[Contribution from the Noyes Chemical Laboratory, University of Illinois]

THE REACTION OF BENZYLMAGNESIUM CHLORIDE WITH MESITYL 1-METHYL-2-NAPHTHYL KETONE

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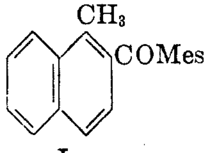
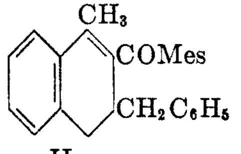
The ability of Grignard reagents to undergo conjugate addition with mesityl 2-naphthyl ketone (1) suggested that attack at the 3-position might be possible provided the 1-position were blocked by a suitable substituent. Accordingly, mesityl 1-methyl-2-naphthyl ketone (I) has been treated with benzylmagnesium chloride. Decomposition of the reaction mixture in air gave a hydroperoxide, showing the enol to be fairly stable. The enol could be ketonized, however, by heating with methanolic hydrogen chloride to give a product having the composition of the 3-benzyl derivative (II) that might have been expected. The properties of the benzyl derivative, however, corresponded rather to those to be expected of a compound having structure III, in which the benzyl radical is attached to the carbon atom that holds the methyl group.



I



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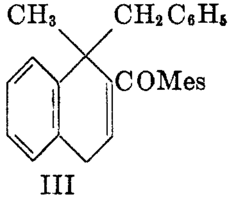

III

Treatment of the compound with a palladium-charcoal catalyst at 300° eliminated the benzyl group, yielding mesityl 1-methyl-2-naphthyl ketone. The same change was observed when the benzyl compound was treated with alkaline permanganate for 30 hours at 100°. Apparently pyrolysis occurred faster than oxidation. This behavior is interpreted to mean that the benzyl group is attached to a quaternary carbon atom.

The infrared spectrum had absorption bands assignable to *ortho*-substituted phenyl, doubly-conjugated carbonyl, and monosubstituted phenyl structural elements and showed no absorption corresponding to the hydroxyl group.[1]

Oxidation of the compound with permanganate under mild conditions or with ozone furnished a derivative ($C_{26}H_{26}O_2$) which formed an oxime. Since the oxidation product must have an unhindered carbonyl group, it was assigned structure IV. The infrared absorption spectrum had bands assignable to doubly-conjugated carbonyl, *ortho*-substituted phenyl, and monosubstituted phenyl structural units.

With ethanolic sodium hydroxide or methanolic hydrogen chloride the benzyl compound was transformed into a high-melting (316–318°) substance, which had been obtained in small amount from the mild permanganate oxidation also. Al-

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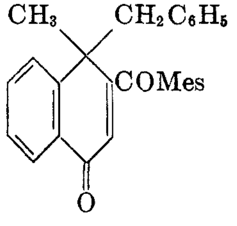
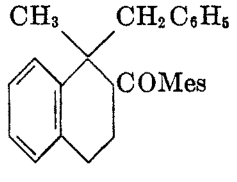
[1] The infrared absorption spectra mentioned in this paper were observed and interpreted by Miss Elizabeth Petersen and Mrs. J. L. Johnson.

though the structure of the compound has not been established, its formation must have involved loss of the benzyl radical. Actually it was first encountered



IV



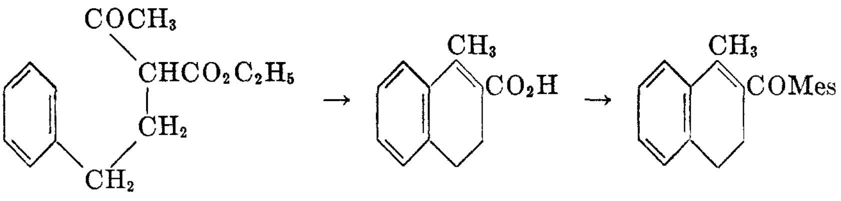
V

as a product of the reaction between methylmagnesium iodide and mesityl 2-naphthyl ketone. It is thought to be 4,4′-dimethyl-3,3′-dimesitoyl-1,1′-binaphthyl.

The correctness of structure III for the benzylation product was established by way of its hydrogenation product (V), obtained by catalytic hydrogenation in the presence of Raney nickel.

The structure of the hydrogenation product (V) was confirmed by the independent synthesis from 1-methyl-3,4-dihydro-2-naphthoic acid (VII). This acid was made from ethyl phenethylacetoacetate (VI) by the method of von Auwers and Moeller (2).

Treatment of this acid with phosphorus trichloride gave 1-methyl-3,4-dihydro-2-naphthoyl chloride. Friedel-Crafts acylation of mesitylene with this acid chloride yielded mesityl 1-methyl-3,4-dihydro-2-naphthyl ketone (VIII). The structure of this compound was established by dehydrogenation with palladium-charcoal to mesityl 1-methyl-2-naphthyl ketone. Condensation of mesityl 1-methyl-3,4-dihydro-2-naphthyl ketone with benzylmagnesium chloride and subsequent ketonization with methanolic hydrogen chloride produced mesityl 1-benzyl-1-methyl-1,2,3,4-tetrahydro-2-naphthyl ketone. This ketone was proved to be identical with that obtained by catalytic hydrogenation of mesityl 1-benzyl-1-methyl-1,4-dihydro-2-naphthyl ketone by use of mixture melting points and by comparison of infrared absorption spectra.



VI VII VIII

EXPERIMENTAL

The benzyl derivative of mesityl 1-methyl-2-naphthyl ketone. A solution of 20.5 g. of mesityl 1-methyl-2-naphthyl ketone in 200 ml. of dry ether was added slowly to a Grignard reagent prepared from 6.8 g. of magnesium, 35.5 g. of freshly-distilled benzyl chloride, and 200 ml. of dry ether. The addition was carried out at such a rate as to maintain gentle reflux. The mixture was heated under reflux for 3 hours after mixing was complete, cooled, and decomposed by the addition of 100 ml. of 1.2 *N* hydrochloric acid and 200 ml. of water. The preceding operations were conducted in an oxygen-free nitrogen atmosphere.

The ether solution was removed, dried over sodium sulfate, and returned to the nitrogen atmosphere. The ether was distilled, and 150 ml. of saturated methanolic hydrogen chloride was added to the residue. The mixture was heated for 15 hours under reflux in a nitrogen atmosphere. When part of the methanol was removed at the water-pump, the product crystallized. After trituration with ethanol it weighed 14.8 g. (55%). It was purified by recrystallization from ethanol; m.p. 128.5–129.5°.

Anal.[2] Calc'd for $C_{26}H_{28}O$: C, 88.38; H, 7.42.
Found: C, 88.34; H, 7.46.

The infrared spectrum of the benzyl compound has an absorption band at 1658 cm^{-1} which is assignable to a doubly conjugated carbonyl group. The benzyl compound appears to deteriorate slowly. A pure sample, kept in a drying pistol near 100° for 12 hours, acquired a yellow tinge and melted over a range beginning at 122°. After being stored for a year the analytical sample was found to have a melting point that was not sharp. Melting point samples of pure material introduced into a bath held at 120° soon softened and melted completely within 25 minutes.

Attempted dehydrogenation of the dihydro compound (III). A mixture of 0.5 g. of the crude ketone and 0.05 g. of a 10% palladium-charcoal catalyst was heated at 300° for 40 minutes and cooled. The methanol extract, after filtration, deposited 0.22 g. (58% yield) of colorless crystals which, after recrystallization from ethanol, melted at 97–98°. A mixture of this product with an authentic sample of 2-mesitoyl-1-methylnaphthalene [m.p. 98.5–100° (4)] melted at 97.5–98.5°.

The peroxide of the enol form of the dihydro ketone (III) was obtained by adding petroleum ether to the ethyl ether solution of the enol and passing a stream of oxygen through the resulting solution for 4 hours. A total of 1.78 g. (68% yield) of peroxide was obtained as colorless crystals. Recrystallization of the peroxide from a mixture of benzene and high-boiling petroleum ether gave white needles. The melting point depended on the rate of heating, the highest value obtainable being 175–177° (corr.). Melting was accompanied by the evolution of gas.

Anal. Calc'd for $C_{28}H_{28}O_3$: C, 81.52; H, 6.84.
Found: C, 81.66; H, 7.06.

The infrared absorption spectrum possesses bands assignable to the hydroxyl group (3326 cm^{-1}), the mesityl radical (1615 and 851 cm^{-1}), and the phenyl group (1579, 1490, and 707.5 cm^{-1}). The band assignable to the carbonyl group is missing.

Oxidation of the benzyl compound. A. With neutral permanganate. A 2% solution (50 ml.) of potassium permanganate was added gradually over a period of 80 minutes, with stirring, to a solution of 2 g. of the benzyl compound in 150 ml. of acetone. The temperature of the reaction mixture was held at −5–0° during the addition and for 25 minutes thereafter. After excess permanganate had been destroyed with ethanol, the manganese dioxide was removed by filtration, and most of the acetone was distilled. The yellow product was treated with boiling ethanol and the mixture filtered. A white, insoluble powder (0.035 g.) was collected on the filter and from the filtrate 0.69 g. of yellow crystals separated; m.p. 143–146°. The mother liquors yielded an additional 0.34 g. of the compound. After repeated recrystallization from ethanol the yellow crystals melted at 149.5–150°.

Anal. Calc'd for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64.
Found: C, 85.00; H, 6.82.

The same compound was obtained when the benzyl derivative was treated with ozone in glacial acetic acid at 20° according to the procedure of Smith, Greenwood, and Hudrlik (3).

An *oxime* was formed by treating the oxidation product with hydroxylamine in the usual way. It was recrystallized from dilute ethanol; m.p. 199–201°.

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[2] The microanalyses reported in this paper were carried out by Miss Emily Davis, Miss Rachel Kopel, and Mrs. Jean Fortney.

Anal. Calc'd for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42.
Found: C, 82.45; H, 6.86; N, 3.75.

The infrared absorption spectrum of the benzyl compound has bands ascribable to the presence of a doubly-conjugated carbonyl group (1666 cm^{-1}) as well as *o*-phenyl and monosubstituted phenyl groupings (742 cm^{-1}, 762 cm^{-1}).

The ethanol-insoluble powder was recrystallized from glacial acetic acid; m.p. 315–317°. A mixture melting point showed this compound to be identical with that obtained previously in the preparation of mesityl 1-methyl-2-naphthyl ketone (4). This compound was obtained also as a by-product in one of the condensations of benzylmagnesium chloride with mesityl 1-methyl-2-naphthyl ketone. The infrared spectrum of the high-melting compound had bands assignable to a doubly-conjugated carbonyl group (1666 cm^{-1}) and an *ortho*-substituted phenyl group (762 cm^{-1}).

Anal. Calc'd for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66.
Found: C, 87.76; H, 6.74.

B. With alkaline permanganate. The method employed was similar to that of Randall, Benger, and Groocock (5) in the oxidation of aromatic hydrocarbons. A mixture of 2 g. of the benzyl compound, 5 g. of potassium hydroxide, and 300 ml. of water was heated to reflux, and a 2% solution of potassium permanganate was added, with stirring, until no further decolorization took place (24 hours). The total period of heating and stirring was 30 hours. When the mixture was cooled, a film of oil collected on the surface of the liquid. Introduction of an additional 5 ml. of permanganate solution followed by an hour of stirring at 98–100° did not cause the oil to dissolve. After the mixture had been recooled, the oil was removed mechanically, and the manganese dioxide was removed by filtration. No organic material could be obtained from the filtrate.

After the reaction product had stood for several months it was partially crystalline. The crystalline compound, obtained in small amount, melted at 99.5–100° and was shown by the method of mixture melting points to be mesityl 1-methyl-2-naphthyl ketone.

Mesityl 1-benzyl-1-methyl-1,2,3,4-tetrahydro-2-naphthyl ketone (V). A solution of 2 g. of mesityl 1-benzyl-1-methyl-1,4-dihydro-2-naphthyl ketone in 50 ml. of dry methanol was heated for 8 hours at 105–110° and shaken with ¼ teaspoonful of Raney nickel catalyst in a bomb while subjected to 2400 p.s.i. of hydrogen. The mixture was then cooled and filtered. The filtrate was saturated with dry hydrogen chloride and heated at reflux for 12 hours. After the solvent had been removed by distillation at water-pump pressure, the residue was taken up in hot ethanol. When the solution was cooled to room temperature, an oily liquid was deposited. Decantation of the solution left an oil which could not be induced to crystallize. The decanted solution, when chilled in a refrigerator overnight, deposited 0.7 g. (35%) of white needles: m.p. 150–153°. After recrystallization of the compound from ethanol the melting point was 152.5–153.5°.

Anal. Calc'd for $C_{28}H_{30}O$: C, 87.91; H, 7.91.
Found: C, 87.71; H, 8.08.

Mesityl 1-methyl-3,4-dihydro-2-naphthyl ketone. Ethyl phenethylacetoacetate, prepared in 76% yield from ethyl acetoacetate and phenethyl bromide, was subjected to cyclization by the method of von Auwers and Moeller (2). A mixture of the resulting 1-methyl-3,4-dihydro-2-naphthoic acid (25 g.) and 27.4 g. of phosphorus trichloride was heated at reflux for 1½ hours. After the mixture had cooled, 50 ml. of carbon disulfide was added and the solution was decanted. To the solution were added 21.6 g. of mesitylene and 100 ml. of carbon disulfide. The solution was stirred vigorously, and 23.2 g. of aluminum chloride was added over a period of one hour, the temperature being maintained at 0–5°. The mixture was allowed to warm up to room temperature, was stirred for an additional 1½ hours, and was decomposed by pouring over a mixture of cracked ice and concentrated hydrochloric acid. The residue obtained from the organic layer by evaporation of the carbon disulfide by an air blast was taken up in ether, washed with 10% sodium carbonate solution and with water, and dried over magnesium sulfate. The ether was removed, and the residue was recrystallized from ethyl alcohol. The yield of mesityl 1-methyl-3,4-dihydro-2-naphthyl ketone melting at 60–61°, was 23.6 g. (61%).

Anal. Calc'd for $C_{21}H_{22}O$: C, 86.87; H, 7.64.
Found: C, 86.74; H, 7.52.

The infrared absorption spectrum of this compound has bands assignable to a doubly-conjugated carbonyl group (1656 cm^{-1}) and a carbon-carbon double bond conjugated with a carbonyl group (1627 cm^{-1}).

Dehydrogenation of mesityl 1-methyl-3,4-dihydro-2-naphthyl ketone. A mixture of 2 g. of mesityl 1-methyl-3,4-dihydro-2-naphthyl ketone and 0.25 g. of 10% palladium-charcoal catalyst was heated for a period of one hour at 300–310° in a flask swept out with nitrogen. The mixture was cooled, warmed with 20 ml. of dry ether, and filtered. The ether was removed and the solid residue recrystallized from ethyl alcohol. The mesityl 1-methyl-2-naphthyl ketone formed white needles; m.p. 98–99°; yield 1.3 g. (65%). A mixture melting point with an authentic sample of mesityl 1-methyl-2-naphthyl ketone was not depressed.

Mesityl 1-benzyl-1-methyl-1,2,3,4-tetrahydro-2-naphthyl ketone. To a solution of benzylmagnesium chloride, prepared from 21.5 g. of benzyl chloride, 20.6 g. of magnesium turnings, and 150 ml. of dry ether, was added with stirring, over a period of 10 minutes, a solution of 10 g. of mesityl 1-methyl-3,4-dihydro-2-naphthyl ketone in 100 ml. of dry ether. As the solution of ketone came in contact with the solution of Grignard reagent a characteristic, transient, purple color was noted. The mixture was stirred and heated at reflux for an additional 30 minutes and decomposed by pouring on a mixture of cracked ice and concentrated hydrochloric acid. After the ethereal layer had been dried over magnesium sulfate, the solvent was removed, and the residue was heated at reflux for 10 hours with 100 ml. of methanol which had been saturated with dry hydrogen chloride. The methanol was removed by distillation at reduced pressure, and the semi-solid residue was recrystallized from ethanol. Mesityl 1-benzyl-1-methyl-1,2,3,4-tetrahydro-2-naphthyl ketone formed white needles; m.p. 153–154°; yield 8.6 g. (66%).

Anal. Calc'd for $C_{28}H_{30}O$: C, 87.91; H, 7.91.
Found: C, 88.06; H7.82.

The infrared absorption spectrum of this compound had a band assignable to a conjugated carbonyl group (1675 cm^{-1}). This spectrum and that of the compound obtained by catalytic hydrogenation of mesityl 1-benzyl-1-methyl-1,4-dihydro-2-naphthyl ketone are superimposable. The melting point of a mixture of samples was not depressed.

SUMMARY

Mesityl 1-methyl-2-naphthyl ketone (I) has been found to react with benzylmagnesium chloride to produce the enolic modification of mesityl 1-benzyl-1-methyl-1,4-dihydro-2-naphthyl ketone (III), which forms a hydroperoxide and is readily ketonized.

Catalytic hydrogenation converted the dihydronaphthalene derivative (III) to the corresponding tetrahydro derivative (V), the structure of which was established by an independent synthesis.

URBANA, ILLINOIS

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