[Contribution from the Department of Chemistry,
University of Southern California]

ACETYLATION OF 1,2-DIETHYLNAPHTHALENE. I.[1]

MILTON C. KLOETZEL and HERSHEL L. HERZOG

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The reaction of 1,2-diethylnaphthalene with acetyl chloride and aluminum chloride in nitrobenzene has been reported to yield a solid acetyl derivative, m.p. 61.5–62.5° (1). This ketone has now been identified as 1-aceto-3,4-diethylnaphthalene. A small quantity (3% yield) of an isomeric ketone, possibly 2-aceto-5,6-diethylnaphthalene,[2] has also been isolated from the acetylation reaction.

1-Aceto-3,4-diethylnaphthalene was reduced, by the Clemmensen method, to 1,2,4-triethylnaphthalene, which was shown to be identical with a sample of the hydrocarbon prepared in an unequivocal manner (formulas I–VII) similar to that previously employed for the synthesis of 1,2,4-trimethylnaphthalene (3).

Methyl β-benzoylpropionate reacted with ethylmagnesium bromide to yield 4-phenyl-3-hexenoic acid (I), which was quantitatively reduced over Adams' catalyst. The resulting 4-phenylhexanoic acid was converted to 4-ethyl-1-tetralone (II) in 70–80% yield through a Friedel-Crafts intramolecular condensation of the acid chloride. This method was found to be superior to ring closure of 4-phenylhexanoic acid with 80% sulfuric acid (4), which afforded only 50–55% yields of II. Condensation of the cyclic ketone (II) with dimethyl oxalate yielded a glyoxalate, from which carbon monoxide was eliminated by heating with powdered soft glass (5). When the sodio derivative of the resulting methyl 4-ethyl-1-tetralone-2-carboxylate (III) reacted with ethyl iodide, methyl 2,4-diethyl-1-tetralone-2-carboxylate (IV) was obtained. Hydrolysis and subsequent decarboxylation of this ester yielded 2,4-diethyl-1-tetralone (V). Treatment of this cyclic ketone with ethylmagnesium bromide in the usual manner yielded 1,2,4-triethyl-1-tetralol (VI), which was dehydrated with anhydrous formic acid and dehydrogenated at 290° over a palladium on charcoal catalyst to give the desired 1,2,4-triethylnaphthalene (VII).

The liquid hydrocarbon, 1,2,4-triethylnaphthalene, formed a solid derivative, m.p. 95–96°, with 1,3,5-trinitrobenzene, but failed to form a satisfactory picrate.

Recently it was shown (6) that certain alkylnaphthalenes can be made to undergo a Diels-Alder type reaction with maleic anhydride, similar to that which has been demonstrated for anthracene derivatives (7, 8). When 1,2,4-triethylnaphthalene was heated to 100° with excess maleic anhydride, it likewise yielded an adduct. This substance, 1,2,4-triethyl-1,4-dihydronaphthalene-1,4-*endo*-α-β-

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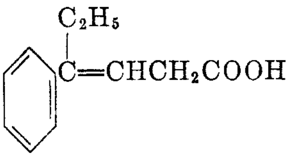
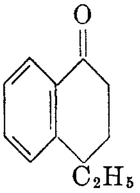
[1] Abstracted from the thesis submitted by Hershel L. Herzog to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Master of Science.

[2] Bachmann and Cronyn (2) have shown that acetylation of 1,2,3,4-tetrahydrophenanthrene results in the formation of 9- and 7-aceto-1,2,3,4-tetrahydrophenanthrene, in the ratio of 2:1.

succinic anhydride (VIII), proved to be useful as an additional solid derivative suitable for characterization of the liquid hydrocarbon.



I



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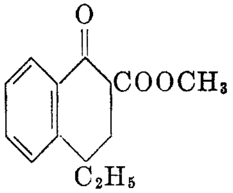

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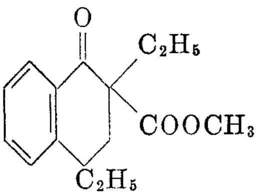

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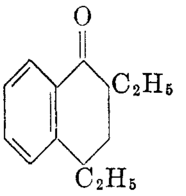

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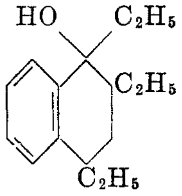

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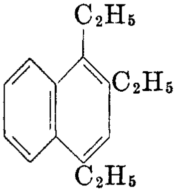

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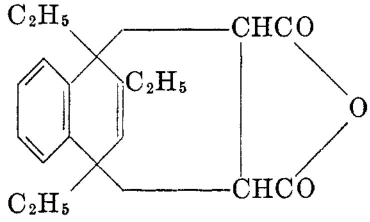

VIII

EXPERIMENTAL[3]

4-Ethyl-1-tetralone (II). Methyl β-benzolypropionate was allowed to react with ethylmagnesium bromide as described for the analogous reaction with methylmagnesium iodide (3). When the Grignard reaction mixture had warmed up to 25°, 150 c.c. of dry toluene was added and ether was removed as completely as possible by distillation on a steam-bath. After being heated on the steam-bath for five hours, the mixture was hydrolyzed with 3 *N* hydrochloric acid and worked up in the customary manner; yield, 60–70% of *4-phenyl-3-hexenoic acid* (I), b.p. 163–167° at 5 mm.

Hydrogenation of 96.5 g. of 4-phenyl-3-hexenoic acid in 250 c.c. of glacial acetic acid over 500 mg. of Adams' catalyst, at 10–40 lbs. pressure, was complete within two hours, and yielded 89.5 g. (92%) of *4-phenylhexanoic acid*, b.p. 160–163° at 5 mm. Levy (9), who prepared this acid in a different manner, reported a b.p. of 185° at 22 mm.

The *acid chloride* prepared by warming a mixture of 31.5 g. of 4-phenylhexanoic acid and 16.5 g. of thionyl chloride on a steam-bath for fifteen minutes, and removing excess thionyl chloride by distillation under reduced pressure, was dissolved in 175 c.c. of carbon disulfide. To the solution, at 0°, was added 25 g. of anhydrous aluminum chloride and the mixture was then refluxed for ten minutes. After hydrolysis in the customary manner, 4-

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[3] Melting points are uncorrected. Analyses are by Dr. G. Oppenheimer, California Institute of Technology.

ethyl-1-tetralone (II), b.p. 131–135° at 4 mm., was obtained in 70–80% yield, and formed a *semicarbazone*, m.p. 182–183°. Levy (9) reported the cyclization of 4-phenylhexanoyl chloride to yield 60% of 4-ethyl-1-tetralone; semicarbazone, m.p. 183°

Methyl 2,4-diethyl-1-tetralone-2-carboxylate (IV). 4-Ethyl-1-tetralone was condensed with dimethyl oxalate, following the procedure described for 1-tetralone by Bachmann and Thomas (5), to yield 92% of liquid *methyl 4-ethyl-1-tetralone-2-glyoxalate.* Carbon monoxide was evolved when 30.5 g. of the glyoxalate was heated to 150° with 15 g. of powdered soft glass. The temperature was finally raised to 180° until gas evolution ceased (total period of heating, 25 minutes) and the resulting *methyl 4-ethyl-1-tetralone-2-carboxylate* (III) was purified by distillation in a vacuum; yield, 18 g. (66%), b.p. 164–170° at 4 mm.

The sodio derivative was prepared from 40 g. of the aforementioned β-keto ester, and was treated with ethyl iodide as described for methyl 1-tetralone-2-carboxylate (1). There was isolated 13.5 g. of unreacted keto ester and 20.5 g. of *methyl 2,4-diethyl-1-tetralone-2-carboxylate* (IV), b.p. 152–155° at 1 mm.

Anal. Calc'd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74.

Found: C, 73.92; H, 7.93.

2,4-Diethyl-1-tetralone (V). Hydrolysis of ester IV (20.5 g.) was accomplished by refluxing for three hours with ethanol (36 c.c.) and 20% sodium hydroxide solution (140 c.c.). Acidification of the resulting solution with sulfuric acid caused a vigorous evolution of carbon dioxide. Complete decarboxylation was effected by warming the mixture on a steam-bath and the *2,4-diethyl-1-tetralone* was extracted with benzene; yield, 11 g. (69%), b.p. 118–121° at 1 mm.

The *semicarbazone* of *2,4-diethyl-1-tetralone*, prepared in ethanolic pyridine solution as previously described for 2,4-dimethyl-1-tetralone (3), melted at 181–183°.

Anal. Calc'd for $C_{15}H_{21}N_3O$: N, 16.20.

Found: N, 15.94.

1,2,4-Triethyl-3,4-dihydronaphthalene. To the ice-cold Grignard reagent prepared from 10.9 g. of ethyl bromide, 2.43 g. of magnesium, and 80 c.c. of ether was added dropwise, with swirling, 10 g. of 2,4-diethyl-1-tetralone dissolved in 40 c.c. of ether. The reaction mixture was allowed to warm up to room temperature and was then refluxed for 2½ hours. Hydrolysis with ice and ammonium chloride, followed by extraction of the reaction mixture with ether, yielded 10 g. of liquid *1,2,4-triethyl-1-tetralol* (VI).

The crude carbinol was added to 40 c.c. of anhydrous formic acid and, after standing for two hours at room temperature, the mixture was diluted with 200 c.c. of water and extracted with several portions of ether. Evaporation of the washed extracts left an oil which was distilled from metallic sodium; yield, 6 g. (57%) of colorless *1,2,4-triethyl-3,4-dihydronaphthalene*, b.p. 106–109° at 1 mm.

Anal. Calc'd for $C_{16}H_{22}$: C, 89.65; H, 10.34.

Found: C, 89.46; H, 10.52.

1,2,4-Triethylnaphthalene (VII) was obtained in 86% yield by heating the aforementioned dihydronaphthalene with one-tenth of its weight of palladium on charcoal catalyst (10) to 290° until evolution of hydrogen ceased. The hydrocarbon distilled as a colorless oil, b.p. 125–127° at 1 mm.

Anal. Calc'd for $C_{16}H_{20}$: C, 90.50; H, 9.49.

Found: C, 90.49; H, 9.57.

The *1,3,5-irinitrobenzene derivative* of *1,2,4-triethylnaphthalene* separated from methanol in flat yellow needles, m.p. 95–96°.

Anal. Calc'd for $C_{22}H_{23}N_3O_6$: N, 9.88.

Found: N, 9.93.

1,2,4-Triethyl-1,4-dihydronaphthalene-1,4-endo-α,β-succinic anhydride (VIII). One gram of 1,2,4-triethylnaphthalene was heated in a sealed tube for 24 hours at 100° with 13.9 g. of maleic anhydride. The resulting solution was poured into 100 c.c. of water and the mixture was stirred until all excess maleic anhydride had dissolved. Separation of the oily residue was accomplished with the aid of ether and, after evaporation of the ether, the mixture of adduct and unreacted hydrocarbon was allowed to stand at room temperature for 24 hours with 20 c.c. of 5% aqueous potassium hydroxide. Unreacted hydrocarbon was extracted with ether and the alkaline solution was acidified with 10% hydrochloric acid. There was precipitated 0.25 g. of 1,2,4-triethyl-1,4-dihydronaphthalene-1,4-*endo*-α,β-succinic acid, which was converted to the corresponding anhydride (VIII) by dissolving in several c.c. of warm acetyl chloride and finally evaporating the excess acetyl chloride. The anhydride (VIII) separated from ether-hexane in colorless massive prisms, m.p. 136–137°.

Anal. Calc'd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14.
Found: C, 77.00; H, 7.15.

Acetylation of 1,2-diethylnaphthalene (10 g.) was effected in nitrobenzene as previously described (1). When the mother liquor from crystallization of *1-aceto-3,4-diethylnaphthalene* was evaporated, there remained an oily residue (1.9 g.) which could not be induced to crystallize. This material yielded 0.8 g. of the picrate of an isomeric *acetodiethylnaphthalene* upon treatment with a saturated ethanolic solution of picric acid; yellow needles, m.p. 118–118.5°.

Anal. Calc'd for $C_{22}H_{21}N_3O_8$: N, 9.22.
Found: N, 9.26

The isomeric acetodiethylnaphthalene, liberated by shaking a benzene solution (20 c.c.) of the aforedescribed picrate (0.8 g.) with 10% aqueous lithium hydroxide until all color had been extracted from the benzene solution, was refluxed for two hours with a solution of semicarbazide hydrochloride (0.4 g.) and pyridine (1 c.c.) in ethanol (20 c.c.). The *semicarbazone*, which precipitated when the reaction mixture was poured into water, separated from dioxane-ethanol in colorless leaflets, m.p. 234–235°.

Anal. Calc'd for $C_{17}H_{21}N_3O$: N, 14.83.
Found: N, 14.68.

Reduction of 1-aceto-3,4-diethylnaphthalene was accomplished by refluxing for 24 hours a mixture of 11.9 g. of the ketone, 35 c.c. of benzene, 68 c.c. of methanol, 45 c.c. of concentrated hydrochloric acid, and 29 g. of amalgamated mossy zinc. The organic layer yielded 8 g. (72%) of colorless *1,2,4-triethylnaphthalene*, b.p. 125–127° at 1 mm., whose solid 1,3,5-trinitrobenzene derivative and maleic anhydride adduct caused no depression of m.p. when mixed with samples of these respective derivatives prepared as described from authentic 1,2,4-triethylnaphthalene.

SUMMARY

Acetylation of 1,2-diethylnaphthalene has been shown to yield 1-aceto-3,4-diethylnaphthalene and a small amount of an isomeric ketone. Clemmensen reduction of the 1-aceto-3,4-diethylnaphthalene yielded 1,2,4-triethylnaphthalene, which was shown to be identical with the hydrocarbon synthesized in an unequivocal manner.

LOS ANGELES, CALIF.

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