the hydrolysis of waxy maize starch than those reported in Table II showed that maltose was present in significant concentrations from the very early stages of the hydrolysis of this substrate, at stages which corresponded to approximately 2 to 5% of theoretical maltose. On the other hand, reaction mixtures at these very early stages of hydrolysis gave no evidence of the presence of glucose even when the concentrated hydrolyzates were examined by the sensitive manometric technique. Concentrated dialyzates of these early reaction mixtures, also, failed to show traces of glucose. At later stages of the reaction, whenever both sugars appear in the hydrolyzates of waxy maize starch, the concentrations of glucose are much lower than those of maltose.

The data given in Table II are also of interest because they show that the relative concentrations of the products were different in comparable hydrolyzates which had reached stages of very slow rates of change in the same time (five hours) under the influence of different concentrations of maltase-free pancreatic amylase. These data confirm and extend previous observations[2] that the slowing down of the hydrolysis of starch by pancreatic amylase under conditions which prevent its inactivation[2] is due largely to the replacement of the original substrate by products which the amylase hydrolyzes slowly, for which it has low affinities.

While the results obtained in the earlier stages of the hydrolysis suggest that pancreatic amylase causes a random hydrolysis of waxy maize starch, the accumulation of low molecular weight dextrins in the later stages of the hydrolysis indicates that the action of the amylase is not perfectly random.

Summary and Conclusions

A study has been made of the hydrolysis of the branched chain substrate, waxy maize starch, by highly purified maltase-free pancreatic amylase.

It has been found that the extent of the hydrolysis of waxy maize starch like that of other starches and of their linear components depends within wide limits upon the concentration of pancreatic amylase.

Under comparable conditions and judged by the total reducing values of the reaction mixtures, waxy maize starch is hydrolyzed more slowly by pancreatic amylase than unfractionated corn starch and much more slowly than the linear fraction from corn starch.

Maltose is present in significant concentrations from the very early stages of the hydrolysis of waxy maize starch by purified pancreatic amylase.

Glucose, also, is liberated in the hydrolysis of waxy maize starch by purified maltase-free pancreatic amylase but this sugar is set free in smaller concentrations than maltose and does not appear in the very early stages of the hydrolysis.

Waxy maize starch is hydrolyzed rapidly by pancreatic amylase to products of relatively low average molecular weights and of relatively high reducing values.

The attack of pancreatic amylase on waxy maize starch appears to be random in the early stages of the hydrolysis but the accumulation of low molecular weight products in the later stages of the hydrolysis indicates that the action of the amylase is not perfectly random.

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

The Dienone-Phenol Rearrangement. II. Rearrangement of 1-Keto-4-methyl-4-phenyl-1,4-dihydronaphthalene

BY RICHARD T. ARNOLD AND JAY S. BUCKLEY, JR.

If the dienone–phenol rearrangement proceeds by a mechanism[1,2] similar to that for the conversion of pinacols to pinacolones, the same migratory aptitudes of groups should be observed in both rearrangements. It is well established[3,4] that a phenyl group migrates preferentially with respect to a methyl group in the pinacol rearrangement, and now the same migratory aptitude has been found in the dienone–phenol rearrangement of 1-keto-4-methyl-4-phenyl-1,4-dihydronaphthalene (VI) to 4-methyl-3-phenyl-1-naphthol (VIII).

Synthesis of the dienone VI involved the preparation of γ,γ-diphenylvaleric acid[5] and the cyclization of this acid to 4-methyl-4-phenyl-1-tetralone (IV).[6c] Bromination of this ketone gave a

(1) Arnold, Buckley and Richter, THIS JOURNAL, **69**, 2322 (1947).

(2) Huang-Minlon, *ibid.*, **70**, 611 (1948).

(3) Kon, *Annual Reports*, **30**, 182 (1933).

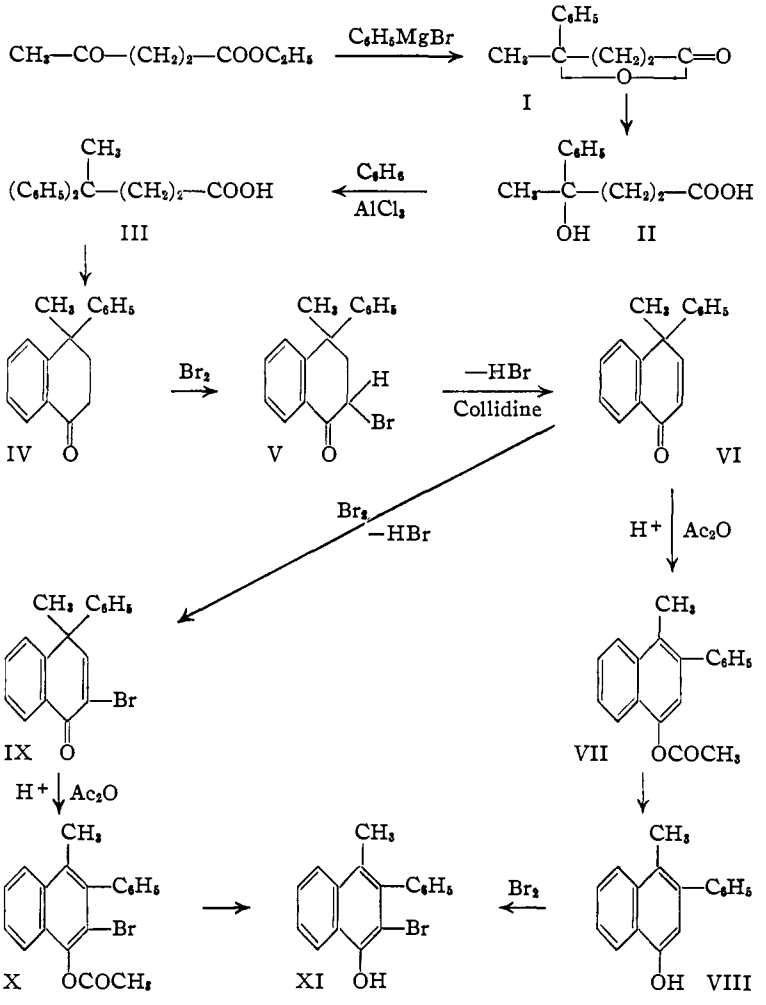
(4) Thorner and Zincke, *Ber.*, **13**, 644 (1880).

(5) This acid has been obtained as a side product in the preparation of phenacylacetone from "Lävulinsäurechlorides" by Helberger (*Ann.*, **522**, 270 (1936)). It has been prepared also by Eykman (*Chemisch Weekblad*, **4**, 727 (1907)) by treating $\Delta\beta$-angelica lactone with benzene and aluminum chloride. We have found that under normal conditions for the condensation of lactones with benzene[6a] a 46% yield of phenacyl acetone can be obtained from $\Delta\beta$-angelica lactone. This cleavage between the carbonyl carbon and the oxygen is similar to that observed by Boese[6b] in the reaction of diketene with benzene and aluminum chloride.

(6a) Beyer, *Ber.*, **70**, 1101, 1482 (1937).

(6b) Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

(6c) Preliminary experiments under varied conditions showed that it was not feasible to prepare this ketone by a direct Friedel–Crafts reaction between γ-methyl-γ-phenylbutyrolactone and benzene, as originally proposed (1).



mixture of racemates of the bromoketone V which was dehydrobrominated directly to obtain 1-keto-4-methyl-4-phenyl-1,4-dihydronaphthalene (VI). Rearrangement of this dienone in acetic anhydride solution with sulfuric acid gave the acetate of 4-methyl-3-phenyl-1-naphthol (VII).

The dienone VI absorbed one equivalent of bromine to form an unstable dibromide which readily eliminated hydrogen bromide to form 2-bromo-1-keto-4-methyl-4-phenyl-1,4-dihydronaphthalene (IX). Rearrangement of this bromodienone gave a 92% yield of the acetate of 2-bromo-4-methyl-3-phenyl-1-naphthol (X).

To prove the structures of the rearrangement products, 4-methyl-3-phenyl-1-naphthol (VIII) was synthesized by an independent route involving the preparation of 4-methyl-3-phenyl-1-tetralone (XV) previously described by Spring.[7] Since Spring reported products that differed stereochemically from ours, the preparation of XV is reported in detail.

A Reformatsky reaction with α-phenylpropiophenone (XII) gave a mixture of racemates of the hydroxy acid XIII which, except for identification, was not separated but reduced with hydriodic acid and red phosphorus to obtain a mixture of racemates of β,γ-diphenylvaleric acid (XIV).[8] Cyclization of this mixture yielded a mixture of racemates of 4-methyl-3-phenyl-1-tetralone (XV) from which the racemate reported by Spring was separated. Bromination and subsequent dehydrobromination of these ketones gave 4-methyl-3-phenyl-1-naphthol (VIII) which was identical in all respects with the product obtained by the dienone–phenol rearrangement. Bromination of the naphthol VIII gave 2-bromo-4-methyl-3-phenyl-1-naphthol (XI) which was identical with the product from rearrangement of the bromodienone IX.

Experimental

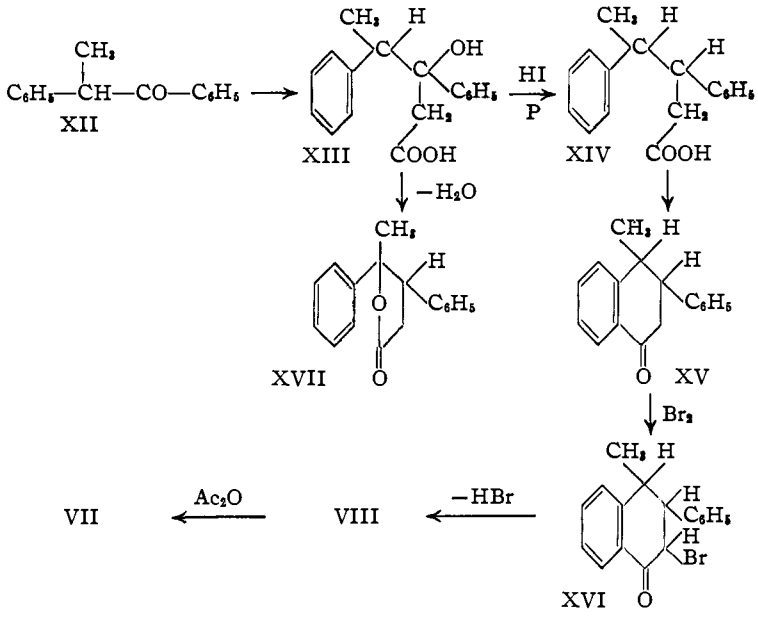
γ-Methyl-γ-phenylbutyrolactone (I)[9].—A Grignard solution was prepared from 329.7 g. of bromobenzene and 51 g. of magnesium in 800 ml. of ether. Half of the ether was removed by distillation and replaced with benzene. The resulting solution was added under nitrogen, during 1.5 hours, to a stirred solution of 288 g. of ethyl levulinate in 1200 ml. of benzene at 0°. After stirring for one hour at room temperature, the mixture was decomposed on ice and dilute sulfuric acid. The organic layer was washed successively with sodium bicarbonate, water, and saturated sodium chloride solution and the solvents distilled. The residue yielded 174 g. (49.5%) of the lactone, b. p. 128–130° (3 mm.); $n^{20}D$ 1.5310.

γ-Hydroxy-γ-phenylvaleric Acid (II)[9].—γ-Methyl-γ-phenylbutyrolactone (102 g.) was stirred with a hot solution of 34 g. of sodium hydroxide in 1500 ml. of water for forty-five minutes. After one extraction with benzene, the aqueous solution was cooled to 0° and acidified with vigorous stirring. The precipitated hydroxy acid was washed with water, and the dried product was suspended in petroleum ether (b. p. 60–68°). Filtration yielded 104.5 g. of the hydroxy acid, m. p. 103.5–104.5°.

(7) Spring, *J. Chem. Soc.*, 1332 (1934).

(8) This acid mixture was not separated since the racemates have been described by Spring[7] and Meerwein (*J. prakt. Chem.*, **97**, 269 (1918)), respectively. A mixture of racemates of the acid XIV was obtained upon reduction of the pure racemates of the hydroxy acid XIII due, perhaps, to the formation by an S_N1 mechanism of the same intermediary cation (C_6H_5—CH(CH$_3$)—C$^+$(C_6H_5)—CH_2—COOH) from each racemate. An attempted reduction of a mixture of racemates of the hydroxy acid XIII with phosphorus and iodine in acetic acid solution gave a racemate of β,γ-diphenyl-γ-valerolactone (XVII) as the major product. Attempts to prepare the naphthol VIII by the methods by Borsche (*Ann.*, **526**, 1 (1936)) were unsuccessful, for the lactone XVII distilled unchanged at 400° and was unaffected upon refluxing with phosphorus trichloride as well as stannic chloride.

(9) Johnson, Petersen and Schneider, THIS JOURNAL, **69**, 77 (1947).



γ,γ-Diphenylvaleric Acid (III).[5]—A stirred suspension of 33 g. of aluminum chloride in 200 ml. of benzene at 0° was treated, during thirty minutes, with 16 g. of γ-hydroxy-γ-phenylvaleric acid (II). The mixture was stirred for five hours during which the bath temperature rose to 15°; it was then hydrolyzed with ice and dilute hydrochloric acid. Extraction of the benzene solution with 5% sodium hydroxide solution followed by acidification of the alkaline extracts gave a semi-solid product that was crystallized from aqueous methanol. This material (11.8 g., m. p. 113–115°) was recrystallized to obtain the acid, m. p. 115–116°, that did not depress the melting point of a sample obtained by Helberger's method.[5]

4-Methyl-4-phenyl-1-tetralone (IV).—Phosphorus pentachloride (18.7 g.) was added to a solution of 20.3 g. of γ,γ-diphenylvaleric acid (III) in 100 ml. of benzene. After thirty minutes at room temperature and boiling for ten minutes, the solution was treated with 41.7 g. of stannic chloride.[10] The neutral product was distilled to obtain 15.1 g. of viscous ketone, b. p. 172° (6 mm.).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.11; H, 6.86.

The oxime of the ketone melted at 170–171°.

Anal. Calcd. for $C_{17}H_{17}ON$: C, 81.24; H, 6.82. Found: C, 80.84; H, 6.63.

The 2,4-dinitrophenylhydrazone, crystallized from ethyl acetate–alcohol, melted at 211–213°.

Anal. Calcd. for $C_{23}H_{20}O_4N_4$: C, 66.33; H, 4.84. Found: C, 66.17; H, 4.90.

1-Keto-4-methyl-4-phenyl-1,4-dihydronaphthalene (VI).—Bromine (9.6 g.) was vaporized in a stream of dry nitrogen and absorbed, during two hours, in a solution of 14.2 g. of 4-methyl-4-phenyl-1-tetralone in 175 ml. of carbon tetrachloride.[11,12] After one hour at room temperature, the solution was washed with sodium bicarbonate solution, dried over calcium chloride, and the solvent distilled. The viscous residue did not yield any solid material, so it was refluxed for seventy minutes with 50 ml. of γ-collidine, cooled, acidified, and the dienone extracted with ether. Distillation gave 10.5 g. of the dienone VI,[13] b. p. 165–170° (3 mm.). This material crystallized from petroleum ether at −80°, but became liquid at room temperature. Since this product could not be purified conveniently, it was converted to its bromo derivative IX, as well as rearranged into VII without further purification.

4-Methyl-3-phenyl-1-naphthyl Acetate (VII).—A solution of 4.7 g. of 1-keto-4-methyl-4-phenyl-1,4-dihydronaphthalene (VI) in 50 ml. of acetic anhydride was treated with 1.0 g. of sulfuric acid in 20 ml. of acetic anhydride. After five hours at room temperature, followed by slow addition to ice water, 4.6 g. of material, m. p. 81–84°, was obtained. Crystallization from aqueous methanol yielded 3.9 g. (70%) of the acetate, m. p. 95–96° after drying *in vacuo*.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.69; H, 5.87.

4-Methyl-3-phenyl-1-naphthol (VIII).—4-Methyl-3-phenyl-1-naphthyl acetate (2.32 g.) was refluxed for one hour with 60 ml. of 5% methanolic potassium hydroxide. Acidification of the solution and crystallization of the product from carbon tetrachloride–petroleum ether (b. p. 60–68°) yielded a colored product (1.74 g., m. p. 127–128°). Vacuum sublimation of the product and recrystallization gave the colorless naphthol, m. p. 127–128°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.04; H, 6.12.

2-Bromo-1-keto-4-methyl-4-phenyl-1,4-dihydronaphthalene (IX).—A solution of 3.29 g. of the dienone VI in 30 ml. of carbon tetrachloride was treated with a solution of approximately 1 molar equivalent of bromine in 20 ml. of carbon tetrachloride until there was a persisting orange color. Evaporation of the solvent on a steam-bath resulted in a vigorous evolution of hydrogen bromide. Two crystallizations of the residue from aqueous methanol gave 3.41 g. (77%) of the bromodienone, m. p. 116–119°. An additional crystallization gave the colorless bromodienone, m. p. 118.5–119.5°.

Anal. Calcd. for $C_{17}H_{13}OBr$: C, 65.19; H, 4.18. Found: C, 65.28; H, 4.20.

2-Bromo-4-methyl-3-phenyl-1-naphthyl Acetate (X).—A solution of 2.78 g. of the bromodienone IX in 25 ml. of acetic anhydride was treated with 500 mg. of sulfuric acid in 10 ml. of acetic anhydride. Isolation of the product after five hours at room temperature yielded 3.15 g. of colorless material, m. p. 136–141°. One crystallization from aqueous ethanol gave 2.86 g. (92%) of the acetate, m. p. 142.5–144°.

Anal. Calcd. for $C_{19}H_{15}O_2Br$: C, 64.24; H, 4.26. Found: C, 64.27; H, 4.35.

2-Bromo-4-methyl-3-phenyl-1-naphthol (XI).—Hydrolysis of 2.46 g. of the acetate X with 50 ml. of 5% alcoholic potassium hydroxide gave the bromonaphthol XI which, after crystallization from aqueous ethanol, weighed 1.88 g. and melted at 100–101°.

A solution of approximately 1 molar equivalent of bromine in 5 ml. of acetic acid was added to a solution of 0.74 g. of 4-methyl-3-phenyl-1-naphthol in 10 ml. of acetic acid. The resulting solution was poured into water, and the precipitated pink powder, by crystallization from aqueous ethanol containing a trace of sodium bisulfite, yielded 0.86 g. of the bromonaphthol, m. p. 99–100.5°.

Anal. Calcd. for $C_{17}H_{13}OBr$: C, 65.19; H, 4.18. Found: C, 65.27; H, 4.20.

This bromonaphthol did not depress the melting point

(10) Wilds, THIS JOURNAL, **64**, 1421 (1942).

(11) Bourcart, *Ber.*, **22**, 1368 (1889).

(12) Maeder, *Helv. Chim. Acta*, 124 (1946).

(13) This product (*Anal.* Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.33; H, 6.37) undoubtedly contains some of the ketone IV. The impurities probably account for the low melting point of the crude product formed upon rearrangement, as well as the diminished yield.

of the hydrolysis product from 2-bromo-4-methyl-3-phenyl-1-naphthyl acetate (X).

β,γ-Diphenyl-β-hydroxyvaleric Acid (XIII).[7]—A mixture of 40 g. of α-phenylpropiophenone, 34 g. of ethyl bromoacetate, 200 ml. of benzene, and 17 g. of zinc strips (sandpapered under benzene) was refluxed for two hours. The resulting ester was refluxed for two hours with 300 g. of 20% alcoholic potassium hydroxide, the alcohol distilled *in vacuo*, and 500 ml. of water was added. Unchanged ketone was removed by extraction with ether. Acidification of the alkaline solution gave an oil which was taken up in ether and the ether evaporated. The residue was dissolved in 150 ml. of hot benzene, and 150 ml. of petroleum ether (b. p. 60–68°) was added to precipitate 30 g. of a mixture of racemates of the hydroxy acid XIII, m. p. 112–140°.

Fractional crystallization of 26 g. of this mixture from aqueous methanol gave 7 g. of the higher melting racemate, m. p. 176.5–177.5° (reported m. p. 178°). The more soluble fraction was crystallized from benzene–petroleum ether to obtain 8 g. of the lower melting racemate, m. p. 108–110°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.56; H, 6.87.

β,γ-Diphenylvaleric Acid (XIV).[7,8]—A mixture of the racemates of β,γ-diphenyl-β-hydroxyvaleric acid (17.5 g.) was refluxed for five hours with 105 g. of hydriodic acid (sp. gr. 1.7) and 17.5 g. of red phosphorus. The viscous, oily product was dissolved in 300 ml. of warm 5% ammonium hydroxide, filtered, and the filtrate acidified. The precipitated acid was crystallized from aqueous methanol to yield 10.6 g. of a mixture of racemates of β,γ-diphenylvaleric acid, m. p. 90–115°.

Reduction[7] of the higher melting racemate of the hydroxy acid XIII (6.6 g.) gave 4.5 g. of a mixture of the racemates of β,γ-diphenylvaleric acid, m. p. 95–120°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.43; H, 7.26.

β,γ-Diphenyl-γ-valerolactone (XVII).—A mixture of the racemates of β,γ-diphenyl-β-hydroxyvaleric acid (33 g.) was treated with 1.4 g. of iodine, 4.2 g. of red phosphorus, 1.4 ml. of water, and 80 ml. of acetic acid according to "Organic Syntheses."[14] The oily product was dissolved in ether, and the dried ether solution evaporated to give a residue which was crystallized from petroleum ether (b. p. 60–68°). This material (14 g.) was recrystallized from petroleum ether and finally from aqueous ethanol to yield 9.5 g. of the lactone, m. p. 113–114.5°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.09; H, 6.46.

The lactone XVII dissolved very slowly in boiling sodium hydroxide solution, but more rapidly in potassium hydroxide solution. Saponification of 0.83 g. of the lactone was complete after boiling for forty-five minutes with 50 ml. of 10% potassium hydroxide. Acidification of the cold alkaline solution precipitated the hydroxy acid which lactonized at room temperature. Crystallization of the material from aqueous ethanol yielded 0.60 g. of the lactone, m. p. 113–114.5°.

4-Methyl-3-phenyl-1-tetralone (XV).[7]—A mixture of the racemates of β,γ-diphenylvaleric acid (10.5 g.), 31 ml. of concentrated sulfuric acid, and 10 ml. of water was heated for seventy minutes at 100° with stirring and the reaction was worked up as previously reported.[7] The neutral product (6.3 g., b. p. 184–185° (2 mm.)) partially solidified; it was melted prior to analysis.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.47; H, 6.81.

The higher melting racemate, m. p. 68–69.5° (reported m. p. 68°), was isolated from this mixture by crystallization from petroleum ether (b. p. 60–68°), but attempts to isolate the lower melting form were unsuccessful.

4-Methyl-3-phenyl-1-naphthol (VII).—A mixture of the racemates of 4-methyl-3-phenyl-1-tetralone (1.03 g.) in 50 ml. of dry ether was treated with 0.224 ml. of bromine at 0°. After fifteen minutes, the solution was poured into water, washed with bicarbonate solution, dried, and the ether evaporated. The residue was refluxed for seventy minutes with 10 ml. of γ-collidine, cooled, and acidified. The product was taken up in ether, and the solution was extracted five times with 5% potassium hydroxide and the ether layer dried. Distillation yielded 0.77 g. of an oil, b. p. 192–200° (2 mm.) which, after crystallization from aqueous methanol, yielded 0.64 g. of 4-methyl-3-phenyl-1-naphthol, m. p. 122–125°. This material was dissolved in 50 ml. of 3% potassium hydroxide solution, and the naphthol was extracted with ether from the filtered alkaline solution. Evaporation of the ether and crystallization of the residue from carbon tetrachloride–petroleum ether gave the naphthol, m. p. 125.5–127°.

The acetate of this naphthol was prepared by refluxing 300 mg. of the naphthol with 3 ml. of acetic acid, 3 ml. of acetic anhydride, and a drop of sulfuric acid. The recrystallized acetate, m. p. 94.5–96°, and the naphthol described above did not depress the melting points of the products obtained by rearranging 1-keto-4-methyl-4-phenyl-1,4-dihydronaphthalene (VI).

Summary

1. 1-Keto-4-methyl-4-phenyl-1,4-dihydronaphthalene and 2-bromo-1-keto-4-methyl-4-phenyl-1,4-dihydronaphthalene have been prepared and rearranged to 4-methyl-3-phenyl-1-naphthol and 2-bromo-4-methyl-3-phenyl-1-naphthol, respectively.

2. Evidence for a pinacol–pinacolone type mechanism in the dienone-phenol rearrangement has been obtained by a comparison of group migratory aptitudes.

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(14) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 224.