no picrate after dehydrogenation.

6,7-Di-*n*-propyltetralin (18 g.) gave less than 1 cc. of yellow oil from which no identifiable material could be isolated.

1-Tetralone was prepared from tetralin in 36% yield by the procedure of Thompson.[6] The product boiled at 125–126° (8 mm.), and gave a semicarbazone which, after crystallization from aqueous ethanol, melted at 215–217°.[7]

1-Methyl-1-tetralol.—To an ethereal solution of methylmagnesium iodide (prepared from magnesium 1.7 g.,

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[4] For example, see Newton, THIS JOURNAL, 65, 2439 (1943).

[5] Microanalyses by Sherman Sundet, Roger Amidon, Jay S. Buckley.

[6] Thompson, *Org. Syntheses*, 20, 94 (1940).

[7] Kipping and Hill, *J. Chem. Soc.*, 75, 148 (1899), reported the m. p. as 217°.

methyl iodide 5.5 cc. and ether 30 cc.) was added a solution of 1-tetralone (6.7 g.) in ether (10 cc.). The mixture was refluxed. and then decomposed by addition of iced ammonium chloride solution. The mixture was extracted with ether, the extract was washed with ammonium chloride solution, and the solvent was removed. The residue (7 g., 94%) solidified and then melted at 77–79°. After recrystallization from petroleum ether, the substance melted at 86–87°.[8]

1-Methylnaphthalene.—A mixture of 1-methyl-1-tetralol (3 g.) and a palladium–charcoal catalyst (0.3 g., 10%) was heated at 230–270° for three hours. The product was dissolved in ether. the catalyst was removed. and the solution was washed with aqueous sodium hydroxide (5%). Removal of the ether left 2.5 g. (95%) of residual oil which boiled at 94–96° (5 mm.). and had $n^{20}\mathrm{D}$ 1.6037.[9]

Picrate.—The above oil (0.5 cc.) was added to methanolic picric acid and the solution was cooled. The yellow needles were removed and recrystallized from methanol. The product then melted at 141–142°.[10] *Anal.* Calcd. for $C_{17}H_{13}O_7N_3$: C. 54.99: H, 3.53. Found: C. 54.54: H, 3.56.

6-Propionyltetralin.[11]—Propionic anhydride (43.4 g.) was slowly (one hour) added to a cooled (0°) and stirred mixture of tetralin (6.6 g.). nitrobenzene (200 cc.) and aluminum chloride (150 g.). The mixture was gradually (two and one-half hours) allowed to attain room temperature and then was poured over ice and hydrochloric acid (100 cc.) and extracted with benzene. The extract was washed with water. aqueous sodium carbonate (10%) and water and dried over calcium chloride. Benzene, tetralin and nitrobenzene were removed by distillation under reduced pressure, and the residue was distilled. The product weighed 43 g. (68%). boiled at 160–163° (11 mm.) and had $n^{29}\mathrm{D}$ 1.5508.

The semicarbazone. after crystallization from ethanol, melted at 209°.[12] *Anal.* Calcd. for $C_{14}H_{19}ON_3$: C. 69.11: H. 7.87. Found: C. 69.33; H, 8.06.

6-*n*-Propyltetralin.—A mixture of amalgamated zinc (360 g.. 20 mesh), water (360 cc.). acetic acid (480 cc.). hydrochloric acid (720 cc.) and 6-propionyltetralin (61 g.) was refluxed for seventy-six hours. more hydrochloric acid (total 900 cc.) being added from time to time. The cooled mixture was extracted with ether. the extract was washed with water. aqueous sodium hydroxide (10%). and water, the solvent was removed. and the residue was distilled. The product. a colorless liquid, weighed 53 g. (92%). boiled at 123–125° (10 mm.) and had $n^{29}\mathrm{D}$ 1.5253. *Anal.* Calcd. for $C_{13}H_{18}$: C. 89.60: H. 10.41. Found: C. 89.29: H. 10.47.

Trinitro-6-*n*-propyltetralin.—The tetralin (1 g.) was slowly dropped into a cold (0°) mixture of sulfuric acid (5 cc.) and fuming nitric acid (5 cc.). The mixture was allowed to stand for ten minutes and was then poured over ice and extracted with ether. The extract was washed with water. dilute sodium hydroxide. water, and was dried. The solvent was removed and the residue was crystallized twice from methanol. The colorless prisms (0.5 g.) melted at 97–98° and became first yellow. then red. when allowed to stand in the light. No attempt was made to determine the position of the nitro groups. *Anal.* Calcd. for $C_{13}H_{15}O_6N_3$: C, 50.5: H. 4.85. Found: C. 50.7: H, 5.12.

6-*n*-Propyltetralin Sulfonamide.—Chlorosulfonic acid (5 cc.) was added dropwise to a cold solution of the tetralin (1 g.) in chloroform (5 cc.). The mixture was allowed to attain room temperature and was poured over ice. The organic layer was removed, washed with water, and evaporated. The residual sulfonyl chloride was an oil which was converted directly to the sulfonamide by boiling it with ammonium hydroxide (5 cc.) for five minutes. The solid was dissolved in aqueous sodium hydroxide (5%), the solution was filtered, and the filtrate was acidified. The solid. after crystallization from ethanol, melted at 117–119°. No attempt was made to determine the position of the sulfonamide group. *Anal.* Calcd. for $C_{13}H_{19}O_2NS$: C. 61.5: H. 7.5. Found: C, 61.8; H, 8.1.

β-(4-*n*-Propyl)-benzoylpropionic Acid.—Aluminum chloride (75 g.) was added, in small portions, to a cooled (0°) mixture of succinic anhydride (25 g.). nitrobenzene (250 cc.) and *n*-propylbenzene (33 g.).[13] The mixture was stirred for two hours and then poured over iced hydrochloric acid and steam-distilled. The oily residue, which solidified on cooling, was dissolved in aqueous sodium carbonate (10%), the solution was warmed with charcoal. filtered. and the filtrate was acidified. The solid was removed and crystallized from methanol. It weighed 35 g. (63%) and melted at 108–115°. After two recrystallizations from benzene. the substance melted at 120–121°. *Anal.* Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C. 70.97: H, 7.60.

The *p*-phenylphenacyl ester, recrystallized twice from ethanol. melted at 85–86°. *Anal.* Calcd. for $C_{27}H_{26}O_4$: C, 78.3: H. 6.28. Found: C. 78.7: H, 6.51.

The semicarbazone, after crystallization from dilute ethanol. melted at 171–172°. *Anal.* Calcd. for $C_{14}H_{19}O_3N_3$: C, 60.6: H. 6.91. Found: C. 60.1: H, 7.15.

3-(4-*n*-Propyl)-phenylpyridazinone-6, prepared from the acid by the procedure of Gabriel and Colman,[14] and crystallized from dilute ethanol, melted at 103.5–104.5°. *Anal.* Calcd. for $C_{13}H_{16}ON_2$: C, 72.2; H. 7.46. Found: C. 72.6: H. 7.62.

γ-(4-*n*-Propyl)-phenylbutyric Acid.—The above keto acid (55 g.) was refluxed with amalgamated zinc (100 g.), hydrochloric acid (175 cc.) and water (75 cc.) for twenty-four hours. during which time three 50-cc. portions of hydrochloric acid were added. The top layer solidified when the mixture was cooled; the solid was removed and crystallized from petroleum ether (b. p. 30–60°), when it weighed 36.5 g. (71%) and melted at 65–66°. *Anal.* Calcd. for $C_{13}H_{18}O_2$: C. 75.69: H. 8.79. Found: C. 75.93: H. 9.01.

The *p*-phenylphenacyl ester. crystallized from ethanol. melted at 105–106°. *Anal.* Calcd. for $C_{27}H_{28}O_3$: C. 80.97: H. 7.05. Found: C, 81.23: H, 7.19.

7-*n*-Propyl-1-tetralone.—Sulfuric acid (150 cc.. 80%) and γ-(4-*n*-propyl)-phenylbutyric acid (30 g.) were heated on the steam bath for one hour. The cooled solution was poured over ice and extracted with ether. The ether extract was washed with aqueous sodium hydroxide (5%). dried, and the solvent was removed. The residue. on distillation. gave 19.5 g. (71%) of a colorless liquid which boiled at 150–155° (8 mm.) and had $n^{29}\mathrm{D}$ 1.5455. *Anal.* Calcd. for $C_{13}H_{16}O$: C. 82.93: H. 8.57. Found: C. 82.51: H. 8.70.

The semicarbazone. crystallized twice from ethanol. melted at 197–198°. *Anal.* Calcd. for $C_{14}H_{19}ON_3$: C, 68.54: H, 7.81. Found: C, 68.70; H, 7.86.

6-*n*-Propyltetralin.—The above 7-*n*-propyltetralone (14.5 g.) reduced by the method of Clemmensen as previously described, gave the hydrocarbon (6.6 g.. 49%) boiling at 105–109° (5 mm.). Converted to the sulfonamide. as described above. the product melted at 117.5–118.5° alone or when mixed with the sulfonamide prepared from the tetralin resulting from reduction of 6-propionyltetralin.

2-*n*-Propylnaphthalene Picrate.—6-*n*-Propyltetralin (1 cc.) and a palladium–charcoal catalyst (10%. 0.1 g.)[15] were heated at 200–240° under a current of carbon dioxide for three hours. The product was taken up in ethanol,

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[8] von Auwers. *Ann.*, **415**. 169 (1918). reported the m. p. as 88–89°.

[9] Anderson and Short. *J. Chem. Soc.*, 485 (1933). reported the b. p. as 100–105° (5 mm.).

[10] Lesser, *Ann.*, **402**, 10 (1913), and Meyer and Fricke. *Ber.*, **47**. 2770 (1914). reported the m. p. as 141–142°.

[11] Barnes. Ph.D. Thesis. University of Minnesota. 1943.

[12] Barbot. *Bull. soc. chim.*, [4] **47**. 1314 (1930). reported 224–225°. but gave no analysis.

[13] Gilman and Catlin. "Org. Syntheses." Coll. Vol. I. 471 (1941).

[14] Gabriel and Colman. *Ber.*, **32**. 399 (1899).

[15] Linstead and Thomas. *J. Chem. Soc.*, 1127 (1940).

the catalyst was removed and ethanolic picric acid (15 cc.) was added to the filtrate. The cooled solution deposited yellow needles which, after crystallization from ethanol, melted at 91°.[16]

6-Acetyltetralin.—This was prepared by the procedure of Barnes[11] essentially as described for the propionyl derivative, but substituting acetic anhydride for propionic anhydride. The product, obtained in 60% yield, was a yellow oil which boiled at 151–156° (10 mm.) and had n^{29}_D 1.5593.

The semicarbazone, recrystallized from ethanol, melted at 233–234°.[17]

6-Tetralyldimethylcarbinol.—A solution of 6-acetyltetralin (43.5 g.) in ether (20 cc.) was slowly (forty-five minutes) added to a Grignard reagent prepared from magnesium (6 g.), methyl iodide (36 g.) and ether (120 cc.). After addition was complete, the mixture was refluxed for thirty minutes, then cooled and poured carefully over iced ammonium chloride. The ether layer was removed and the aqueous layer was extracted with ether. The combined organic solutions were washed with ammonium chloride solution and dried over sodium sulfate. The solvent was removed and the residue was distilled. The product (39.3 g., 83%) boiled at 138–141° (5 mm.), and had n^{20}_D 1.5497. *Anal.* Calcd. for $C_{13}H_{18}O$: C. 82.1; H, 9.53. Found: C, 82.5; H. 9.23. Although water (1.8 cc., calcd. 2.7 cc.) was eliminated from the carbinol (29 g.) when it was heated to 150–160° with fused potassium acid sulfate (25 g.). the product (12.5 g.) was a mixture (b. p. 133–160° (10 mm.)) from which no pure material could be isolated. When heated with hydriodic acid and red phosphorus, the carbinol was converted into a thick oil which did not distill at 200° (5 mm.).

6-Isopropyltetralin.—The above carbinol (24 g.) was dissolved in ethanol (24 cc.) and the solution was refluxed with Raney nickel catalyst (1 g.) for an hour. The catalyst was removed, the filtrate was diluted with ethanol to 60 cc. and reduced over copper chromite catalyst (6 g.)[18] in a bomb at a temperature of 225° and initial hydrogen pressure of 1670 lb. The reduction was complete in one hour. The reaction product. processed in the usual way, yielded 19 g. (86%) of a colorless liquid which boiled at 120–123° (12 mm.), and had n^{29}_D 1.5246. *Anal.* Calcd. for $C_{13}H_{18}$: C, 89.6: H, 10.41. Found: C, 89.9: H. 10.58.

Trinitro-6-isopropyltetralin.—The trinitro compound, prepared as described above for the *n*-propyl isomer, melted at 141–142°. It also became yellow, then red, in the light. *Anal.* Calcd. for $C_{13}H_{15}O_6N_3$: C, 50.5; H, 4.85. Found: C, 50.9; H, 5.27.

6-Isopropylsulfonamide.—The hydrocarbon was converted into the sulfonamide by the procedure described above for the *n*-propyl isomer. The product, after crystallization twice from dilute methanol, melted at 157–158°. The position of the sulfonamide group was not determined. *Anal.* Calcd. for $C_{13}H_{19}O_2NS$: C, 61.5: H, 7.51. Found: C, 61.6: H, 7.95.

6-Isopropyltetralin was also prepared by direct alkylation of tetralin (396 g.) with isopropyl bromide (123 g.) at 60° in the presence of aluminum chloride (20 g.). The product was processed in the usual way. The fraction boiling at 123-125° (15 mm.) weighed 43 g. (24%), had n^{20}_D 1.5429, and gave the same sulfonamide, m. p. 158°, described above. When tetralin (500 cc.) and isopropyl acetate (52 g.) reacted in the presence of aluminum chloride (80 g.). a product resulted from which, on distillation, a fraction (30 g., 34%) was isolated having n^{29}_D 1.5250 and boiling at 113–115° (8–9 mm.). This likewise gave the sulfonamide. m. p. 157°. The middle fraction (25 g.), b. p. 149–152° (8–9 mm.), solidified on cooling and. after two crystallizations from ethanol, melted at 73–74°. It was identified as octahydroanthracene by the m. p. and analysis.[19] *Anal.* Calcd. for $C_{14}H_{18}$: C, 90.33; H, 9.68. Found: C, 90.45: H, 9.68. The mother liquor from this solid was a colorless oil boiling at 150–155° (10 mm.). and having n^{29}_D 1.5579. It was identified as 6-acetyltetralin by the m. p. and mixed m. p. (232–235°) of the semicarbazone. The high boiling fraction was a yellow oil, b. p. 215–220° (9 mm.) having the composition $C_{20}H_{24}$. Analysis and b. p. indicated that this was α-phenyl-δ-2-tetralylbutane.[20] *Anal.* Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.99;. H, 9.11.

β-(4-Isopropyl)-benzoylpropionic acid (64.8 g., 59%) was prepared from succinic anhydride (50 g.) and isopropylbenzene (66 g.) by action of aluminum chloride (150 g.) in nitrobenzene (500 cc.) essentially according to Barnett and Sanders.[21] The product, crystallized twice from benzene. melted at 141°. The *p*-phenylphenacyl ester, crystallized from ethanol, melted at 101.5–102.5°. *Anal.* Calcd. for $C_{27}H_{26}O_4$: C, 78.26; H, 6.28. Found: C, 78.42; H, 6.42. The semicarbazone, crystallized from ethanol, melted at 182–182.5° (dec.). *Anal.* Calcd. for $C_{14}H_{19}O_3N_3$: C, 60.63; H, 6.91. Found: C, 60.48: H. 7.08. 3-(4-Isopropyl)-phenylpyridazinone, prepared by action of hydrazine and alkali upon the keto acid, and crystallized from ethanol. melted at 166–167°. *Anal.* Calcd. for $C_{13}H_{16}O_2N_2$: C, 72.19; H, 7.46. Found: C, 72.18: H, 7.16.

γ-4-(Isopropyl)-phenylbutyric acid (37 g., 72%) was prepared from the above keto acid (55 g.) by Clemmensen reduction, according to the procedure of Barnett and Sanders.[22] The product boiled at 180–185° (11 mm.) and solidified on standing. Recrystallized from petroleum ether (b. p. 30–60°) it formed colorless prisms melting at 48–50°. The *p*-phenylphenacyl ester, after crystallization from ethanol. melted at 91–92.5°. *Anal.* Calcd. for $C_{27}H_{28}O_3$: C, 80.97: H, 7.05. Found: C. 81.22: H, 7.25.

7-Isopropyl-1-tetralone (16.5 g., 72%) was obtained by action of sulfuric acid (80%, 125 cc.) upon the above phenylbutyric acid.[23] The product boiled at 153–155° (12 mm.) and melted at 36°. The semicarbazone, after crystallization from ethanol, melted at 199-200°. *Anal.* Calcd. for $C_{14}H_{19}ON_3$: C, 68.54; H, 7.81. Found: C, 68.65: H. 7.97.

This tetralone (14.5 g.) was refluxed with amalgamated zinc (100 g.), water (75 cc.) and hydrochloric acid (175 cc.) for ten hours, during which two 50-cc. portions of hydrochloric acid were added. There resulted 9.7 g. (72%) of 6-isopropyltetralin, which boiled at 123–125° (9 mm.) and had n^{29}_D 1.5245. The sulfonamide melted at 158–159° and was identical with the one described above.

2-Isopropylnaphthalene.—The tetralin (17.4 g.) and sulfur (6.4 g.) were heated at 200° (temperature of the metal-bath) for one hour, and then at 265–270° for thirty minutes. The reaction mixture was distilled: the distillate weighed 12 g. (70%), boiled at 126–129° (10 mm.) and had n^{20}_D 1.5730. The picrate, obtained by dissolving the hydrocarbon in methanolic picric acid and cooling the solution. melted at 93–94°.[24]

6-Methyltetralin was prepared by catalytic reduction of 2-methylnaphthalene, according to the procedure of Fieser and Jones,[25] although it was found that the starting material had to be pre-treated with Raney nickel catalyst before a smooth reduction occurred. The product, obtained in 94% yield, boiled at 220–222° (736 mm.). 100–103° (12 mm.), and had n^{20}_D 1.5358.

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[16] Haworth, Letsky and Mavin, *J. Chem. Soc.*, 1784 (1932), gave the m. p. as 89–90°.

[17] Hesse, *Ber.*, **53**, 1645 (1920), reported 234–235°; Barbot (ref. 12) reported 257–258°.

[18] Catalyst 37 KAF, Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1140 (1932).

[19] Schroeter, *Ber.*, **57**, 1990 (1924), reported the m. p. as 73–74°

[20] Schroeter, Ref. 19, reported the b. p. of this substance as 236–237° (13 mm.).

[21] Barnett and Sanders, *J. Chem. Soc.*, 435 (1933), who give the m. p. as 142°.

[22] Ref. 21. The m. p. is here given at 50°.

[23] Barnett and Sanders, ref. 21. The m. p. is here given as 36°

[24] Haworth, Letsky and Mavin, Ref. 16, reported the m. p. as 93–95°.

[25] Fieser and Jones, THIS JOURNAL, **60**, 1940 (1938).

6-Acyl-7-alkyltetralins.—These were prepared from the alkyltetralins, by action of the corresponding acid anhydride in the presence of aluminum chloride, with nitrobenzene as the solvent. A representative procedure is given.

6-Acetyl-7-methyltetralin.—Acetic anhydride (50 cc.) was added slowly (forty minutes) to a cooled (0°) and stirred mixture of 6-methyltetralin (62 g.), nitrobenzene (350 cc.). and aluminum chloride (143 g.). The mixture was stirred at room temperature for two hours and then was decomposed by pouring it into iced hydrochloric acid. The mixture was extracted with benzene and the extract was washed successively with hydrochloric acid, aqueous sodium hydroxide (10%), and water. The solvents were removed by distillation under reduced pressure and the residue was distilled. There resulted 62 g. (77%) of a yellow oil which boiled at 155–159° (10 mm.) and had n^{20}D 1.5511. *Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.04: H, 8.78. The 2,4-dinitrophenylhydrazone, crystallized once from acetone and twice from a mixture of ethyl acetate and methanol, melted at 172–173°. *Anal.* Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.92: H, 5.47. Found: C. 62.09; H, 5.67.

6-Propionyl-7-methyltetralin: yield 76%, b. p. 162–166° (11 mm.), n^{20}D 1.5479. *Anal.* Calcd. for $C_{14}H_{18}O$: C, 83.12: H, 8.97. Found: C, 82.72; H, 8.84. The 2.4-dinitrophenylhydrazone, crystallized twice from ethyl acetate, melted at 153–154°. *Anal.* Calcd. for $C_{20}H_{22}O_4N_4$: C, 62.81: H, 5.80. Found: C, 63.07; H, 5.78.

6-Acetyl-7-*n*-propyltetralin: yield 72%, b. p. 150–155° (5 mm.): n^{20}D 1.5445. *Anal.* Calcd. for $C_{15}H_{20}O$: C, 83.28: H, 9.32. Found: C, 82.94: H, 9.20. The 2.4-dinitrophenylhydrazone. crystallized twice from ethyl acetate–methanol, melted at 133–134°. *Anal.* Calcd. for $C_{21}H_{24}O_4N_4$: C, 63.69: H, 6.25. Found: C, 63.81; H, 6.31.

6-Propionyl-7-*n*-propyltetralin: yield 78%, b. p. 182–186° (16 mm.), n^{20}D 1.5350. *Anal.* Calcd. for $C_{16}H_{22}O$: C, 84.42; H, 9.63. Found: C, 83.84; H, 9.95. The 2.4-dinitrophenylhydrazone crystallized twice from ethyl acetate–methanol, melted at 123–124°. *Anal.* Calcd. for $C_{22}H_{26}O_4N_4$: C, 64.37; H, 6.38. Found: C, 64.63; H, 6.51.

6-Acetyl-7-isopropyltetralin: yield 66%: b. p., 147–150° (4 mm.). n^{20}D 1.5460. *Anal.* Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 82.73; H, 9.45. The 2.4-dinitrophenylhydrazone, crystallized twice from ethyl acetate–methanol, melted at 166–167°. *Anal.* Calcd. for $C_{21}H_{24}O_4N_4$: C, 63.69: H, 6.25. Found: C, 63.84; H, 6.31. It was planned to convert 6-acetyl-7-isopropyltetralin into 6,7-diisopropyltetralin, *via* the dimethyl carbinol which would result by addition of methylmagnesium iodide to the acetyl compound. However, the only product isolated as a result of this reaction was unchanged 6-acetyl-7-isopropyltetralin (20 g. from 30 g. used), b. p., 138–141° (2 mm.), n^{20}D 1.5408, m. p. and mixed m. p. of the semicarbazone, 166–167°. No further study of this reaction was made: it is likely that the reaction involved almost entirely enolization of the ketone, but this was not investigated.

6-Propionyl-7-isopropyltetralin: yield 57%, b. p. 170–175° (14.5 mm.), n^{20}D 1.5382. *Anal.* Calcd. for $C_{16}H_{22}O$: C, 83.42; H, 9.63. Found: C, 83.53; H, 9.69. The 2,4-dinitrophenylhydrazone, crystallized twice from ethyl acetate–methanol, melted at 141–142°. *Anal.* Calcd. for $C_{22}H_{26}O_4N_4$: C, 64.37; H, 6.38. Found: C, 64.85: H, 6.57.

6,7-Dialkyltetralins.—These were, except where noted otherwise, prepared from the corresponding 6-acyl-7-alkyltetralins, by the Clemmensen method. The procedure, in general, followed those already given above for similar reductions.

6,7-Dimethyltetralin (57 g., 89%) was prepared by reduction of 2,3-dimethylnaphthalene (62 g.) in ethanol in the presence of Raney nickel catalyst.[26] The product boiled at 112–115° (9.5 mm.)[27] and had n^{20}D 1.5360.

6,7-Dimethyltetralin-5-sulfonamide.—Chlorosulfonic acid (2.8 cc.) was dropped into a cold (0°) solution of the tetralin (1 cc.) in chloroform (5 cc.). The mixture was allowed to stand at room temperature for twenty minutes, then was poured over ice and extracted with chloroform. The extract was washed with water, dried, the solvent was removed, and the residual oil was boiled with ammonium hydroxide. The mixture was diluted with water, and the solid was removed and crystallized several times from some dilute ethanol. It then melted at 135–136°.[28] *Anal.* Calcd. for $C_{12}H_{17}O_2NS$: C, 60.22: H, 7.16. Found: C, 60.48: H, 7.27. 6-Ethyl-7-methyltetralin, from 6-acetyl-7-methyltetralin: yield 81%, b. p. 121–124° (10 mm.), n^{20}D 1.5272. *Anal.* Calcd. for $C_{13}H_{18}$: C, 89.59: H, 10.41. Found: C, 89.34: H, 10.71.

6-(7-Methyltetralyl)-dimethylcarbinol.—A solution of 6-acetyl-7-methyltetralin (37.6 g.) in ether (20 cc.) was slowly added to a Grignard reagent prepared from magnesium (4.8 g.), methyl iodide (13 cc.) and ether (40 cc.). The mixture was refluxed for thirty minutes, then cooled, poured into iced ammonium chloride solution and extracted with ether. The extract was washed with aqueous ammonium chloride and water, the solvent was removed and the residue was distilled. The carbinol (32 g., 78%) formed a light yellow oil which boiled at 135–136° (3 mm.) and had n^{20}D 1.5435. *Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.3: H, 9.87. Found: C, 83.0: H, 9.50.

6-Isopropyl-7-methyltetralin.—The above carbinol (32 g.) in ethanol (32 cc.) was refluxed with Raney nickel catalyst for one hour. The catalyst was removed and the filtrate was diluted to 70 cc. by addition of ethanol. This solution, together with copper chromite catalyst (9 g.) was heated to 220–225° for two hours in a bomb under an initial hydrogen pressure of 1820 lb. The catalyst was removed by centrifugation, the solvent was removed by distillation under reduced pressure, and the residue was distilled. The product, a colorless liquid, boiled at 113–116° (6 mm.) and had n^{20}D 1.5250. *Anal.* Calcd. for $C_{14}H_{20}$: C, 89.29: H, 10.71. Found: C, 89.46: H, 10.84. The hydrocarbon (8 drops) and nitric acid (3 cc., 1:2) were heated at 190–200° for sixteen hours. The solution was evaporated to dryness and the residue was taken up in ether. Ethereal diazomethane (from 2 g. of nitrosomethylurea) was added, the solution was evaporated, and the residue was crystallized twice from methanol. The product melted at 141–142° alone or when mixed with an authentic specimen of tetramethyl pyromellitate.

6-*n*-Propyl-7-methyltetralin, from 6-propionyl-7-methyltetralin: yield 84%, b. p., 130–135° (11 mm.), n^{20}D 1.5250. *Anal.* Calcd. for $C_{14}H_{20}$: C, 89.30: H, 10.71. Found: C, 88.87; H. 10.62. Oxidation of the hydrocarbon, as described above. gave tetramethyl pyromellitate. m. p. and mixed m. p. 141–142°.

6-*n*-Propyl-7-ethyltetralin, from 6-acetyl-7-*n*-propyltetralin: yield 78%, b. p. 114–117° (2.5 mm.). n^{20}D 1.5228. *Anal.* Calcd. for $C_{15}H_{22}$: C, 89.04: H, 10.96. Found: C, 88.66: H, 10.95.

6,7-Di-*n*-propyltetralin, from 6-propionyl-7-*n*-propyltetralin: yield 80%, b. p. 157–162° (12 mm.), n^{20}D 1.5234. Oxidation of the hydrocarbon, as described above, gave tetramethyl pyromellitate, m. p., and mixed m. p., 141–142°. *Anal.* Calcd. for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.95, 88.61; H, 11.51. 11.15.

6-Isopropyl-7-ethyltetralin, from 6-acetyl-7-isopropyltetralin: yield 61%, b. p. 127–130° (5 mm.), n^{20}D 1.5200. *Anal.* Calcd. for $C_{15}H_{22}$: C, 89.04: H, 10.96. Found: C, 89.50; H, 11.02.

6-Isopropyl-7-*n*-propyltetralin, from 6-propionyl-7-isopropyltetralin: yield 53%, b. p. 157–160° (15 mm.), n^{20}D 1.5238. *Anal.* Calcd. for $C_{16}H_{24}$: C, 88.82: H, 11.18. Found: C, 88.59: H, 11.04.

2,3-Dialkylnaphthalenes.—These were prepared by dehydrogenation of the corresponding 6,7-dialkyltetralins by heating them to 220–250° in a current of carbon dioxide and in the presence of a palladium-charcoal (10%)

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[26] Craig. Ph.D. Thesis. University of Minnesota. 1947.

[27] Coulson. *J. Chem. Soc.*, 1305 (1938). reported the b. p. as 244–246°.

[28] Coulson. ref. 27. reported the m. p. as 135°.

catalyst for approximately three hours. The catalyst was used in an amount roughly 10% of that of the dialkyltetralin taken. The reaction product was taken up in ether, the catalyst was removed, and the naphthalene was distilled. The picrates were prepared by dissolving the hydrocarbon in methanolic picric acid and cooling the solution. They were recrystallized from ethanol or methanol.

2-Ethyl-3-methylnaphthalene, from 6-ethyl-7-methyltetralin: yield 85%, b. p. 109–112° (3 mm.), n^{20}_D 1.5658. *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.17; H, 8.67. Picrate, yellow needles, m. p., 129–130°. *Anal.* Calcd. for $C_{19}H_{17}O_7N_3$: C, 57.14; H, 4.29. Found: C, 57.45; H, 4.57.

2-Isopropyl-3-methylnaphthalene, from 6-isopropyl-7-methyltetralin: yield 99%, b. p. 130–132° (7 mm.), n^{20}_D 1.5599. *Anal.* Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.54; H, 8.83. Picrate, yellow needles, m. p., 133–136°. *Anal.* Calcd. for $C_{20}H_{19}O_7N_3$: C, 58.11; H, 4.63. Found: C, 58.17: H, 4.66.

2-*n*-Propyl-3-methylnaphthalene, from 6-*n*-propyl-7-methyltetralin: yield 70%, b. p. 121–123° (3 mm.), n^{20}_D 1.5647. *Anal.* Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.20: H, 8.95. Picrate, yellow needles, m. p., 110–112°. *Anal.* Calcd. for $C_{20}H_{19}O_7N_3$: C, 58.11; H, 4.63. Found: C, 57.85: H, 4.87.

2-*n*-Propyl-3-ethylnaphthalene from 6-*n*-propyl-7-ethyltetralin: yield 81%, b. p. 131–134° (4 mm.), n^{20}_D 1.5752. *Anal.* Calcd. for $C_{15}H_{18}$: C, 90.85: H, 9.15. Found: C, 90.47; H, 9.02. Picrate, yellow needles, m. p., 92–93°. *Anal.* Calcd. for $C_{21}H_{21}O_7N_3$: C, 59.01; H, 4.95. Found: C, 59.15; H, 5.09.

2,3-Di-*n*-propylnaphthalene from 6,7-di-*n*-propyltetralin: The tetralin (17.2 g.) and sulfur (4.8 g.) were heated at 200–205° for one hour and then at 270–275° for one hour. The product was distilled, then allowed to stand over sodium for several hours, and redistilled. It weighed 13 g. (77%), boiled at 155–158° (8.5 mm.), and had n^{23}_D 1.5601. *Anal.* Calcd. for $C_{16}H_{20}$: C, 90.50: H, 9.50. Found: C, 90.33; H, 9.56. Picrate, yellow needles, m. p., 83–84°. *Anal.* Calcd. for $C_{22}H_{23}O_7N_3$: C, 59.86; H, 5.25. Found: C, 59.70; H, 5.38.

2-Isopropyl-3-ethylnaphthalene, from 6-isopropyl-7-ethyltetralin: yield 95%, b. p., 132–135° (5 mm.), n^{20}_D 1.5742. *Anal.* Calcd. for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.58; H, 9.11. Picrate, yellow needles, m. p., 117–119°. *Anal.* Calcd. for $C_{21}H_{21}O_7N_3$: C. 59.01: H, 4.95. Found: C, 58.66: H, 5.06.

2-Isopropyl-3-*n*-propylnaphthalene, from 6-isopropyl-7-*n*-propyltetralin: yield 95%, b. p., 135–138° (5 mm.), n^{20}_D 1.5604. *Anal.* Calcd. for $C_{16}H_{20}$: C, 90.50; H, 9.49. Found: C, 90.27; H, 9.90. This naphthalene failed to form a picrate when treated with methanolic picric acid.

2-Methoxalyl-1-tetralone, m. p., 64–65°, was prepared from 1-tetralone in 59% yield by the procedure of Bachmann and Thomas,[29] who reported it to melt at 65.5–66.5°.

2-Carbomethoxy-1-tetralone was prepared from the methoxalyl compound in 91% yield, according to Bachmann and Thomas.[29]

2-Methyl-2-carbomethoxy-1-tetralone, m. p., 58–59.5°, was prepared in 80% yield by alkylation of the carbomethoxytetralone with methyl iodide, following Bachmann and Thomas[29] who reported the m. p. as 56.5–57.5°.

2-Methyl-1-tetralone, b. p. 138–140° (15 mm.),[30] was obtained in 91% yield by alkaline hydrolysis of 2-methyl-2-carbomethoxy-1-tetralone according to the general procedure of Kloetzel.[31] The semicarbazone, crystallized from ethanol, melted at 201–202°.[32]

2-Methyl-1-*n*-propyltetralol.—A solution of *n*-propylmagnesium bromide (prepared from magnesium 1.1 g., *n*-propyl bromide 4.5 cc., and ether 30 cc.) was cooled and stirred while a solution of 2-methyl-1-tetralone (5 g.) in ether (20 cc.) was slowly added. The mixture was refluxed for one and one-half hours, then poured into ammonium chloride solution and extracted with ether. The extract was washed successively with aqueous ammonium chloride and water, the solvent was removed, and the residue was distilled. The product, 4.8 g. (75%) was a colorless liquid boiling at 146–150° (14–15 mm.), which solidified on cooling. Twice crystallized from petroleum ether (b. p. 30–60°), the substance melted at 82–83°. *Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.4; H, 9.8. Found: C, 83.1; H, 9.7.

2-Methyl-1-*n*-propylnaphthalene.—The above tetralol (3 g.) was heated to 230–270° for three hours with palladium–charcoal catalyst (0.3 g., 10%). The mixture was taken up in ether, the catalyst was removed, and the solvent was evaporated. There resulted 2.4 g. of oil which boiled at 102–105° (5 mm.). and had n^{20}_D 1.5961. *Anal.* Calcd. for $C_{14}H_{16}$: C, 91.25: H, 8.75. Found: C, 91.08; H, 8.97.

Picrate.—The naphthalene (0.5 cc.) was dissolved in methanolic picric acid (6 cc.), the solution was cooled and the yellow crystals were removed and crystallized from methanol. The picrate then melted at 118–119°. *Anal.* Calcd. for $C_{20}H_{19}O_7N_3$: C, 58.11: H, 4.63. Found: C, 57.98: H, 4.49.

2-Methyl-1-isopropyl-1-tetralol.—A solution of isopropylmagnesium bromide (prepared from magnesium 1.5 g., isopropyl bromide 6 cc., and ether 30 cc.) was cooled and to it was added a solution of 2-methyl-1-tetralone (6.4 g.) in ether (20 cc.). The reaction mixture was then processed as described for the *n*-propyl isomer. The product (5.4 g.) boiled at 126–129° (14 mm.), and had n^{20}_D 1.5562. *Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.4; H, 9.8. Found: C. 84.0; H, 8.4. This tetralol (4 g.) was not dehydrated when it was refluxed with acetic acid (40 cc.) for one hour; there was recovered 3 g. of unchanged material, b. p. 127–131° (14 mm.), having n^{20}_D 1.5568.

2-Methyl-1-isopropylnaphthalene.—The above tetralol (3 g.) was dehydrated and dehydrogenated in one operation by heating it to 230–270° for three hours with palladium–charcoal catalyst (0.3 g., 10%). Isolated as described above for the *n*-propyl isomer, the product (1.8 g.) boiled at 92–95° (4 mm.). and had n^{20}_D 1.5992. *Anal.* Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.02; H, 8.62.

Picrate, prepared as described above and crystallized from methanol, formed needles melting at 142–143°. *Anal.* Calcd. for $C_{20}H_{19}O_7N_3$: C. 58.11; H, 4.63. Found: C, 58.15: H, 4.85.

The methods used for synthesis of the 2-methyl-1-propylnaphthalenes failed when applied to the synthesis of the 1-methyl-2-propyl isomers. Thus, 2-carbomethoxy-1-tetralone could not be alkylated with *n*-propyl bromide, by the procedure of Bachmann and Thomas[29]: the only product that could be isolated was recovered 2-carbomethoxy-1-tetralone (75%). Nor was the direct alkylation of 1-tetralone successful. Action of methyl iodide upon the sodium derivative of the tetralone in liquid ammonia failed to produce any methyltetralone: action of isopropyl bromide upon the sodium derivative of the tetralone, formed in benzene by action of freshly prepared sodamide likewise failed: nor was the action of potassium *t*-butoxide in butanol effective in bringing about any reaction between 1-tetralone and isopropyl bromide.

Summary

1. Five 6,7-dialkyltetralins have been subjected to the conditions of the Jacobsen rearrangement. 6,7-Dimethyltetralin rearranged to 5,6-dimethyltetralin; 6-methyl-7-*n*-propyltetralin rearranged to 6-methyl-5-*n*-propyltetralin, the struc-

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(29) Bachmann and Thomas, THIS JOURNAL, **63**, 598 (1941).

(30) Tishler, Fieser and Wendler, *ibid.*, **62**, 2866 (1940), reported the b. p. as 136–137° (16 mm.).

(31) Kloetzel, *ibid.*, **62**, 1708 (1940).

(32) Krollpfeiffer and Schaefer, *Ber.*, **56**, 631 (1923), give 199–201°; Mayer and Stamm, *Ber.*, **56**, 1424 (1923), give 200–201°; Kloetzel, Ref. 31, gives 203–205°; and Tishler, Fieser and Wendler, Ref. 30, give 205–206°.

ture of the *n*-propyl group remaining unaltered. 6-Isopropyl-7-methyltetralin gave 6-methyltetralin, the isopropyl group being eliminated. 6-Isopropyl-7-ethyltetralin and 6,7-di-*n*-propyltetralin were largely decomposed to products obtained in small yields only, and which could not be identified.

2. The theoretical aspects of these results have been discussed with reference to the theory of Arnold and Barnes on the mechanism of the Jacobsen rearrangement.

3. Satisfactory laboratory methods for preparation of the two 6-propyltetralins, *n*- and *iso*-, have been developed, and it has been shown that the structure of the *n*-propyl group remains unaltered when *n*-propylbenzene undergoes a Friedel–Crafts reaction with succinic anhydride.

4. Seven new 6,7-dialkyltetralins have been synthesized, in which one or both of the alkyl groups is methyl, ethyl, *n*-propyl or isopropyl.

5. The corresponding 2,3-dialkylnaphthalenes (and their picrates) have been prepared by dehydrogenation of the 6,7-dialkyltetralins. Syntheses of 1-isopropyl-2-methylnaphthalene and of 1-methylnaphthalene have been developed.

6. Several new intermediate ketones (acyl tetralins) and carbinols have been synthesized and characterized.

MINNEAPOLIS 14, MINNESOTA

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

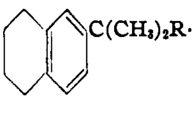
The Reaction between Tetralin and β,β-Dimethylacrylic Acid

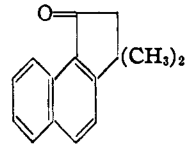
BY LEE IRVIN SMITH AND CHIEN-PEN LO[1]

The reaction between benzene or an alkylbenzene and β,β-dimethylacrylic acid in the presence of aluminum chloride leads to a β-aryl-isovaleric acid.[2] However, when a polyalkylbenzene is used in this reaction, one or more of the following abnormal transformations may occur: (a) the condensation may occur at a position other than the one involved when the acid chloride (ordinary Friedel–Crafts reaction) is used, as is the case with 1,2,3-trimethylbenzene[3]; (b) one of the alkyl groups may rearrange to another position on the benzene nucleus, as is the case with 1,2,4-trimethylbenzene[3]; (c) one of the alkyl groups may be eliminated during the reaction, as is the case with 1,3,5-trimethylbenzene.[4]

In order to explore the limits of this reaction, tetralin has been condensed with β,β-dimethylacrylic acid in the presence of aluminum chloride. Only one acid (70% yield) was isolated; this was identified as β-(6-tetralyl)-isovaleric acid, I, by comparison with a specimen synthesized by an independent method. Thus tetralin, unlike other polyalkylbenzenes, behaves normally in this condensation.

6-(Tetralyl)-dimethylcarbinol, II,[5] was converted by action of hydrochloric acid into the chloride III, which (without isolation) was used to alkylate diethyl malonate. The substituted malonic ester IV (also without isolation) was hydrolyzed to the malonic acid V, and V, on decarboxylation, gave the isovaleric acid I, identical with the product obtained from β,β-dimethylacrylic acid and tetralin.





VI

I. R = $-CH_2COOH$
II, R = OH
III. R = Cl
IV. R = $-CH(COOC_2H_5)_2$
V. R = $-CH(COOH)_2$

Cyclization of the acid I, by action of sulfuric acid, in view of the work of Cauquil and Barrera[6] on the closely related β-(6-tetralyl)-butyric acid, should lead to a mixture of two tetrahydrobenzhydrindones, linear and angular. However, cyclization of β-(2-naphthyl)-propionic acids generally leads to only one benzindanone, the angular.[7] The acid I was therefore converted into the methyl ester and the latter was smoothly dehydrogenated to methyl β-(2-naphthyl)-isovalerate by action of palladium–charcoal catalyst—a result substantiating the findings of Newman and Zahm[8] that a carbomethoxy group is not affected by the hydrogen evolved during dehydrogenation. The methyl ester was hydrolyzed to β-(2-naphthyl)-isovaleric acid, and the acid, subjected to the action of sulfuric acid was dehydrated to a single benzhydrindone assigned structure VI.

Experimental[9]

β-(6-Tetralyl)-isovaleric Acid (I).—To a stirred and cooled (−10°) solution of β,β-dimethylacrylic acid (7.5 g.) in tetralin (37.5 g.), powdered aluminum chloride (13.3 g.) was added (fifteen minutes) in small portions. The mixture was thereafter stirred at −10° for one hour, at room temperature for two hours, and poured into iced hydrochloric acid. The acid fraction of the product, a

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[1] Abstracted from a thesis by Chien-Pen Lo, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, September, 1947.

[2] (a) Eijkman, *Chem. Weekblad*, **5**, 655 (1908); (b) Hoffman, THIS JOURNAL, **51**, 2542 (1929).

[3] Smith and Prichard, THIS JOURNAL, **62**, 771 (1940).

[4] Smith and Spillane, *ibid.*, **65**, 202 (1943).

[5] Smith and Lo, *ibid.*, **70**, 2209 (1948).

[6] Cauquil and Barrera, *Compt. rend.*, **223**, 679 (1946).

[7] Johnson, "Org. Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 125.

[8] Newman and Zahm, THIS JOURNAL, **65**, 1097 (1943).

[9] Microanalyses by R. Amidon and S. Sundet.