pound could be obtained sufficiently pure for analysis, since they decomposed readily on heating. Both compounds were viscous yellow liquids.

**2-(2-Diethylaminoethylsulfo)-ethylamine.**—A derivative of this compound could not be made.

**3-(2-Diethylaminoethylsulfo)-1-propylamine dithiocarbamate** formed tiny white needles from dilute acetone, melting at 130–132°.

*Anal.* Calcd. for $C_{10}H_{22}O_2N_2S_3$: C, 40.24; H, 7.43; N, 9.39. Found: C, 40.23; H, 7.11; N, 9.35.

**2-(2-Cyanoethylthio)-triethylamine.**—To 17.5 g. of acrylonitrile was added, with external cooling, 42.5 g. of 2-diethylaminoethanethiol.[7] The spontaneous exothermic reaction was controlled by frequent cooling in ice. After standing overnight at room temperature the reaction product was distilled *in vacuo*. There was obtained 54.7 g. (92%) of pure colorless product, boiling at 111.0° at 2.5 mm., $n^{20}_D$ 1.4885.

*Anal.* Calcd. for $C_9H_{18}N_2S$: C, 58.02; H, 9.74; N, 15.04. Found: C, 58.05; H, 9.83; N, 14.76.

The picrate crystallized from absolute alcohol–acetone in yellow needles, melting at 74–75°.

*Anal.* Calcd. for $C_{15}H_{22}O_7N_5S$: C, 43.37; H, 5.10. Found: C, 43.49; H, 5.23.

2-(2-Cyanoethylthio)-triethylamine was also obtained in 67% yield by the reaction between II, as the free base, and potassium cyanide in aqueous alcohol.

## Summary

The preparation of a series of diethylaminoethylthioalkyl chlorides and amines, their corresponding sulfones, and related compounds is described.

RENSSELAER, NEW YORK RECEIVED DECEMBER 21, 1944

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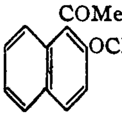
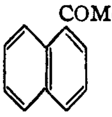
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Grignard Reactions Involving the Naphthalene Nucleus

BY REYNOLD C. FUSON, B. C. MCKUSICK[1] AND FRED W. SPANGLER[2]

Because of the ease with which Grignard reagents reacted with 1-mesitoyl-2-methoxynaphthalene (I),[3] to replace the methoxyl group by an alkyl or aryl group, attempts have been made to condense this type of reagent with the mesitoylnaphthalenes. The present paper is a report of an investigation of the action of methylmagnesium iodide on these ketones. Similar studies with benzoylmesitylene, *p*-toluylmesitylene and benzoylisodurene[4] had indicated that 1,2-addition might be expected with the methyl Grignard reagent. On the other hand, it had been established that phenylmagnesium bromide condensed with 1-mesitoylnaphthalene (II) in the 1,4 manner.[5] Moreover, the fixed nature of the naphthalene bond structure might be expected to facilitate 1,4-addition to naphthyl ketones.


I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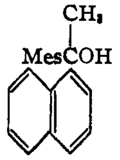
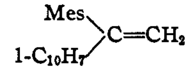
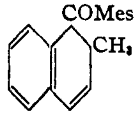

III

In the present work it was found that treatment of 1-mesitoylnaphthalene (II) with methylmagnesium iodide produced a 58% yield of an addition compound. At first it was thought to be the carbinol (III) which would result from 1,2-addition. It gave a mole of gas in the Kohler–Richtmyer apparatus[6] and could be converted to an acetate. Hydrolysis of the acetate regenerated the original condensation product.

In an attempt to synthesize the carbinol, mesitylmagnesium bromide was condensed with 1-acetonaphthone. Although enolization occurred to the extent of 61%, addition to the carbonyl group did take place. The product, however, was not the carbinol but the corresponding olefin, 1-mesityl-1-(1-naphthyl)-ethylene (IV).


IV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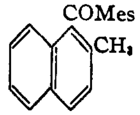
VI

This olefin could not be made by dehydration of the supposed carbinol, the latter being unaffected by treatment with dehydrating agents.

Accordingly the carbinol structure had to be abandoned. It seemed likely that conjugate addition involving the naphthalene nucleus had occurred. 1,4-Addition might be expected to lead to the formation of 1,2-dihydro-1-mesitoyl-2-methylnaphthalene (V)—a compound which would possess active hydrogen and would be expected to yield an acetate.

This structure was finally established by dehydrogenation of the compound in the presence of a palladium-charcoal catalyst. The possibility that the addition was 1,6 could not be ignored. For this reason 1-mesitoyl-4-methylnaphthalene as well as 1-mesitoyl-2-methylnaphthalene (VI) was prepared for reference. The dehydrogenation product proved to be identical with the latter (VI). The dihydro structure was confirmed by the identification of the cleavage products of the enol peroxide (VII) prepared by the method of Kohler and Thompson.[7]

The products to be expected from the decomposition of the peroxide are mesitoic acid and 2-

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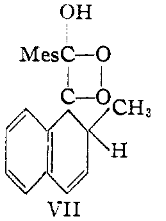
[3] Fuson and Speck, THIS JOURNAL, 64, 2446 (1942).

[4] Fuson, Armstrong, Wallace and Kneisley, *ibid.*, 66, 681 (1944).

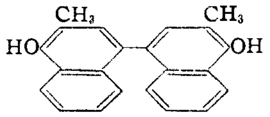
[5] Fuson, Armstrong and Speck, *J. Org. Chem.*, 7, 297 (1942).

[6] Kohler and Richtmyer, THIS JOURNAL, 52, 3736 (1930).

[7] Kohler and Thompson, *ibid.*, 59, 887 (1937).



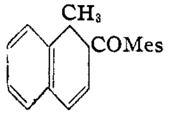
VII



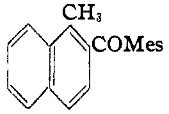
VIII

methyl-1-naphthol. The acid was identified; the naphthol was not isolated as such but in the form of its oxidation product, 4,4'-dihydroxy-3,3'-dimethyl-1,1'-dinaphthyl (VIII). The melting point of this compound and that of its acetate correspond to those given in the literature.[8]

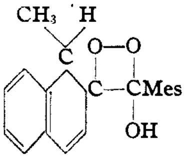
The reaction of methylmagnesium iodide with 2-mesitoylnaphthalene (XIII) was also found to proceed in the 1,4 manner. In the absence of air the resulting enol ketonized to 1,2-dihydro-2-mesitoyl-1-methylnaphthalene (IX). Dehydrogenation of the hydroaromatic compound produced the corresponding aromatic ketone, 2-mesitoyl-1-methylnaphthalene (X). When the Grignard reaction mixture was decomposed in the presence of air a small amount of the completely aromatized ketone (X) was obtained along with large quantities of a yellow, high-melting substance which appeared to be a bimolecular product.



IX



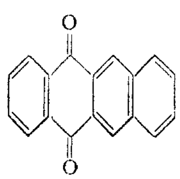
X



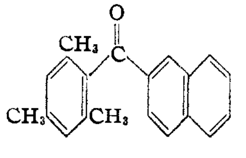
XI

The structure of 2-mesitoyl-1-methylnaphthalene (X) was confirmed by an independent synthesis. 1-Methyl-2-naphthoic acid, prepared by the method of Mayer and Schnecko,[9] was converted to the acid chloride, and the latter was condensed with mesitylene by the Friedel–Crafts method.

By the method of Kohler and Thompson[7] it was possible to obtain the peroxide (XI) of the enol in 74% yield. This corresponds to a much higher yield of 1,4-addition product than any previously observed Grignard condensation to a conjugated system involving a double bond of an aromatic nucleus. In structure, 2-mesitoylnaphthalene (XIII) bears a striking resemblance to naphthacenequinone (XII)[10] which likewise undergoes lateral-nuclear condensation with the Grignard reagent. The results obtained with the mesitoylnaphthalenes are noteworthy not only because of the extent to which 1,4-addition occurs but also because of the great stability of the dihydro derivatives which form.



XII



XIII

## Experimental

**1-Mesitoylnaphthalene** (II).—This ketone was made by the Friedel–Crafts method of Armstrong.[11] From 190 g. of 1-naphthoyl chloride and 132 g. of mesitylene was obtained 230 g. of the ketone, melting at 158–159°.

**2-Mesitoylnaphthalene** (XIII).[12]—2-Naphthoyl chloride was prepared from naphthoic acid and thionyl chloride in the conventional manner; b. p. 190–192° (3 mm.); m. p. 43–44°; yield 94%. From 190 g. of the 2-naphthoyl chloride and 120 g. of mesitylene was obtained 203 g. of the ketone. It was recrystallized from ethanol; m. p. 97–98°; yield 74%.

*Anal.*[13] Calcd. for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 87.46; H, 6.54.

**1-Mesitoyl-2-methylnaphthalene** (VI).—(a) A Grignard reagent was prepared from 20 g. of 1-bromo-2-methylnaphthalene.[14] The ethereal solution was removed by decantation and to it was added 10 g. of cadmium chloride in accordance with the procedure of Gilman and Nelson.[15] Finally, 10 g. of mesitoyl chloride was added. After being heated for one hour under reflux the mixture was worked up in the usual manner. The oily product was subjected to steam distillation to remove volatile impurities. The residue crystallized partially after several weeks. The crystals were spread on a clay plate, washed with methanol and recrystallized from methanol; m. p. 73–74°; yield 1.5 g.

(b) Thirteen and three-tenths grams of anhydrous aluminum chloride was added in small portions to a solution of 18.5 g. of 2-methyl-1-naphthoyl chloride[14] and 11.9 g. of mesitylene in 90 ml. of carbon disulfide. The yield of crude 2-methyl-1-mesitoylnaphthalene was 62%. The ketone was purified by recrystallization from methanol; m. p. 73–74°.

A mixture of either of the products prepared under *a* and *b* with that made from the dihydro compound or with that prepared from 1-mesitoyl-2-methoxynaphthalene[3] (incorrectly reported as melting at 67°) showed no depression.

**1-Mesitoyl-4-methylnaphthalene.**—4-Methyl-1-naphthoyl chloride was made by the method of Mayer and Sieglitz[14] who reported it as a liquid. It was found to melt at 47–48°. The identity of the solid was checked by treatment with ammonia, which converted it to the known amide; m. p. 192–194°.[14]

The ketone was prepared by a Friedel–Crafts condensation involving 13.5 g. of the acid chloride, 8.6 g. of mesitylene, 9.7 g. of anhydrous aluminum chloride and 80 ml. of carbon disulfide. It crystallized from acetic acid in prisms; m. p. 92.5–94°; yield 13 g.

*Anal.* Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.29; H, 6.96.

**The Condensation of Methylmagnesium Iodide with 1-Mesitoylnaphthalene.**[16]—A solution of 54.8 g. of the ketone in 150 ml. of dry thiophene-free benzene was added slowly over a period of thirty minutes to a Grignard reagent prepared from 42.6 g. of methyl iodide, 7.3 g. of magnesium, 90 ml. of dry ether and 30 ml. of dry, thiophene-free benzene. The color of the reaction mixture changed from yellow to red and finally to green during the fifteen-hour

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[8] Lesser and Aczel, *Ann.*, **402**, 45 (1913).

[9] Mayer and Schnecko, *Ber.*, **56**, 1408 (1923).

[10] Allen and Gilman, THIS JOURNAL, **58**, 937 (1936).

[11] Fuson, Bottorff, Foster and Speck, *ibid.*, **64**, 2573 (1942).

[12] This compound was prepared by Dr. Norman Rabjohn.

[13] The microanalyses reported in this paper were carried out by Miss Margaret McCarthy, Miss Theta Spoor and Miss Dorothy Schneider.

[14] Mayer and Sieglitz, *Ber.*, **55B**, 1835 (1922).

[15] Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

[16] This experiment was carried out by Dr. Stanley B. Speck.

period of heating under reflux. The **1,2-dihydro-1-mesitoyl-2-methylnaphthalene** (V), isolated by conventional means, was an orange-red oil which gradually crystallized. Recrystallization from ethanol gave a 58% yield of a colorless product melting at 86° (cor.).

*Anal.* Calcd. for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.70; H, 7.43.

In certain runs the dihydro compound could be isolated from the reaction mixture only by fractional distillation; b. p. 191–194° (4.5–5 mm.). Addition of ethanol to this fraction caused immediate crystallization. The yield was not appreciably changed by the use of a three-mole excess of the Grignard reagent or of a filtered reagent. Decomposition of the reaction mixture with dilute hydrochloric acid and heating the resulting suspension under reflux for twenty-four hours in a nitrogen atmosphere likewise had no effect on the yield. In each of the runs a small amount (less than 8%) of the original ketone was recovered.

The dihydro compound was not only stable enough to be distilled but was unchanged by heating with 15% sulfuric acid or with phosphorus pentoxide. A solution of bromine in carbon tetrachloride was decolorized immediately by the compound. A solution of potassium permanganate in acetone was decolorized in ten minutes. Treatment of the compound with a 10% solution of sodium methoxide in methanol produced a deep yellow color. This color test is given by dihydro ketones of this type but not by the corresponding fully aromatized ketones. In the Kohler–Richtmyer apparatus[6] the compound gave 0.98 mole of methane.

**Acetate of the Dihydro Ketone.**—(a) A mixture of 2 g. of the dihydro compound (V), 10 g. of acetic anhydride and 20 ml. of dry pyridine was heated for fifteen hours under reflux and poured on crushed ice. The acetate, when recrystallized from ethanol in the presence of Darco, formed small white needles; m. p. 114–115° (cor.); yield 0.9 g.

*Anal.* Calcd. for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 83.03; H, 7.29.

(b) A mixture of 1 g. of the dihydro compound, 2 g. of powdered, freshly fused potassium acetate and 25 ml. of acetic anhydride was refluxed gently for three hours. The dark colored solution was then poured into 400 ml. of cold water and allowed to stand overnight to decompose the excess acetic anhydride. The acetate separated from methanol in small, colorless needles which melted at 114–115° (cor.).

(c) To a Grignard reagent prepared from 1.46 g. of magnesium and 8.52 g. of methyl iodide in 20 ml. of anhydrous ether and 35 ml. of anhydrous thiophene-free benzene was added 11 g. of 1-mesitoylnaphthalene. After the reaction mixture had been stirred at 65° for eight hours and then cooled, 5 g. of acetyl chloride dissolved in 10 ml. of anhydrous ether was added dropwise. The mixture was stirred for one hour longer under gentle reflux, cooled and decomposed with crushed ice and hydrochloric acid. The acetate separated from methanol in small, colorless needles; m. p. 114–115° (cor.).

When 1 g. of the acetate was heated for three hours under reflux in a solution of 1 g. of potassium hydroxide in 20 ml. of absolute ethanol, 0.7 g. of the dihydro compound was produced; m. p. 84–85° (cor.).

**Oxidation.**[16]—A mixture of 1 g. of the dihydro compound, 2 g. of chromic acid and 30 ml. of glacial acetic acid was heated on a steam-bath, with occasional shaking, for thirty minutes and poured on crushed ice. The orange solid which formed was recrystallized from ethanol in the presence of Darco. It formed small yellow needles; m. p. 195–196° (cor.).

*Anal.* Calcd. for $C_{21}H_{20}O_3$: C, 78.72; H, 6:29. Found: C, 78.75; H, 6.60.

The oxidation product was not soluble in sodium hydroxide solution. It was evidently a quinone for it yielded a colorless diacetate when subjected to reductive acetylation. A mixture of 1 g. of the oxidation product, 1 g. of zinc dust, 0.2 g. of powdered fused sodium acetate and 10 ml. of acetic anhydride was heated gently on a hot plate until the color was discharged. After the mixture had been boiled for ten minutes longer, 10 ml. of glacial acetic acid was added and the mixture again was heated to boiling and filtered. The solid product, isolated in the usual way, crystallized from ethanol in the presence of Darco. The diacetate formed colorless, diamond-shaped crystals which melted at 159–160° (cor.).

*Anal.* Calcd. for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. Found: C, 73.83; H, 6.33.

When 1-mesitoylnaphthalene was subjected to oxidation in a similar manner the product was a yellow solid which, after recrystallization from ethanol, melted at 178–180° (cor.).

*Anal.* Calcd. for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 79.00; H, 5.58.

Similarly, 1-mesitoyl-2-methylnaphthalene yielded a yellow oxidation product melting, after recrystallization from absolute ethanol, at 180–182° (cor.).

*Anal.* Calcd. for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.23; H, 5.84.

The three yellow oxidation products, presumably quinones, were shown by the mixed melting point method to be different.

**Dehydrogenation.**—One gram of the dihydro compound (V) and 0.1 g. of 10% palladium–charcoal catalyst were placed in a test-tube which had been swept out with nitrogen. The mixture was heated at 300° under nitrogen for one hour and fifteen minutes. It was then cooled, extracted with ether, and filtered to remove the catalyst. Evaporation of the solvent left a light colored oil which was taken up in methanol and set in the ice box overnight. Six-tenths gram of colorless cubes separated; m. p. 73–74° (cor.). A mixed melting point with an authentic specimen of 1-mesitoyl-2-methylnaphthalene (VI) showed no depression.

**Cleavage of the Peroxide (VII) of the Enol Form of 1,2-Dihydro-1-mesitoyl-2-methylnaphthalene.**—A solution of 2.9 g. of the dihydro compound (V) was added to a solution of ethylmagnesium bromide containing a three-fold excess of the Grignard reagent and the mixture was heated for one hour under reflux. The enol was liberated and converted to the peroxide by the method of Kohler and Thompson.[7] The crude peroxide, isolated as an oil, was heated gently until decomposition was complete. One of the products was soluble in sodium bicarbonate solution and was shown by the mixed melting point method to be mesitoic acid. The other product was a light brown solid which dissolved in sodium hydroxide solution. It melted at 232–235°, the melting point given by Lesser and Aczel for 4,4′-dihydroxy-3,3′-dimethyl-1,1′-binaphthyl (VIII).[8] Acetylation of the compound with acetic anhydride in the presence of potassium acetate yielded an acetate melting at 233–236°. The melting point of the diacetate of the binaphthol found by Lesser and Aczel[8] was 235–236°.

**Reaction of Mesitylmagnesium Bromide with 1-Acetonaphthone.**—To a Grignard reagent prepared from 9.7 g. of magnesium and 63.7 g. of bromomesitylene in 200 ml. of anhydrous ether was added gradually 42.5 g. of 1-acetonaphthone dissolved in 50 ml. of anhydrous thiophene-free benzene. Stirring and heating under gentle reflux were continued for six hours. Decomposition of the reaction mixture in the usual way yielded an oil, which was fractionally distilled. In this way were isolated 20 g. of mesitylene, 26 g. (61% recovery) of 1-acetonaphthone and 8.2 g. of a light colored, viscous oil. Addition of absolute ethanol to this oil caused the **1-mesityl-1-(1-naphthyl)-ethylene** (IV) to separate as a colorless crystalline solid; m. p. 91–94°. After several recrystallizations from absolute ethanol, the product melted at 98–99° (cor.).

*Anal.* Calcd. for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.24; H, 7.49.

The olefin (IV) gave a deep blue color with concentrated sulfuric acid. It readily decolorized bromine in carbon tetrachloride but failed to reduce potassium permanganate in acetone.

**Oxidation of the Olefin.**—One and five-tenths grams of chromic anhydride was added to a solution of 0.75 g. of the olefin (IV) in 25 ml. of glacial acetic acid. After the initial reaction had subsided, the mixture was warmed on a steam-bath for thirty minutes and then poured into ice water. The product, isolated by conventional procedures, was a yellow crystalline solid melting at 156–158°. A mixed melting point with an authentic specimen of 1-mesitoylnaphthalene showed no depression.

**The Condensation of Methylmagnesium Iodide with 2-Mesitoylnaphthalene (XIII).**—By treatment of 27.4 g. of 2-mesitoylnaphthalene with an excess of methylmagnesium iodide, according to a procedure similar to that outlined for 1-mesitoylnaphthalene, it was converted in part to a yellow solid melting at 209–210° (cor.). This compound was purified by recrystallization from benzene.

*Anal.* Calcd. for $C_{42}H_{42}O_2$: C, 87.15; H, 7.32. Found: C, 87.36; H, 7.09.

The compound readily decolorized bromine in carbon tetrachloride but reduced potassium permanganate in acetone only very slowly. It produced a brown color with concentrated sulfuric acid.

When the compound was recrystallized from glacial acetic acid containing a small crystal of iodine small colorless needles separated; m. p. 316–318° (aluminum block). This product was recrystallized from a mixture of benzene and low-boiling petroleum ether.

*Anal.* Found: C, 88.23; H, 6.84.

Neither of these products has been identified.

The mother liquor from the condensation was evaporated and the residual oil distilled under reduced pressure. Addition of ethanol to the distillate caused the separation of 2 g. of **2-mesitoyl-1-methylnaphthalene (X)** in colorless needles; m. p. 92–95°. After several recrystallizations from ethanol, the compound melted at 98.5–100° (cor.).

*Anal.* Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.25; H, 7.16.

The compound did not decolorize bromine in carbon tetrachloride. It failed to reduce potassium permanganate in acetone. Treatment of the compound with a 10% solution of sodium methoxide in methanol produced no color. The compound produced a red color with concentrated sulfuric acid.

In a second run the crude product, obtained by decomposition of the reaction mixture, was subjected to fractional distillation. The chief fraction boiled at 197–200° (2 mm.) and had the properties expected for **1,2-dihydro-2-mesitoyl-1-methylnaphthalene (IX)**.

*Anal.* Calcd. for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.81; H, 7.70.

The redistilled product decolorized bromine in carbon tetrachloride and reduced potassium permanganate in acetone. Treatment with a 10% solution of sodium methoxide in methanol produced a yellow color. It may be that this liquid is the steroisomer of the solid dihydro compound melting at 73–74° (see below).

In a third run, which was carried out in an atmosphere of nitrogen, the mixture resulting from the condensation was divided into three equal parts each of which was treated in a different manner.

**Part 1.**—A stream of dry oxygen was bubbled rapidly for approximately four hours through the solution of the Grignard complex, which was cooled in an ice-bath. Anhydrous ether was added from time to time to replace that lost by evaporation. The solution became dark colored and viscous. It was then decomposed with crushed ice and hydrochloric acid. The organic layer was washed with water and the solvent was evaporated. Addition of acetone to the residual oil caused 3 g. of a yellow solid to separate. After recrystallization from benzene it melted at 208–209°. A mixed melting point determination showed it to be identical with the compound mentioned above which melted at 209–210°.

**Part 2.**—The mixture was cooled and decomposed with crushed ice and hydrochloric acid. The organic layer was separated and rapidly washed three times with ice water. Three volumes of cold low-boiling petroleum ether was added to the solution. A stream of oxygen was then bubbled for approximately eight hours through the solution, which was cooled in an ice-bath. Additional low-boiling petroleum ether was added from time to time to replace that lost by evaporation. At the end of this period 8 g. (74%) of the **peroxide (XI)** had separated: m. p. 170–173°. After several recrystallizations from absolute ethanol, it melted at 172–174° (cor.).

*Anal.* Calcd. for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.45; H, 6.87.

The compound produced a yellow color when treated with 10% sodium hydroxide solution. Treatment with concentrated sulfuric acid gave a brown color. When 2 g. of the compound was heated gently over a yellow flame an exothermic reaction took place. Decomposition was rapid with a large amount of fumes given off. A dark, viscous oil remained. The cleavage products were isolated in amounts too small to be identified.

**Part 3.**—The mixture was cooled and decomposed with 150 ml. of 1.2 *N* hydrochloric acid while still under nitrogen. The resulting suspension was heated under reflux in a nitrogen atmosphere for twenty-four hours. The colorless organic layer was then separated and washed with water. The solvent was evaporated and the residual, light-colored oil was taken up in ethanol. After the solution had stood in the cold for several days, 5.5 g. (57%) of a colorless solid, **1,2-dihydro-2-mesitoyl-1-methylnaphthalene (IX)**, had separated; m. p. 61–64°. After several recrystallizations from methanol, in the presence of Darco, the dihydro compound melted at 73–74° (cor.). In a subsequent run it was found possible to obtain this compound in 74% yield.

*Anal.* Calcd. for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.83; H, 7.79.

The dihydro compound (IX) readily decolorized bromine in carbon tetrachloride and immediately reduced potassium permanganate in acetone. Treatment of the compound with a 10% solution of sodium methoxide in methanol produced a deep yellow color.

**Dehydrogenation.**—A mixture of 1.5 g. of the dihydro compound (IX) and 0.15 g. of 10% palladium–charcoal catalyst was heated at 300–310° under nitrogen for one hour and fifteen minutes. It was then cooled, extracted with ether and filtered to remove the catalyst. Evaporation of the solvent left 1.3 g. of small colorless needles; m. p. 92–95°. After several recrystallizations from absolute ethanol, in the presence of Darco, the compound melted at 98.5–100°. A mixed melting point with a sample of **2-mesitoyl-1-methylnaphthalene (X)** showed no depression.

**Synthesis of 2-Mesitoyl-1-methylnaphthalene.**[17]—1-Methyl-2-naphthoic acid was prepared according to the method of Mayer and Schnecko[9] and converted to the corresponding acid chloride by the action of thionyl chloride. Five and one-half grams of anhydrous aluminum chloride was added in small portions over a period of twenty minutes to a mixture of 5 g. of mesitylene, 3.6 g. of 1-methyl-2-naphthoyl chloride and 100 ml. of carbon disulfide. The mixture was stirred during the addition and for two hours longer. After decomposition of the mixture with dilute hydrochloric acid, the organic layer was separated and extracted with 5% sodium carbonate solution. The carbon disulfide was removed by distillation and the residue steam distilled to remove unchanged mesitylene. The crude ketone was taken up in ether and the ether solution dried. The ether was removed by distillation and the residue was recrystallized twice from ethanol; m. p. 97–98.5°; yield 60%. A mixed melting point determination showed this compound to be identical with the 2-mesitoyl-1-methylnaphthalene obtained from 2-mesitoylnaphthalene.

## Summary

It has been shown that methylmagnesium iodide condenses with 1- and 2-mesitoylnaph-

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(17) This synthesis was carried out by Dr. Jack Mills.

thalene in the 1,4 manner yielding the corresponding enols. The enols absorb oxygen to yield enol peroxides or, if allowed to stand in the absence of oxygen, rearrange to the corresponding ketones. In the case of 2-mesitoylnaphthalene the yield of the 1,4 addition product was 74% of the theoretical.

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# The Chemistry of Acrylonitrile. VI. Cyanoethylation of the Haloforms

BY HERMAN A. BRUSON, WARREN NIEDERHAUSER, THOMAS RIENER AND WILLIAM F. HESTER

The behavior of acrylonitrile with compounds possessing labile hydrogen atoms[1] suggested the possibility that chloroform, if suitably activated, might add to acrylonitrile in the following manner

$$Cl_3CH + CH_2{=}CH{-}CN \longrightarrow Cl_3C{-}CH_2CH_2CN$$

It has now been found that this reaction does occur in the presence of strongly basic catalysts at low temperatures, for example, finely powdered potassium hydroxide, or aqueous 40% trimethylbenzylammonium hydroxide preferably at 0–25°. The γ-trichlorobutyronitrile obtained is a crystalline solid. Its structure follows from the fact that it yields γ-trichlorobutyric acid[2] on mild acid hydrolysis, and succinic acid upon more vigorous alkaline hydrolysis. With alkaline hydrogen peroxide it yields γ-trichlorobutyramide.

In a similar manner acrylonitrile reacted with bromoform to yield γ-tribromobutyronitrile, from which the corresponding acid and amide were in turn prepared. Although the yields are not high, due probably to the poor solubility of the catalysts in the haloforms, the γ-trichloro and γ-tribromobutyronitriles are obtained in very pure form. The reaction affords a simple method for preparing these otherwise relatively inaccessible compounds.

The reaction of iodoform with acrylonitrile in the presence of trimethylbenzylammonium hydroxide yielded a crystalline addition product of iodoform and trimethylbenzylammonium iodide, $C_6H_5CH_2N(CH_3)_3I{\cdot}CHI_3$ instead of the desired γ-tri-iodobutyronitrile. A splitting out of iodine also occurred when KOH was used as a catalyst.

## Experimental

**γ-Trichlorobutyronitrile.**—Forty grams of a 40% aqueous solution of trimethylbenzylammonium hydroxide at 2° was mixed with 447 g. of chloroform previously cooled to 2°, and to the ice-cooled mixture at a temperature not above 5° there was added dropwise with rapid mechanical stirring 202 g. of acrylonitrile during the course of two hours. The mixture was stirred for eight hours longer at 0–5°, at the end of which time an additional 10 g. of 40% aqueous trimethylbenzylammonium hydroxide was added, and the mixture stirred sixteen hours longer at 0–5°. The reaction product was washed twice with water and then distilled. A mixture of 474 g. of chloroform and acrylonitrile boiling between 60 and 80° was recovered. The residual oil was distilled in vacuum to yield 75 g. of γ-trichlorobutyronitrile boiling at 91–103° at 16 mm., which solidified in the receiver; yield 11% based on the acrylonitrile employed. Upon redistillation the compound boiled at 90–95° (12 mm.) or 214–216° at 760 mm. After recrystallization from petroleum ether it formed colorless needles melting at 41° (uncor.). It possesses a pleasant odor and is very soluble in methanol, acetone, benzene, and carbon tetrachloride, but is insoluble in cold water. *Anal.* Calcd. for $C_4H_4Cl_3N$: C, 27.86; H, 2.32; Cl, 61.70; N, 8.12. Found: C, 27.50; H, 2.30; Cl, 60.89; N, 8.16.

An alternative procedure is to gradually add 27 g. of acrylonitrile at 0–5° to a stirred mixture of 10 g. of finely powdered potassium hydroxide and 62 g. of chloroform.[3] After stirring for four hours at 0–5° the product is washed with water and dilute hydrochloric acid. The chloroform layer is then distilled to yield 10.5 g. of γ-trichlorobutyronitrile, b. p. 95–105° (17–18 mm.); yield, 12%.

**Hydrolysis of γ-Trichlorobutyronitrile.**—A mixture of 8.6 g. of γ-trichlorobutyronitrile, 110 g. of water, and 12 g. of sodium hydroxide was boiled under reflux for eleven hours. The product was acidified to congo red with concentrated hydrochloric acid and evaporated to dryness *in vacuo* on a steam-bath. The residue was extracted with acetone. Upon evaporation of the acetone extract a partially solid, dark material was obtained. This was extracted several times with boiling nitroethane and the extract cooled to 5°. The crystals which separated were recrystallized again from nitroethane to yield colorless crystals, m. p. 188–189°, which gave no depression in melting point when mixed with an authentic sample of pure succinic acid.

**γ-Trichlorobutyramide.**—A mixture of 8.6 g. γ-trichlorobutyronitrile, 50 g. of water, 0.4 g. of sodium hydroxide and 25 g. of 27% hydrogen peroxide solution was stirred rapidly at 40–45° for five hours, and allowed to stand overnight. The crystalline product was filtered off, washed with a little water, then air-dried and washed with petroleum ether. The compound was purified by recrystallization from toluene. The analytical sample formed colorless crystals, m. p. 89–90° (uncor.).

*Anal.* Calcd. for $C_4H_6Cl_3NO$: C, 25.20; H, 3.17; Cl, 55.81; N, 7.35. Found: C, 25.50; H, 3.35; Cl, 55.90; N, 7.28.

**γ-Trichlorobutyric Acid.**—A mixture of 8.6 g. of γ-trichlorobutyronitrile and 50 g. of concentrated hydrochloric acid was heated at 60° for six hours with rapid stirring. The mixture was then cooled and the crystalline product filtered off. The crude compound was recrystallized from 400 cc. of hot water from which it separated in colorless needles, m. p. 55°. (uncor.).[4] *Anal.* Calcd. for $C_4H_5Cl_3O_2$: C, 25.07; H, 2.63; Cl, 55.57. Found: C, 24.70; H, 2.72; Cl, 55.30.

**γ-Tribromobutyronitrile.**—Ten grams of aqueous 40% trimethylbenzylammonium hydroxide was added to 126 g. of bromoform at 10°. Acrylonitrile (27 g.) was added

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(1) Bruson and Riener, THIS JOURNAL, **66**, 56 (1944); **65**, 23 (1943); **65**, 18 (1943); **64**, 2850 (1942).

(2) Baroni, *Gazz. chim. ital.*, **63**, 23 (1933).

(3) Since chloroform reacts with powdered potassium hydroxide at room temperature it is advisable to add the powdered potassium hydroxide to the previously chilled chloroform at 0–5° when preparing the mixture.

(4) Baroni ref. 2 reported a m. p. 57° for this compound.