

fur dioxide to give polymeric products. No di-substituted acetylene has been found which gives this addition reaction.

2. Some preliminary work on the exact structure of these addition products has been described.

URBANA, ILLINOIS

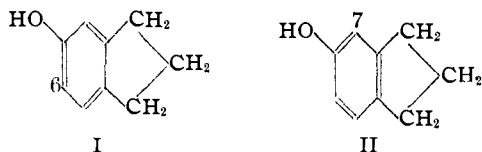
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## An Investigation of the Mills-Nixon Effect

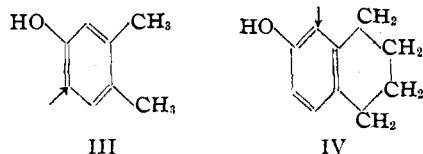
By LOUIS F. FIESER AND WARREN C. LOTHROP

In an important and much-discussed<sup>1</sup> paper, Mills and Nixon<sup>2</sup> advanced the hypothesis that hydrindene, or a given substituted hydrindene, is in a condition of less strain when it has the bond structure shown in formula I than when it exists in the alternate Kekulé form (II) in which the carbon atoms common to the two rings are con-



nected by a double bond. As a means of testing the conclusion that I should be the more stable form of 5-hydroxyhydrindene, or the predominant isomer in the tautomeric equilibrium mixture, these investigators studied the diazo coupling of the substance and its behavior on bromination. Since these are reactions characteristic of enolic systems, substitution should occur at the ortho position joined to the hydroxylated carbon atom by a double linkage, that is, position 6 of I and position 7 of II. It was found that, although substitution does not proceed entirely in a single direction, about 90% of the reaction product is the 6-substituted isomer, indicating that I is the more stable form.

The observation loses some of its significance because of the fact, noted by Mills and Nixon, that *as-o*-xylenol (II) also is attacked chiefly in



the 6-position (arrow), showing that in 5-hydroxyhydrindene the chemical effect of the alicyclic

(1) Thompson, *Chemistry and Industry*, **52**, 61 (1933); Baker, *J. Chem. Soc.*, 1678, 1684 (1934); 274 (1936); Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935); Hampson and Weissberger, *J. Chem. Soc.*, 393 (1936).

(2) Mills and Nixon, *ibid.*, 2510 (1930).

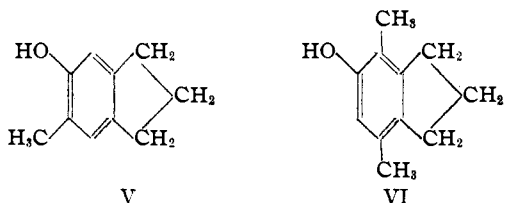
ring may be sufficient, without assistance from a steric factor, to control substitution largely into one of the two available ortho positions. The contrasting behavior of 6-hydroxytetralin (IV), which yields 5-substitution products, afforded the only evidence in the original work of the existence of the Mills-Nixon effect, that is, of a fixation of the bonds in one of the two Kekulé forms as the result of the stereochemical demands of an attached ring. The behavior of IV pointed to the bond structure indicated and, since the 5- and 6-membered rings must be quite similar chemically, the difference was attributed to the different spatial requirements of the two rings. From a theoretical analysis of the configuration of the tetralin molecule, Mills and Nixon concluded, albeit with less conviction than in the other case, that there should be a preference for the Kekulé structure IV.

It seemed to us that the preferential formation of one of two possible isomers may be the result of only a moderate preponderance of one tautomeric form, or of even a very slight difference in reactivities, and that the Mills-Nixon effect may be at most a subtle one in comparison to the fixation of bonds resulting from the fusing together of two aromatic nuclei,<sup>3</sup> and we undertook to apply to hydrindene and to tetralin the much more severe test previously employed in investigating naphthalene,<sup>3</sup> anthracene,<sup>4</sup> and phenanthrene.<sup>5</sup> For this purpose phenolic derivatives in which one of the two ortho positions is blocked by an alkyl group were synthesized and tested for their ability to couple with diazotized amines. If the 5-hydroxyhydrindene derivatives V and VI exist in the stable state suggested by Mills and Nixon, coupling at the free ortho position should occur easily in the case of VI, but only following a migration of the double linkages in the case of V.

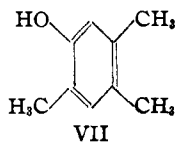
(3) Fieser and Lothrop, *THIS JOURNAL*, **57**, 1459 (1935).

(4) Fieser and Lothrop, *ibid.*, **58**, 749 (1936).

(5) Fieser and Young, *ibid.*, **53**, 4120 (1931).

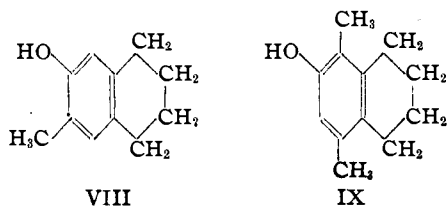


Actually VI readily yielded azo derivatives whereas with V the coupling tests were entirely negative.<sup>6</sup> The observation is particularly strik-



ing when V is compared with pseudocumenol, VII, for the latter substance readily enters into the coupling reaction<sup>7</sup> and therefore is free to react in the Kekulé form shown in the formula. This evidence clearly indicates that the five-membered ring of hydrindene restricts the movement of the double linkages in the benzene nucleus exactly as supposed by Mills and Nixon and to an even greater extent than the results of these investigators would indicate.

In the tetralin series the situation is quite different. If the bond structure is that deduced by Mills and Nixon, and if the fixation imposed by the six-membered ring is comparable with that noted above, VIII should couple and IX should



not. The first of these compounds is already known from the work of Vezelý and Štursa<sup>8</sup> to be capable of coupling with diazotized amines, and on examining IX we found that this substance behaves in a similar manner. Since with typical 6-hydroxytetralins both ortho positions are capable of functioning as enolic groups, it is concluded the double bonds of tetralin are at least fairly free to migrate and that if the Mills-Nixon effect is operative in this case the restriction is comparatively slight.

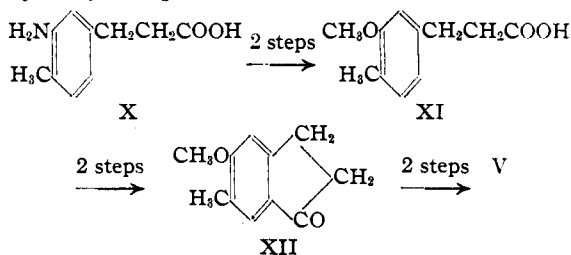
(6) Fisher, Furlong and Grant, *THIS JOURNAL*, **58**, 820 (1936), have reported the failure of the coupling reaction with a similar hydroxyhydrindene of more complicated structure.

(7) Liebermann and Kostanecki, *Ber.*, **17**, 885 (1884).

(8) Vezelý and Štursa, *Collection Czechoslov. Chem. Communications*, **6**, 137 (1934).

Our conclusions with regard to both hydrindene and tetralin agree precisely with those recently reached by Sidgwick and Springall<sup>9</sup> from a study of the dipole moments of *o*-dibromo derivatives of the two hydrocarbons.

For the synthesis of 5-hydroxy-6-methylhydrindene (V), 3-amino-4-methylhydrocinnamic acid<sup>10</sup> (X) was prepared by known methods from 3-nitro-4-methylbenzaldehyde<sup>11</sup> and converted to the hydroxy compound and its ether XI.



This was cyclized through the acid chloride, and the hydrindone XII was reduced by the Clemmensen method and demethylated. That the ring closure takes the expected course is clearly indicated by the failure of V to couple with diazotized amines, for the alternate substance would have available a free para position and would surely react.

For the preparation of VI we at first investigated a synthesis from *p*-xylenol, through the aldehyde and acrylic acid derivatives, which Clemo, Haworth and Walton<sup>12</sup> carried as far as 6-methoxy-4,7-dimethylhydrindone-1, but as considerable difficulty was experienced in methylating the hydroxy aldehyde other methods were investigated. Since 4,7-dimethylhydrindone-1 is readily obtainable from *p*-xylene and  $\beta$ -chloropropionyl chloride,<sup>13</sup> this was reduced to 4,7-dimethylhydrindene and attempts were made to introduce a hydroxyl group through the monosulfonate or the mononitro compound. The sulfonate was obtained without difficulty, but the alkali fusion was wholly unsuccessful, and the nitration of the hydrocarbon under very moderate conditions afforded only a dinitro derivative. The hydrocarbon resembles prehnitene<sup>14</sup> in the latter respect. The following synthesis finally was developed. *p*-Xylyl methyl ether was condensed with  $\beta$ -chloropropionyl chloride in the presence of

(9) Sidgwick and Springall, *Chemistry and Industry*, **55**, 476 (1936).

(10) Salway, *J. Chem. Soc.*, **108**, 1994 (1913).

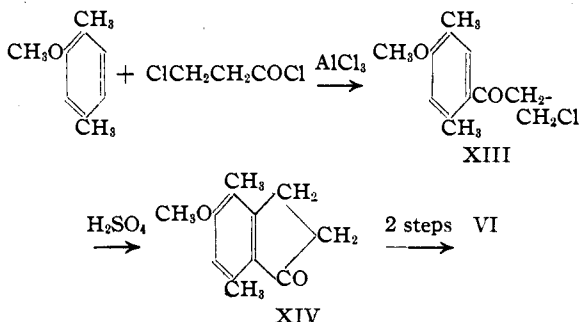
(11) Hanzlik and Bianchi, *Ber.*, **32**, 1288 (1899).

(12) Clemo, Haworth and Walton, *J. Chem. Soc.*, 2368 (1929).

(13) Mayer and Müller, *Ber.*, **60**, 2278 (1927).

(14) Smith and Hac, *THIS JOURNAL*, **56**, 477 (1934).

aluminum chloride, giving in good yield a crystalline chloro ketone. In analogy with other Friedel and Crafts reactions<sup>12</sup> and since the ring closure described below proves that the entering group is not ortho to the methoxyl group, the substance can be assigned the formula XIII. The cycliza-



tion of the chloro ketone with sulfuric acid proceeded poorly (27% yield), but gave a pure ketone, 5-methoxy-4,7-dimethylhydrindone-1 (XIV). It is interesting that this substance melts at the same temperature as the isomeric 6-methoxy compound of Clemo, Haworth and Walton,<sup>12</sup> for the melting points of the 5- and 6-methoxy derivatives of hydrindone-1 are within one degree of each other.<sup>15</sup>

The remaining compound, 6-hydroxy-5,8-dimethyltetralin (IX) was obtained from 7-methoxy-5,8-dimethyltetralone-1, synthesized according to Clemo, Haworth and Walton.<sup>12</sup>

### Experimental Part

**3-Amino-4-methylhydrocinnamic Acid.**<sup>10</sup>—To prepare 3-nitro-4-methylbenzaldehyde<sup>11</sup> 120 g. of tolualdehyde was added in three to four hours to a well-stirred mixture of 600 cc. of concentrated sulfuric acid and 60 cc. of concentrated nitric acid, keeping the solution at 0–3°. After pouring the solution onto ice the pale yellow product was washed free of acid, dried in ether with calcium chloride, and vacuum distilled; yield 132 g. (80%), m. p. 43°. 3-Nitro-4-methylcinnamic acid was prepared from the aldehyde both by the Perkin reaction<sup>11</sup> (63% yield), and by condensation with malonic acid in the presence of pyridine and piperidine (70% yield), following the procedure given by Brand and Horn<sup>16</sup> for an analogous case.

The reduction of the nitro group and simultaneous saturation of the double bond was accomplished conveniently by the hydrogenation of the unsaturated acid (20.7 g.) dissolved in 95% alcohol (275 cc.) using Adams catalyst (0.2 g.). Some solid material which separated was dissolved by warming and the filtered solution was diluted with 1 liter of water and cooled well. The product separated in slightly pink crystal aggregates; yield 13.6 g. (76%), m. p. 140–141°.

(15) Ingold and Piggott, *J. Chem. Soc.*, **123**, 1469 (1923).

(16) Brand and Horn, *J. prakt. Chem.*, **115**, 374 (1927).

**3-Hydroxy-4-methylhydrocinnamic Acid.**—A solution of 8.96 g. of the above amine and 2.65 g. of sodium carbonate in 100 cc. of water was cooled, treated with an aqueous solution of 3.7 g. of sodium nitrite, and poured into a mixture of 10 cc. of concentrated hydrochloric acid, 50 g. of ice and 4.7 g. of boric acid. The mixture was gradually warmed, with stirring, and finally boiled for a few minutes and clarified with Norite. After cooling, the hydroxy acid was obtained by extraction with ether as a crystalline mass, m. p. 154–156°. Recrystallization from a very small volume of water gave slightly buff colored flat needles, m. p. 156–157°; yield 5.5 g. (61%).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{12}\text{O}_3$ : C, 66.63; H, 6.72. Found: C, 66.58; H, 6.95.

**3-Methoxy-4-methylhydrocinnamic acid** was obtained by the action of dimethyl sulfate on the above acid in warm alkaline solution. The substance crystallized from 50% alcohol as fine, colorless needles, m. p. 82–83°.

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{14}\text{O}_3$ : C, 68.02; H, 7.27. Found: C, 67.78; H, 7.35.

**5-Methoxy-6-methylhydrindone-1.**—The acid (9.25 g.) was warmed with thionyl chloride (4.6 cc.) and after the completion of the reaction and the removal of the excess reagent at the water pump the acid chloride was taken into 200 cc. of carbon bisulfide. Treatment with Norite gave a clear yellow solution, which was then cooled to 0° and treated with 14 g. of aluminum chloride. An oily complex separated, and after refluxing for four hours the mixture was cooled and treated with ice and hydrochloric acid. The residue remaining on removing the solvent by steam distillation was extracted with ether, which left much tarry material undissolved. On extracting the ethereal solution with sodium carbonate solution, 2.1 g. of starting material was recovered, while the residual ethereal solution yielded 2.7 g. of the hydrindone (42% conversion). The substance dissolves readily in petroleum ether and crystallizes from this solvent as lustrous, colorless needles, m. p. 114–115°.

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{12}\text{O}_2$ : C, 74.97; H, 6.87. Found: C, 75.24; H, 7.05.

An attempt to demethylate the hydrindone (2.7 g.) with 48% hydrobromic acid (3.5 cc.) and glacial acetic acid (30 cc.) led to the formation of a dimer. After boiling the solution for one hour a considerable quantity of orange-red needles had deposited and the mixture was cooled and filtered. From the mother liquor 1.7 g. of unchanged hydrindone was recovered. The orange-red needles (0.65 g., m. p. 215–217°, dec.) became yellow when boiled with dilute alkali, and this material on crystallization from acetic acid formed small yellow needles, m. p. 237–240°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{24}\text{O}_4$ : C, 74.97; H, 6.87; mol. wt., 396. Found: C, 75.47, 75.62; H, 6.85, 6.90; mol. wt. (Rast), 346.

**5-Hydroxy-6-methylhydrindone.**—A mixture of 1.7 g. of the hydrindone, 13.5 g. of amalgamated zinc, 34 cc. of concentrated hydrochloric acid, 10 cc. of water and 13 cc. of toluene was refluxed for eighteen hours. After steam distillation of the solvent the product was extracted with ether, but as the crude material (1.3 g.) appeared sensitive to oxidation and turned blue, it was demethylated without

further purification by refluxing under nitrogen with 25 cc. of glacial acetic acid, 1.8 cc. of 48% hydrobromic acid and 1 cc. of 45% hydriodic acid for three and one-half hours. After pouring the solution into 200 cc. of water and neutralizing the acids with sodium carbonate, the hydroxy compound separated as large, buff colored plates, m. p. 74–76°. Recrystallization from petroleum ether gave material melting at 83–84°, but the color was not entirely removed; yield 0.7 g. (49%). The compound has an odor reminiscent of that of  $\beta$ -naphthol.

*Anal.* Calcd. for  $C_{10}H_{12}O$ : C, 81.02; H, 8.17. Found: C, 80.84; H, 8.37.

Coupling tests in alkaline solution with diazotized sulfanilic acid were somewhat indecisive for there was considerable discoloration. With diazotized *p*-nitroaniline test solutions remained quite clear and were hardly distinguishable from alkaline solutions containing only the diazo component.

The benzoyl derivative crystallized from dilute alcohol as small, colorless plates, m. p. 111–112°.

*Anal.* Calcd. for  $C_{17}H_{16}O_2$ : C, 80.92; H, 6.39. Found: C, 80.79; H, 6.74.

**4,7-Dimethylhydrindene.**—4,7-Dimethylhydrindone-1 (m. p. 77°) was prepared according to Mayer and Müller<sup>13</sup> in 71% yield. Reduction by the Clemmensen method and recovery of the product by steam distillation gave a product boiling at 223–225° at atmospheric pressure and solidifying in a freezing mixture, m. p. –1.5°, yield 73%. The substance did not form a picrate.

*Anal.* Calcd. for  $C_{11}H_{14}$ : C, 90.35; H, 9.65. Found: C, 90.00; H, 10.10.

**Sodium 4,7-Dimethylhydrindene-5-sulfonate.**—A mixture of 6.5 g. of the hydrocarbon and 75 cc. of concentrated sulfuric acid was stirred mechanically for fifteen minutes on the steam-bath and the resulting solution was poured onto 500 cc. of ice. After neutralization with soda the solution was saturated at the boiling point with sodium chloride and on cooling the sulfonate separated as large white flakes. The yield after recrystallization was 8.7 g. (79%). For characterization and analysis the substance was converted into the *p*-toluidine salt, which formed long glistening needles from water, m. p. 248–249°, dec.

*Anal.* Calcd. for  $C_{18}H_{20}O_3NS$ : C, 64.83; H, 6.96. Found: C, 64.95; H, 7.16.

Attempted fusions of the sodium salt with potassium hydroxide gave either unchanged material or intractable tars.

**5,6-Dinitro-4,7-dimethylhydrindene.**—To a mixture of 1.6 cc. of concentrated nitric acid and 17 cc. of concentrated sulfuric acid at 0°, 3 g. of 4,7-dimethylhydrindene was added with stirring in one-half hour. The pasty mixture was poured onto ice and the pale yellow solid obtained was crystallized twice from glacial acetic acid, giving 2.3 g. of buff colored plates, m. p. 191–192°.

*Anal.* Calcd. for  $C_{11}H_{12}O_4N_2$ : C, 55.91; H, 5.13. Found: C, 56.28; H, 5.20.

**2-Methoxy-5- $\beta$ -chloropropionyl-*p*-xylene (XIII).**—Sodium *p*-xylene sulfonate, obtained in 85–95% yield after heating the hydrocarbon (20 g.) with concentrated sulfuric acid (100 cc.) for about fifteen minutes on the steam-bath,

gave *p*-xylenol in 66% yield on fusion with potassium hydroxide at 280–290°, and the methyl ether was prepared in the usual way.<sup>13</sup> After several trials the following procedure was found most satisfactory for the Friedel and Crafts reaction.

To a vigorously stirred suspension of 37.2 g. of finely powdered aluminum chloride in 250 cc. of carbon disulfide there was added over a half-hour period 35.6 g. of  $\beta$ -chloropropionyl chloride, a bright yellow complex separating as a solid. After cooling to 0°, 34 g. of *p*-xylyl methyl ether was added by drops with stirring in the course of forty-five minutes. On allowing the mixture to come to room temperature hydrogen chloride was evolved copiously and a dark purple complex collected as a heavy oil. After standing overnight ice and hydrochloric acid were added and the carbon disulfide layer was separated and combined with ether extracts of the aqueous layer. After washing with dilute acid, dilute alkali and water, the solution was dried over sodium sulfate and the solvent removed by distillation. The residual yellow oil solidified on cooling and pure material was easily obtained by crystallization from petroleum ether; yield, 41.9 g. (74%). The ketone forms colorless, prismatic plates melting at 85–86°; it is volatile with steam but decomposes on attempted distillation at reduced pressure.

*Anal.* Calcd. for  $C_{12}H_{16}O_2Cl$ : C, 63.55; H, 6.66. Found: C, 63.38; H, 7.01.

A derivative, **1-phenyl-3-(2',5'-dimethyl-3'-methoxyphenyl)- $\Delta^2$ -pyrazoline**, was obtained by heating the chloro ketone (0.5 g.) in absolute alcohol (7 cc.) with phenylhydrazine (0.5 g.) on the steam-bath. The difficultly soluble product separated rapidly and was recrystallized from its faintly fluorescent solution in alcohol, giving nearly colorless small plates, m. p. 171–172°.

*Anal.* Calcd. for  $C_{18}H_{20}ON_2$ : C, 77.09; H, 7.21. Found: C, 76.69; H, 7.49.

**5-Methoxy-4,7-dimethylhydrindone-1 (XIV).**—In trial cyclizations of the above chloro ketone warm concentrated sulfuric acid either left the material largely unchanged or gave extensive sulfonation. Formic acid at 100° was without effect, and aluminum chloride in carbon disulfide solution gave an alkali-soluble product. The following procedure, although far from satisfactory, was the best found. To a cold solution of 1.5 g. of the chloro ketone in 8 cc. of glacial acetic acid, 12 cc. of concentrated sulfuric acid was added and the clear red solution was warmed on the steam-bath for one hour and poured onto ice. The somewhat orange material which precipitated was collected and crystallized twice from glacial acetic acid, giving almost colorless needles, m. p. 163–165°; yield 0.35 g. (27%).

*Anal.* Calcd. for  $C_{12}H_{14}O_2$ : C, 75.76; H, 7.41. Found: C, 75.54; H, 7.25.

**5-Methoxy-4,7-dimethylhydrindene.**—A solution of 4 g. of the hydrindone in warm alcohol was added in small portions in one and one-half hours to a refluxing mixture of 42 g. of amalgamated zinc, 29 cc. of concentrated hydrochloric acid and 14 cc. of water, waiting after each addition until the yellow color had disappeared before adding a fresh portion. After adding 20 cc. more of the concentrated acid and refluxing for three hours, the reduction

product was recovered by steam distillation as a colorless oil. Further purification was effected by steam distillation from an alkaline medium, and on cooling the distillate with ice the substance solidified to a mass of colorless needles, m. p. 25–26°; yield 3.25 g. (90%).

*Anal.* Calcd. for  $C_{12}H_{16}O$ : C, 81.79; H, 9.14. Found: C, 81.49; H, 9.32.

**5-Hydroxy-4,7-dimethylhydrindene (VI).**—The above ether (3.25 g.) was refluxed with 25 cc. of glacial acetic acid and 4 cc. of 48% hydrobromic acid for three hours in a nitrogen atmosphere, and on pouring the solution into water the hydroxy compound separated as a pink solid. It was taken up in dilute alkali, the solution was clarified with Norite and acidified, and the dried product was crystallized twice from petroleum ether; yield 2 g. (66%). The substance forms fine colorless needles melting at 111–112°.

*Anal.* Calcd. for  $C_{11}H_{14}O$ : C, 81.44; H, 8.70. Found: C, 81.32; H, 8.76.

The benzoyl derivative forms colorless plates, m. p. 72–73°, from dilute alcohol.

*Anal.* Calcd. for  $C_{13}H_{18}O_2$ : C, 81.18; H, 6.80. Found: C, 80.82; H, 6.95.

**5-Hydroxy-4,7-dimethyl-6-*p*-nitrobenzeneazohydrindene** was obtained by coupling the components in 1% alkali at 0°. A red precipitate separated at once and it was unaffected by rendering the solution acidic and boiling the mixture to coagulate the material. Recrystallized from glacial acetic acid, in which it is sparingly soluble, the azo compound formed brownish-red needles, m. p. 220–222°, dec. It is insoluble in alkali.

*Anal.* Calcd. for  $C_{17}H_{17}O_3N_3$ : C, 65.58; H, 5.50. Found: C, 65.72; H, 5.85.

**6-Methoxy-5,8-dimethyltetralin.**—On condensing *p*-xylyl methyl ether and succinic anhydride with aluminum chloride in benzene solution as described by Clemons, Haworth and Walton,<sup>12</sup> the yield was even lower than that (70%) reported by these investigators, but the general procedure described by Fieser and Hershberg<sup>17</sup> proved very satisfactory. Using 0.2 mole of the ether, 0.21 mole of succinic anhydride, 200 cc. of tetrachloroethane, 50 cc. of nitrobenzene and 0.42 mole of aluminum chloride, stirring at 0° until solution was complete, and allowing the mixture to stand for four days at 0°,  $\beta$ -4-methoxy-2,5-dimethylbenzoylpropionic acid, recovered as usual and crystallized from dilute alcohol, was obtained as colorless crystals, m. p. 130–131°, in 86% yield. The reduction to  $\gamma$ -4-methoxy-2,5-dimethylphenylbutyric acid (m. p. 98–99°) by the Clemmensen–Martin method has been described<sup>18</sup> already. Cyclization was effected according to Clemons, Haworth and Walton<sup>12</sup> in 64% yield.

(17) Fieser and Hershberg, Part IV, in press.

(18) Martin, *THIS JOURNAL*, **58**, 1438 (1936).

**7-Methoxy-5,8-dimethyltetralone-1** (6 g.) was reduced by the ordinary Clemmensen method, refluxing for twenty-one hours, and the material extracted with ether after distillation (b. p. 116–125° at 12–13 mm.) was obtained as a solid, m. p. 36–38°; yield 4.25 g. (76%). Crystallization from petroleum ether gave colorless needles melting at 38–39°.

*Anal.* Calcd. for  $C_{13}H_{18}O$ : C, 82.06; H, 9.52. Found: C, 82.36; H, 9.76.

**6-Hydroxy-5,8-dimethyltetralin (IX).**—For demethylation the ether (4.25 g.) was refluxed with glacial acetic acid (25 cc.) and 45% hydriodic acid (9.75 g.) for three hours. The crude product was precipitated from a clarified solution in dilute alkali and crystallized from petroleum ether, giving nearly colorless needles, m. p. 104–105°, yield 2.45 g. (62%). The substance dissolves in dilute alkali slowly on warming.

*Anal.* Calcd. for  $C_{12}H_{16}O$ : C, 81.79; H, 9.14. Found: C, 81.78; H, 9.48.

The benzoyl derivative forms very long, slender, colorless needles, m. p. 119–120°, from dilute alcohol.

*Anal.* Calcd. for  $C_{14}H_{20}O_2$ : C, 81.38; H, 7.18. Found: C, 81.44; H, 7.26.

**6-Hydroxy-5,8-dimethyl-7-*p*-nitrobenzeneazotetralin** was obtained by coupling as described above and crystallized from glacial acetic acid, in which it is sparingly soluble. The substance forms bronze-red needles, m. p. 220–231°. It is insoluble in alkali and stable to acids.

*Anal.* Calcd. for  $C_{13}H_{19}O_3N_3$ : C, 66.42; H, 5.90. Found: C, 66.50; H, 6.11.

### Summary

$\beta$ -Hydroxy derivatives of hydrindene and of tetralin with one ortho position blocked with a methyl group and the other free have been tested in the coupling reaction to determine if both ortho positions are capable of constituting enolic groups, or if there is any fixation of the bonds in the aromatic nucleus as the result of the spatial requirements of the attached alicyclic rings (Mills–Nixon effect). This test affords a more severe criterion of fixation than that of Mills and Nixon, based upon reactivities, and the results indicate that hydrindene has a rigid bond structure comparable with that of naphthalene, but that tetralin, like all ordinary benzene derivatives, can react in both Kekulé forms.

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