(a) IDENTIFICATION OF PRODUCTS

| Compound | Found m. p., °C. | Lit. m. p., °C. | Derivative | Found m. p., °C. | Lit. m. p., °C. |
|---|---|---|---|---|---|
| Diethyl ketone | ... | ... | Semicarbazone | 138.0 | 138.0[12] |
| Di-*n*-propyl ketone | ... | ... | Semicarbazone | 134–135 | 134.0[12] |
| Di-*n*-butyl ketone | ... | ... | Semicarbazone | 89.5–90.0 | 90.0[13] |
| Di-*n*-amyl ketone | 14–15 | 14.0[7] | Di-*n*-amylcarbinol | 15–16 | 16+[14] |
| Di-*n*-hexyl ketone | 32.0–32.5 | 33.0[7] | Di-*n*-hexylcarbinol | 40.0–40.5 | 41–42[15] |
| Di-*n*-heptyl ketone | 39.0–40.0 | 39.0[8] | Di-*n*-heptylcarbinol | 49.0 | 49.5–50[16] |
| | | | Oxime | 21.5 | 19.5–20[16] |
| Methyl *n*-heptyl ketone | ... | ... | Semicarbazone | 119.0 | 119.0–120[17] |
| *n*-Butyl *n*-nonyl ketone[9] | 25.5–26.0 | ... | *n*-Butyl-*n*-nonylcarbinol[18] | 28.5 | ...... |
| Di-*n*-nonyl ketone | 58.0 | 58–59[10] | Di-*n*-nonylcarbinol[19] | 65.5 | ...... |
| Di-*n*-heptadecyl ketone (Stearone) | 88.0 | 88.0[11] | Di-*n*-heptadecylcarbinol | 89.5–90.0 | 89.5[11] |

**Gas Analysis.**—The gaseous product was analyzed by the Gockel method.[6]

Tables I and Ia represent the results of the experiments. A single experiment was carried out to see whether the yields might be improved with the use of reduced pressure. *n*-Octyl alcohol at 125–135 mm. pressure yielded 73.9% di-*n*-heptyl ketone, compared to 56.0% conversion obtained at atmospheric pressure.

The fact that no acetone was obtained when a mixture of ethyl and *n*-octyl alcohols was subjected to the catalytic reaction is interesting, but will require further study before any detailed discussion can be presented.

## Summary

1. The preparation of ketones by the catalytic dehydrogenation and condensation of primary aliphatic alcohols was extended to *n*-propyl, *n*-butyl, *n*-amyl, *n*-decyl and *n*-octadecyl alcohols.

2. Two mixed ketones, *n*-butyl *n*-nonyl ketone and methyl *n*-heptyl ketone, were prepared by subjecting mixtures of *n*-amyl and *n*-decyl alcohols, and of ethyl and *n*-octyl alcohols to the same reaction.

3. Aldehydes and aldols were found to undergo the same reaction with the production of higher ketones.

4. The following new compounds were prepared for the first time: *n*-butyl *n*-nonyl ketone, *n*-butyl-*n*-nonylcarbinol and di-nonylcarbinol.

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[6] "U. O. P. Laboratory Test Methods for Petroleum and its Products," Chicago, 1940, p. 33.

[7] Sabatier and Mailhe, *Compt. rend.*, **158**, 832 (1914).

[8] Mailhe, *ibid.*, **157**, 220 (1913).

[9] *Anal.* Calcd. for $C_{14}H_{28}O$: C, 79.17; H, 13.29. Found: C, 78.50; H, 12.76.

[10] Briese and McElvain, THIS JOURNAL, **55**, 1697 (1933).

[11] Easterfield and Taylor, *J. Chem. Soc.*, **99**, 2300 (1911).

[12] Michael, THIS JOURNAL, **41**, 417 (1919).

[13] Pickard and Kenyon, *J. Chem. Soc.*, **101**, 629 (1912).

[14] Hess and Bappert, *Ann.*, **441**, 137 (1925).

[15] Kipping, *J. Chem. Soc.*, **57**, 535 (1890).

[16] Kipping, *ibid.*, **63**, 452 (1893).

[17] Haller and Lassieur, *Compt. rend.*, **150**, 1018 (1910).

[18] *Anal.* Calcd. for $C_{14}H_{30}O$: C, 78.43; H, 14.10. Found: C, 78.04; H, 13.57.

[19] *Anal.* Calcd. for $C_{19}H_{40}O$: C, 80.28; H, 14.08. Found: C, 80.64; H, 14.02.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

# Isomerization of Naphthalyl Chloride[1]

BY H. E. FRENCH AND J. E. KIRCHER

The space relationships of the carboxyl groups of 1,8-naphthalic acid permit the easy elimination of water with the formation of the unusually stable cyclic anhydride. The ease of formation, and the stability of this cyclic structure suggest the possibility of a cyclic, unsymmetrical structure for the di-acid chloride, in addition to the symmetrical compound which would normally be expected from this acid. The existence of such isomers appears probable by analogy with the structurally similar phthalyl chloride, which gives reactions of both structures depending on experimental conditions. That the naphthalyl chloride exists in the symmetrical form has been demonstrated. Mason[2] obtained symmetrical dialkyl esters by the action of various alcohols on the chloride, and the symmetrical di-anilide by the action of aniline.

[1] This work is part of the thesis material to be submitted by Mr. Kircher to the graduate faculty of the University of Missouri.

[2] Mason, *J. Chem. Soc.*, **125**, 2116, 2119 (1924).

Davies and Leeper[3] investigated the chloride to see whether isomeric forms could be isolated. They found that neither distillation of the chloride nor heating with aluminum chloride caused any change in the compound, and concluded that the question was still undecided.

Mason, in the work quoted above, treated the di-acid chloride with one equivalent of benzene and aluminum chloride, and obtained a 78% yield of 1-benzoyl-8-naphthoic acid. With an excess of benzene he again obtained some of the benzoylnaphthoic acid, together with a gummy material from which he did not isolate any crystalline compound. With toluene he obtained a ditolyl derivative which he did not characterize.

In the work described in this paper the behavior of the di-acid chloride in the Friedel–Crafts reaction has been investigated in an attempt to obtain products pointing to an unsymmetrical structure for the chloride. When one equivalent of benzene was used, the 1-benzoyl-8-naphthoic acid was obtained, generally in fair yields. In one such reaction however, the yield dropped to 13%. On steam distillation of the solvent there was obtained a crystalline, alkali insoluble compound in a yield of about three times that of the benzoyl compound, together with a trace of naphthalic anhydride. This substance had not previously been isolated from this reaction, nor from any of the other reactions of the acid chloride.

Using an excess of benzene we obtained a 45% yield of the 1-benzoyl-8-naphthoic acid together with the gum reported by Mason. On careful purification of this gum we obtained a 20% yield of diphenylnaphthalide, together with two compounds not yet identified, compound A, melting at 226–228° (cor.), and compound B, melting at 238–239° (cor.), in quantities of 7 and 3% of the total reaction products, respectively. Carbon and hydrogen analyses have been run on all these various compounds, and all have been examined in the Grignard machine for active hydrogen and for carbonyl groups.

The naphthalide had previously been prepared by Wittig and Wiemer[4] by the action of phenyllithium on naphthalic anhydride. Our analyses for carbon and hydrogen correspond to theory, and the Grignard machine showed the presence of one carbonyl group and no active hydrogen. Geissman and Morris[5] point out that this compound does not give carbonyl reactions in general, and is highly stable toward alkali. This corresponds to the behavior of the compound obtained in our reaction, since it did not form an oxime or phenylhydrazone, and was unchanged by long boiling with up to 50% potassium hydroxide solutions.

In the earlier runs of the diphenylnaphthalide in the Grignard machine, small quantities of hydrocarbon gas were evolved. Geissman and Morris found that the compounds formed by the action of Grignard reagents on diphenylnaphthalide liberated hydrocarbon gases at high temperatures and it was thought that our magnesium complexes were decomposing in the same manner. The difficulty was eliminated by lowering the temperature and increasing the time of reaction in the Grignard machine.

Mason[2] obtained 1-toluyl-8-naphthoic acid by the action of one equivalent of toluene on the di-acid chloride, but did not demonstrate the position of the methyl group. By decarboxylation we obtained the known $\alpha$-naphthyl *p*-tolyl ketone. Using an excess of toluene we obtained the ditolyl compound previously reported by Mason, who did not demonstrate its structure. This compound we have found in the Grignard machine to have no active hydrogen, but it does possess one carbonyl group. It does not undergo ketone reactions, and is stable toward hot, concentrated solutions of potassium hydroxide. We have shown that the compound is *p*,*p*-ditolylnaphthalide by its synthesis from naphthalic anhydride and *p*-tolyllithium, using the method of Wittig and Wiemer.

As yet we have been unable to obtain a symmetrical diaroylnaphthalene by the Friedel–Crafts reaction. The evidence of Mason and of Davies and Leeper, however, demonstrates the symmetrical structure for the acid chloride. The formation of the naphthalide in the work reported here points to the unsymmetrical structure for the acid chloride. In our reactions using an excess of benzene we obtained both the naphthalide and the benzoylbenzoic acid, indicating a simultaneous reaction of both forms of the chloride in these mixtures.

Further work on the reactions of naphthalyl chloride and certain of its derivatives is in progress.

## Experimental

**1,8-Naphthalyl Dichloride.**—This compound was prepared by the method described by Mason.[2]

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[3] Davies and Leeper, *J. Chem. Soc.*, 1124 (1927).

[4] Wittig and Wiemer, *Ber.*, **64**, 2405 (1931).

[5] Geissman and Morris, THIS JOURNAL, **63**, 1111 (1941).

**1-Benzoyl-8-naphthoic Acid.**—This compound was prepared by the method of Mason, using the acid chloride with aluminum chloride and one equivalent of benzene in tetrachloroethane solution. The acid was isolated by sodium carbonate extraction of the reaction solution after hydrolysis. Various quantities of naphthalic acid were recovered by extraction with hot 10% potassium hydroxide solution. Yields of benzoylnaphthoic acid were generally of the order of 50–60%, as white crystals from acetic acid, m. p. 110–112°. On one occasion when the yield of benzoylnaphthoic acid was very small, the tetrachloroethane was steam distilled, leaving a solid residue in the flask; white crystals from glacial acetic acid, m. p. 235–236°. *Anal.* C, 85.51; H, 5.91. Further characterization was not made.

**Diphenylnaphthalide.**—Fifty-eight grams of aluminum chloride was added in small portions to 200 cc. of partly frozen benzene. After standing for two hours at room temperature, the mixture was gradually added to 61 g. of 1,8-naphthalyl dichloride in 300 cc. of benzene which had previously been cooled to near the freezing point. After four hours the deep purplish solution was heated to 40° and after six hours the temperature was raised to 80°, and finally the mixture was heated on a water-bath for one hour, the mixture being stirred constantly throughout the reaction time. The reaction mixture was decomposed with ice and dilute hydrochloric acid, washed with water and extracted repeatedly with 10% sodium carbonate solution. Acidification of the carbonate solution caused the precipitation of the benzoylnaphthoic acid, which was formed in varying quantities. The benzene solution was washed with water, treated with charcoal, filtered, and concentrated under reduced pressure. A red, gummy residue remained. This was taken up in the minimum amount of boiling ethyl alcohol, about one-third of its volume of 10% potassium hydroxide solution was added and the mixture was boiled for about ten minutes. The precipitate thus obtained was filtered off; white crystals of diphenylnaphthalide from glacial acetic acid, m. p. 202–203° (cor.), yield 20%.

*Anal.* Calcd. for $C_{24}H_{16}O_2$: C, 85.71; H, 4.76. Found: C, 85.60; H, 4.69. The Grignard machine showed the presence of one carbonyl group and no active hydrogen.

The filtrate from the diphenylnaphthalide was largely diluted with water and allowed to stand for several hours, and filtered; white crystals from glacial acetic acid, m. p. 226–228° (cor.). This is the compound A previously mentioned; yield, 7% of the reaction products. *Anal.* C, 86.22; H, 5.61.

Acidification of the potassium hydroxide solution precipitated an acid, m. p. 238–239° (cor.) from benzene. This is the compound B previously mentioned; yield 3% of the total products. *Anal.* C, 78.40; H, 4.09. Further characterization of A and B was not made.

**1-Toluyl-8-naphthoic Acid.**—This compound was prepared as described by Mason.

***p*-Toluyl α-Naphthyl Ketone.**—This compound was prepared by the decarboxylation of 1-toluyl-8-naphthoic acid, using the method of Dougherty.[6]

**Ditolylnaphthalide.**—This compound was prepared in the same manner as the diphenyl compound. The yields were generally of the order of 80%, m. p. 235–236° (cor.).

Repeated analyses in the Grignard machine showed the presence of one carbonyl group and no active hydrogen. The Grignard complex of this compound was more soluble than the corresponding diphenyl compound, and the analyses were correspondingly easier to run. Hot concentrated solutions of potassium hydroxide were without action on the naphthalide. The compound had previously been isolated by Mason, who determined the percentage composition.

The identity of the compound was established by its synthesis from tolyllithium and naphthalic anhydride according to the method of Wittig and Wiemer.[4]

## Summary

Naphthalyl chloride has been found to enter into the Friedel–Crafts reaction to produce the naphthalide and the aroyl-naphthoic acid simultaneously. This, together with information from other sources on the symmetrical structure, is evidence for the existence of isomeric forms for the acid chloride.

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[6] Dougherty, This Journal, 50, 571 (1928).