This acid, 8 g. (0.023 mole) was reduced by refluxing for 4 hr. with 1.5 g. (0.04 mole) of lithium aluminum hydride in ethyl ether. After hydrolysis the alcohol was distilled at 0.3 mm.; after some weeks it solidified: m.p. 76°. A small sample was converted into 2,2-dibenzyl-4-phenylbutyl 3,5-dinitrobenzoate, m.p. 174–175°, from methanol, whose infrared spectrum was identical with that of the analytical sample previously described.

Allylation of 2-phenylethanol. The alkoxide, 0.25 mole, was made and treated as previously described, but using benzaldehyde as promoter and allyl chloride, 0.028 mole, as alkylating agent. The product, after hydrolysis, was distilled at 5 mm. into eight fractions. Approximately 50% of the 2-phenylethanol was recovered. The last fraction, b.p. 135–137° at 5.5 mm., n_D^{25} 1.5416 was redistilled into three fractions, most of the material, *2,2-diallyl-2-phenylethanol* distilling at 98–99° at 0.6 mm., n_D^{25} 1.5406. With palladium-charcoal in acetic acid it absorbed 97% of the hydrogen required for two double bonds, and a Zerewitinoff determination showed 1.1 equivalents of active hydrogen.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.9; H, 8.9.

Evanston, Ill.

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

Conjugate Bimolecular Reduction of Hindered Ketones Involving Replacement of Methoxyl Groups. IV. Mesityl 2-Methoxy-1-naphthyl Ketone[1]

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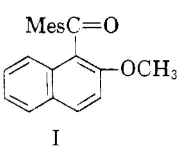
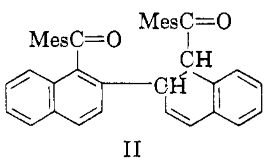
Received February 25, 1960

Reduction of mesityl 2-methoxy-1-naphthyl ketone with the binary mixture, magnesium–magnesium iodide, gave 1,2-dihydro-1,1′-dimesitoyl-2,2′-binaphthyl and 1,1′-dimesitoyl-2,2′-binaphthyl. The dihydro diketone underwent cleavage with chloranil to give a monoketone, 1-mesitoyl-2,2′-binaphthyl, and mesitoic acid. The monoketone, synthesized independently, was cyclized with polyphosphoric acid. Conversion of the dihydro diketone to the aromatic diketone was effected with palladium-on-charcoal.

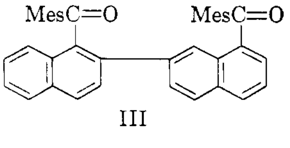
It has been shown that hindered *o*-methoxyphenyl ketones undergo reductive coupling and cyclization to yield the corresponding 9,10-diarylphenanthrenes.[3] The analogous behavior of mesityl 2-methoxy-1-naphthyl ketone (I) would afford a new entry into the picene family. A greater tendency for coupling might be expected in the naphthalene series as the methoxy ketone, because of the greater double bond quality of the 1,2-linkage, would be expected to behave more like an ester than does the benzene analog. Under reaction conditions very similar to those employed previously, the naphthyl ketone gave coupling products in comparatively high yields. The transformation stopped, however, at the diketone stage. The principal product II proved to be the dihydro derivative of the completely aromatized diketone III. The latter was obtained also but in much smaller amounts.



I

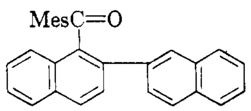


II

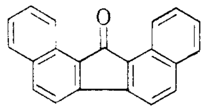


III

Of special interest was the transformation realized when the dihydroaromatic diketone II was treated with chloranil in anisole. The products were a monoketone, 1-mesitoyl-2,2′-binaphthyl (IV), and mesitoic acid. This result is unusual; the treatment with chloranil was expected to give the aromatized diketone. Aromatization was accomplished, however, by heating with palladium-on-charcoal.



IV



V

The monoketone IV was synthesized independently by displacement of the methoxyl group of the methoxy ketone I by the action of the 2-naphthyl Grignard reagent. Ring closure of the monoketone was effected with polyphosphoric acid, the product being the known 13H-dibenzo[a,i]fluoren-13-one (V).

The aromatic diketone presumably was produced by dimerization of the ketyl formed by the interaction of the methoxy ketone and the binary mixture, magnesium–magnesium iodide.[4] The dihydro diketone could conceivably be the intramolecular reduction product of the aromatic diketone, if ring closure were prevented by steric factors. Further reduction of the diketone pre-

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(1) This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

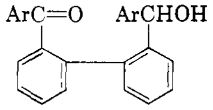
(2) American Cyanamid Company Fellow, 1958–1959.

(3) R. C. Fuson and R. O. Kerr, *J. Org. Chem.*, 19, 373 (1954).

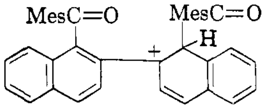
(4) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, 49, 236 (1927).

sumably would give a dienol, which, after ketonization, could then undergo an acid-catalyzed rearrangement to the dihydro product, the driving force being formation of the aromatic ring. The dihydro diketone is analogous to the keto alcohols VI, which have been isolated[5] by the reduction of hindered *o*-methoxyphenyl ketones, except that an aromatic ring underwent reduction rather than a carbonyl group.

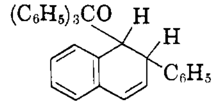
The cleavage of the dihydro diketone is somewhat similar to the pyrolysis of 1,2-dihydro-2-phenyl-1-naphthyl triphenylmethyl ketone (VIII), which yields 2-phenylnaphthalene, triphenylmethane, and carbon monoxide.[6]



VI



VII



VIII

The cleavage of the dihydrodiketone II is not a pyrolysis, however, as evidence has been accumulated that chloranil is necessary; cleavage was not brought about by boiling in anisole without chloranil or by boiling with methoxide ion. An acid and not carbon monoxide is formed, so it seems that the two cleavage reactions are not related. According to the work of Braude, Jackman, and Linstead[7] on the mechanism of the dehydrogenation of dihydroaromatic hydrocarbons with quinones, the last step in the dehydrogenation of the dihydro diketone II would require the expulsion of a proton from the positively charged intermediate VII. Perhaps the mesityl carbonium ion, rather than a proton, is lost; the formation of the monoketone might be favored by steric factors.

EXPERIMENTAL[8]

Mesityl 2-methoxy-1-naphthyl ketone. The procedure used was that of Fuson and Fang[9] as modified by Mon.[10] A solution of 50.4 g. of mesitoyl chloride, prepared from 50 g. of mesitoic acid and 100 g. of thionyl chloride, and 39.6 g. of 2-methoxynaphthalene in 200 ml. of carbon disulfide were added, with stirring, over a period of 3 hr. to an ice-cold slurry of 33.6 g. of aluminum chloride and 200 ml. of carbon disulfide. The red mixture was stirred for 22 hr. while cooled in an ice bath and then poured into 1.5 l. of an ice water mixture to which 90 ml. of concd. hydrochloric acid had been added. The organic layer was washed with 200 ml. of 4% sodium hydroxide and with 200 ml. of water. Acidification of the sodium hydroxide wash gave 4.0 g. of mesitoic acid. The organic phase was dried over sodium sulfate, after which the solvent was evaporated to leave 60.4 g. of crude yellow solid. Three recrystallizations from petroleum ether (b.p. 90–110°) gave 51.5 g. (61.4%) of mesityl 2-methoxy-1-naphthyl ketone, m.p. 129.5–130.5°. A mixture of the sample with an authentic specimen showed no lowering of the melting point.

Reduction of mesityl 2-methoxy-1-naphthyl ketone. Ten grams of iodine was added slowly to a mixture of 9.57 g. of ground magnesium, 44 ml. of *n*-butyl ether, and 40 ml. of toluene. Heat was applied initially, and the reaction proceeded exothermically thereafter. The entire operation was carried out with stirring and in a nitrogen atmosphere. After the last portion of the iodine had been added, the mixture was heated under reflux for 15 min. to give a cloudy, greenish-gray suspension. To the heated mixture was added a solution of 6.00 g. of the ketone in 40 ml. of toluene. The addition took 5 min., after which time the bright red mixture was heated under reflux for 4 hr. and then poured into 200 ml. of 6*N* hydrochloric acid and cooled in an ice bath. The organic layer was washed with 5% sodium bicarbonate, with 5% sodium hydrogen sulfite, and finally with water. After the solution had been dried over sodium sulfate, the solvent was removed. Treatment of the reddish-brown residue with 25 ml. of acetone caused the separation of 1,2-dihydro-1,1′-dimesitoyl-2,2′-binaphthyl; m.p. 213–215°, yield 2.52 g. (46.6%). The analytical sample, crystallized from chloroform-ethanol, melted at 218–219°.

Anal.[11] Calcd. for $C_{40}H_{36}O_2$: C, 87.56; H, 6.61. Found: C, 87.41; H, 6.57.

The infrared spectrum[12] of the compound contains bands attributable to an unconjugated, hindered ketone (1698 cm.$^{-1}$), a conjugated, hindered ketone (1645 cm.$^{-1}$), a 1,2-disubstituted naphthalene ring (828 and 760 cm.$^{-1}$), and a mesityl group (850 cm.$^{-1}$). The ketone band at 1698 cm.$^{-1}$ is also present in the infrared spectrum of 1,2-dihydro-2-methyl-1-naphthyl mesityl ketone.

Evaporation of the acetone from the filtrate left 3.63 g. of dark brown solid, which was chromatographed on a 125-g. alumina column. Elution with 1:1 cyclohexane:ether gave, after combining fractions, 1.36 g. of crude 1,1′-dimesitoyl-2,2′-binaphthyl, m.p. 242–245°. Repeated recrystallization from chloroform-ethanol gave 0.19 g. (1.75%) of analytically pure diketone, m.p. 248–249°.

Anal. Calcd. for $C_{40}H_{34}O_2$: C, 87.77; H, 6.27. Found: C, 88.02; H, 6.39.

The infrared spectrum shows bands assignable to a hindered, conjugated ketone (1655 cm.$^{-1}$), a mesityl group (852 cm.$^{-1}$), and a 1,2-disubstituted naphthalene ring (830 and 740 cm.$^{-1}$). Elution with ether and with methanol gave 1.49 g. of intractable dark red oils, the infrared spectrum of which contains bands at 1687, 1645, and 855 cm.$^{-1}$

During one run the acetone filtrate was treated with copper acetate before removal of solvent. To the acetone solution, made up to a volume of 100 ml., was added 10 ml. of water and 1.50 g. of copper acetate. After the mixture had been shaken for 2 hr., the green complex was collected and hydrolyzed by shaking with 6*N* hydrochloric acid. Extraction with ether and evaporation of solvent gave 0.39 g. (6.8%) of a colorless solid. The infrared spectrum of this material contains a band at 1612 cm.$^{-1}$ attributable to a chelated aromatic ketone. The spectrum is identical with that of a compound which is currently under investigation in this laboratory.

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(5) R. C. Fuson and C. Hornberger, Jr., *J. Org. Chem.*, **16**, 637 (1951).

(6) R. C. Fuson and K. D. Berlin, *J. Am. Chem. Soc.*, **81**, 2130 (1959).

(7) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548 (1954).

(8) All melting points are corrected.

(9) R. C. Fuson and F. T. Fang, *J. Am. Chem. Soc.*, **77**, 3781 (1955).

(10) Private communication.

(11) The microanalyses were carried out by Mr. Rollo Nesset, Mrs. Ruby Ju, Mrs. Alice Terra, and Miss Claire Higham.

(12) The infrared spectra were determined by Mr. James Brader, Mrs. Louise Griffing, and Mr. Sy Portnow.

On certain occasions it was possible to isolate a compound, m.p. 230–231°, which is presumably an isomer of the dihydroaromatic diketone. The infrared spectrum of this material is similar to that of the dihydroaromatic diketone. Conversion of the higher melting to the lower melting form was accomplished by passing the solid, dissolved in benzene, through an alumina column. Treatment with chloranil in *m*-xylene gave 1-mesitoyl-2,2′-binaphthyl in 31.6% yield.

Cleavage of 1,2-dihydro-1,1′-dimesitoyl-2,2′-binaphthyl. A solution of 0.67 g. of the dihydroaromatic diketone and 0.54 g. of chloranil in 12 ml. of anisole was heated under reflux under nitrogen for 36 hr. A test for evolved carbon monoxide was negative. After the reddish-brown solution had cooled, it was extracted twice with 5% sodium hydroxide, benzene and chloroform being added. The organic phase was washed with water and dried over sodium sulfate. Removal of solvent produced 0.59 g. of residue, which was chromatographed on a 25-g. alumina column. Elution with 5:1 cyclohexane:ether gave 0.23 g. (47.3%) of 1-mesitoyl-2,2′-binaphthyl, m.p. 180–181°. A mixture melting point with the monoketone synthesized independently was not depressed, and the infrared spectra of the two samples were superimposable.

When the combined sodium hydroxide extracts were acidified with dilute hydrochloric acid, a dark purple precipitate formed which dissolved readily in ether. The ether layer was washed repeatedly with water and dried over sodium sulfate. Solvent removal left a purple residue, which was then stirred with 5 ml. of concd. sulfuric acid. Ice and water were added, and the mixture was extracted with ether. The ether layer was washed with 5% sodium bicarbonate, the basic extract acidified, and the product taken up in ether, which was then evaporated. The residue was crystallized from methanol-water to give 0.32 g. (16%) of crude mesitoic acid, m.p. 147–150°, identified by reference to its infrared spectrum and by a mixture melting point determination.

1-Mesitoyl-2,2′-binaphthyl. A solution of 3.00 g. of mesityl 2-methoxy-1-naphthyl ketone in 15 ml. of benzene and 15 ml. of ether was added to a Grignard reagent prepared from 12.43 g. of 2-bromonaphthalene and 1.22 g. of ground magnesium in 30 ml. of ether and 30 ml. of benzene. The reaction mixture was heated under reflux for 4 hr. and poured into a saturated ammonium chloride solution. The organic layer was washed with water and dried over sodium sulfate. Evaporation of the solvent left a red residue, which, when treated with ether, gave 1.41 g. of colorless solid. Recrystallization from benzene produced 0.24 g. of 2,2′-binaphthyl, m.p. 183–185°. The benzene filtrate was taken to dryness; the residue crystallized from chloroform-ethanol to give 0.41 g. (10.4%) of 1-mesitoyl-2,2′-binaphthyl, m.p. 180–181°.

Anal. Calcd. for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 89.89; H, 5.92.

The infrared spectrum of this compound has bands attributable to a hindered, conjugated ketone at 1650 cm.$^{-1}$, to the mesityl group at 850 cm.$^{-1}$, and to a 1,2-disubstituted naphthalene ring at 740 and 825 cm.$^{-1}$.

Ring closure of 1-mesitoyl-2,2′-binaphthyl. Two milliliters of polyphosphoric acid and 0.11 g. of the monoketone were heated for 4 hr. at 100–110° and then for 1 hr. at 180°. The mixture was poured into ice and water, and the red solid which formed was removed by filtration. One recrystallization from benzene gave 0.023 g. (30.2%) of red plates, m.p. 264–266° (sealed tube). The infrared spectrum of the compound has a strong band at 1690 cm.$^{-1}$ which is also present in the spectrum of the known ketone.[13]

Dehydrogenation of 1,2-dihydro-1,1′-dimesitoyl-2,2′-binaphthyl. A mixture of 0.154 g. of the dihydroaromatic diketone and 0.021 g. of 10% palladium-on-charcoal was heated at 205° for 2 hr., during which time a stream of nitrogen was passed over the molten mixture. When cold the mixture was extracted with chloroform. Filtration gave a light yellow solution, which was boiled on a hot plate, ethanol being added to replace the chloroform removed by distillation. When the solution has cooled, 0.062 g. of the starting diketone crystallized. From the filtrate was obtained 0.019 g. (12.4%) of 1,1′-dimesitoyl-2,2′-binaphthyl, m.p. 248–249°. The infrared spectrum is superimposable on that of the 248–249° compound produced by the reduction of mesityl 2-methoxy-1-naphthyl ketone.

A solution of 0.204 g. of diketone in 4 ml. of anisole was heated under reflux for 36 hr. Evaporation of solvent yielded a residue which, after one recrystallization from chloroform-ethanol, gave 0.202 g. of the starting diketone.

A solution of 0.280 g. of diketone and 0.034 g. of sodium methoxide in 7 ml. of benzene and 3 ml. of methanol was heated under reflux for 12 hr. and then poured into water. The organic phase was washed twice with water and dried over sodium sulfate. Removal of solvent and crystallization of the residue from chloroform-ethanol gave 0.204 g. of the diketone taken as starting material.

URBANA, ILL.

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(13) R. C. Fuson and F. W. Wassmundt, J. Am. Chem. Soc., **78**, 5409 (1956).