

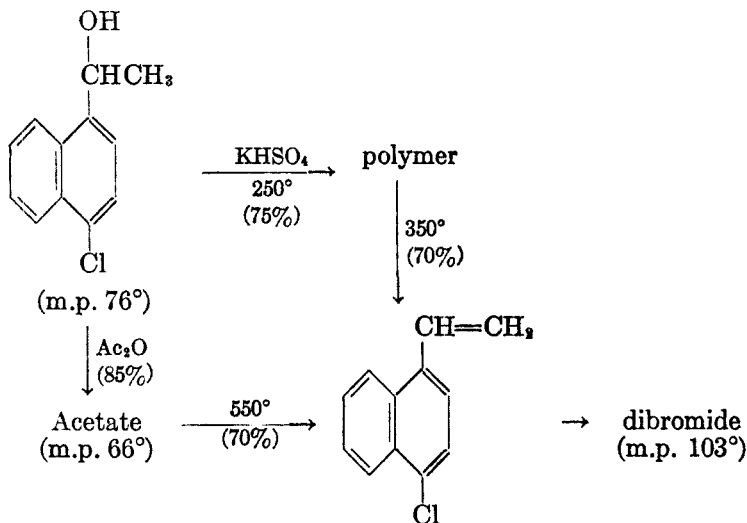
THE PREPARATION OF SEVERAL CHLORINATED 1-VINYLNAPHTHALENES¹

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There are a number of reports of the preparation of 1-vinylnaphthalene by various routes (1-8). It was the purpose of the investigation reported herein to prepare a number of chlorinated derivatives for comparison. Those described are the 4-, 5-, and 7-chloro-, and 5,8-dichloro-1-vinylnaphthalenes.

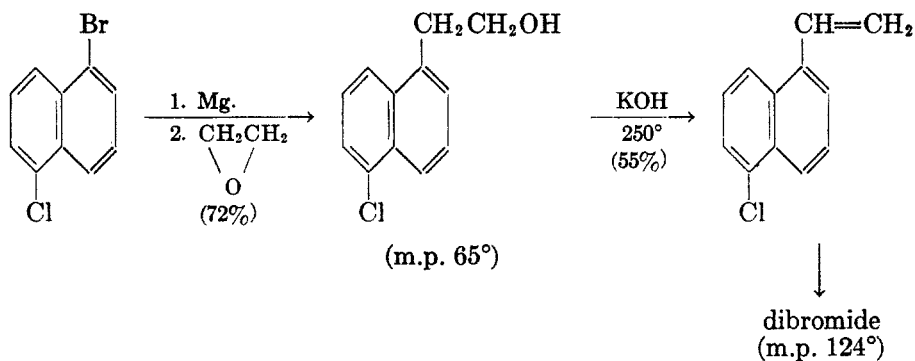
The 4-chloro compound was prepared from 1-chloronaphthalene through Friedel-Crafts acetylation, reduction to the arylmethylcarbinol, and dehydration. The dehydration was effected conveniently by pyrolysis of the acetate or by "dehydration-polymerization" over potassium acid sulfate followed by thermal depolymerization, which proceeded smoothly and in good yield.



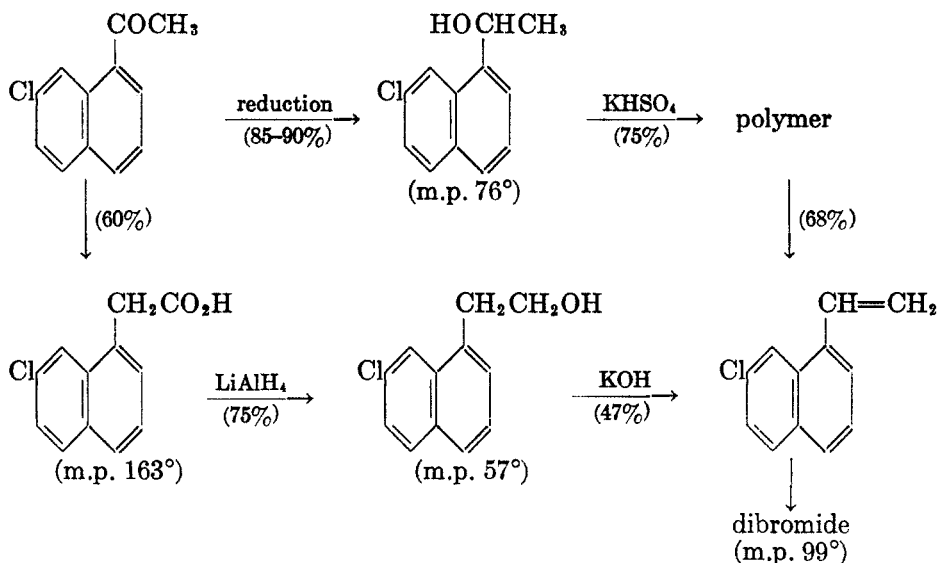
The 5-chloro isomer was prepared from 1-nitronaphthalene through bromination to the 5-bromo derivative. The latter was obtained in 85% yield, a considerable improvement over the 25% reported by Shoesmith (9) and Campbell (10). Reduction and a Sandmeyer reaction produced 1-bromo-5-chloronaphthalene, which was converted to the vinyl compound through the following steps.

¹ Abstracted from a Ph.D. thesis submitted to the graduate school of the University of Notre Dame.

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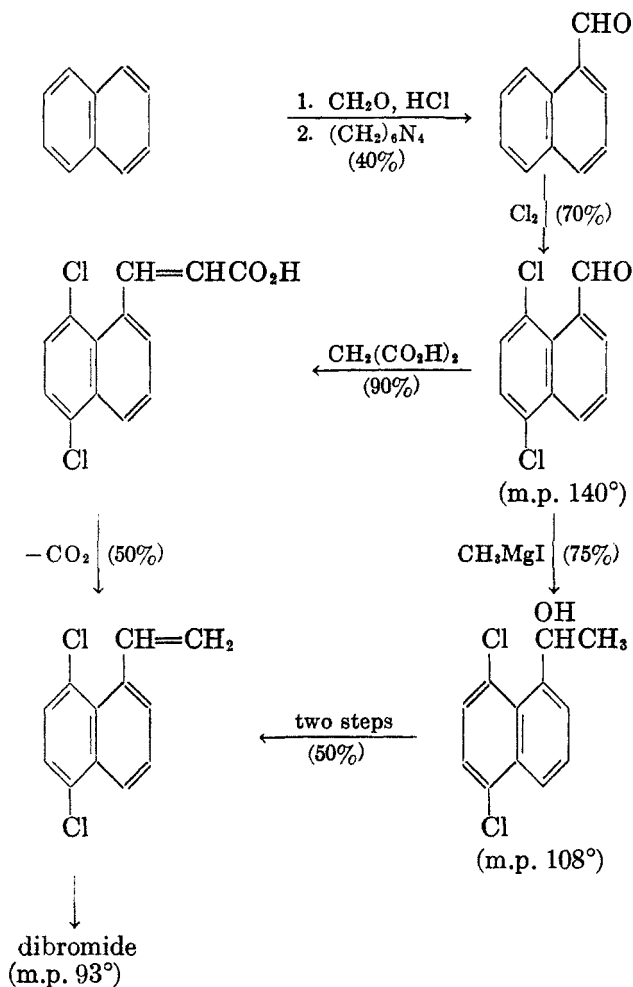


The 7-chloro isomer was prepared through Friedel-Crafts acetylation of 2-acetaminonaphthalene (11). The 7-chloro ketone was then converted to the vinyl compound either by conventional reduction and acid dehydration of the secondary carbinol or by converting to the naphthylacetic acid followed by reduction and alkaline dehydration of the primary carbinol.



5,8-Dichloro-1-vinylnaphthalene was prepared through chlorination of 1-naphthaldehyde *via* two routes, one by addition of methylmagnesium iodide followed by dehydration, the other by condensation with malonic acid followed by decarboxylation.

The preparation of 1-naphthaldehyde from naphthalene was simplified considerably by not isolating the intermediate chloromethyl derivative, depending on purification of the aldehyde through its sodium bisulfite addition compound to separate unreacted naphthalene.

EXPERIMENTAL³

(4-Chloro-1-naphthyl)methylcarbinol was prepared by aluminum isopropoxide reduction of 4-acetyl-1-chloronaphthalene, [b.p. $165\text{--}168^\circ$ (4–5 mm.)], prepared and purified through the picrate (m.p. $87\text{--}88^\circ$) according to Jacobs and co-workers (12). Reduction of 210 g. of the ketone with 200 g. of aluminum isopropoxide in 1000 ml. of isopropyl alcohol required 5 to 6 hours at $55\text{--}60^\circ$. After evaporation of most of the solvent, the mixture was hydrolyzed with dilute hydrochloric acid and extracted with ether. Evaporation of the dried ether extract left 195–204 g. (90–93%) of white solid, m.p. $70\text{--}71^\circ$. Recrystallization from *n*-hexane gave long needles, m.p. $75.5\text{--}76^\circ$.⁴

Anal. Calc'd for $\text{C}_{12}\text{H}_{11}\text{ClO}$: C, 69.72; H, 5.36; Cl, 17.18.

Found: C, 69.56; H, 5.26; Cl, 17.78.

The 3,5-dinitrobenzoate melted at $130\text{--}131^\circ$ after recrystallization from *n*-hexane.

Anal. Calc'd for $\text{C}_{13}\text{H}_{13}\text{ClN}_2\text{O}_7$: N, 6.99. Found: N, 6.69.

³ Analyses by Micro-Tech Laboratories, Skokie, Ill.

⁴ Mowry, Renoll, and Huber (8) reported this carbinol as a liquid, n_D^{25} 1.6200.

The *acetate*, prepared in 85% yield by refluxing the carbinol in acetic anhydride, crystallized from *n*-hexane as long needles, m.p. 65–66°, b.p. 168–170° (2–3 mm.).

Anal. Calc'd for $C_{14}H_{13}ClO_2$: C, 67.59; H, 5.27; Cl, 14.27.

Found: C, 67.55; H, 5.52; Cl, 14.70.

Dehydration of (4-chloro-1-naphthyl)methylcarbinol by the usual procedure, heating at 250° over potassium sulfate under 30–40 mm., gave only a 16% yield of vinyl compound, the major product consisting of an undistilled residue of transparent resin. By raising the pressure to over 50 mm., no vinyl compound was obtained, only resin. This product of "dehydration-polymerization" was then purified by precipitation with methanol from benzene solution to give a 75% yield of white powdery polymer.

Depolymerization was accomplished by heating in a sand bath at about 350° under 0.5–1.0 mm. pressure to yield 65–75% of 4-chloro-1-vinylnaphthalene, b.p. 124–125° (0.5–1 mm.). Pyrolysis of the acetate (containing a small amount of sulfur) at 550° gave the vinyl compound in 71% yield.

The *dibromide* was prepared by adding bromine in carbon tetrachloride. After recrystallization from 80% ethanol, the product melted at 102–103°.

Anal. Calc'd for $C_{12}H_9Br_2Cl$: Halogen, 56.05. Found: Halogen, 55.50.

Polymerization of 4-chloro-1-vinylnaphthalene by heating at 60° with 1% benzoyl peroxide gave a hard, transparent polymer. After reprecipitation from benzene by methanol, it was found to soften at 170–172°.

Anal. Calc'd for $(C_{12}H_9Cl)_n$: C, 76.37; H, 4.81; Cl, 18.81.

Found: C, 75.80; H, 5.10; Cl, 18.84.

5-Bromo-1-nitronaphthalene was prepared by adding 640 g. of bromine to 684 g. of 1-nitronaphthalene and 4.5 g. of ferric chloride warmed to 80–90° on a water-bath. After washing with water and 10% bicarbonate, recrystallization from ethanol yielded 800–850 g. (80–85%) of yellow needles, m.p. 120°, a considerable improvement of the 25% yield previously reported (9, 10).

This was converted to 1-bromo-5-chloronaphthalene by reduction with stannous chloride, diazotization and treatment with cuprous chloride to yield 51% of product, m.p. 115–116° (13).

2-(5-Chloro-1-naphthyl)ethanol. A solution of 120 g. (0.5 mole) of 5-bromo-1-chloronaphthalene and a small crystal of iodine in 150 ml. of ether and 150 ml. of benzene was stirred while 12 g. (0.5 mole) of magnesium turnings was added slowly. When the Grignard preparation was complete, the mixture was cooled to –5° and 20 g. (0.45 mole) of ethylene oxide in 50 ml. of ether was added at 0°. After an hour of reflux, hydrolysis, washing, drying, and evaporation left the solid alcohol, 75 g. (72%), which was recrystallized from hexane, m.p. 64–65°.

Anal. Calc'd for $C_{12}H_{11}ClO$: Cl, 17.18. Found: Cl, 17.55.

The *phenylurethan* was recrystallized from cyclohexane, m.p. 144–145°.

Anal. Calc'd for $C_{19}H_{16}ClNO_2$: Cl, 10.88. Found: Cl, 11.43.

The *p*-nitrobenzoate crystallized from ethanol as colorless needles, m.p. 134–135°.

Anal. Calc'd for $C_{19}H_{14}ClNO_4$: Cl, 10.01. Found: Cl, 10.76.

5-Chloro-1-vinylnaphthalene. A mixture of 40 g. of the alcohol above and 25 g. of potassium hydroxide was heated to 250–260° under 35–40 mm. pressure, yielding 21 g. (55%) of vinyl compound, b.p. 142–144° (2–3 mm.).

The *dibromide* formed yellow crystals, m.p. 122–124°.

Anal. Calc'd for $C_{12}H_9Br_2Cl$: Halogen, 56.05. Found: Halogen, 56.20.

The *polymer* was a yellow powder with a softening point of about 180–185°.

Anal. Calc'd for $(C_{12}H_9Cl)_n$: Cl, 18.81. Found: Cl, 19.00.

7-Amino-1-acetonaphthone was obtained in 60–70% yields as golden-yellow rhombic needles, m.p. 110–111° (13). Diazotization and treatment with cuprous chloride gave an unpromising-looking black tarry solid which, surprisingly, produced a colorless solid on distillation. One recrystallization from ethanol gave 166 g. (65%) of 7-chloro-1-acetonaphthone, m.p. 65–66°, b.p. 158–160° (4 mm.) (14).

(7-Chloro-1-naphthyl)methylcarbinol was obtained in 90–92% yield by aluminum iso-

propoxide reduction and in 85% yield by lithium aluminum hydride. It crystallized from *n*-hexane as needles, m.p. 75-75.5°.

Anal. Calc'd for $C_{12}H_{11}ClO$: Cl, 17.18. Found: Cl, 17.52.

The *phenylurethan* crystallized from ethanol as colorless needles, m.p. 228-230°.

Anal. Calc'd for $C_{13}H_{13}ClNO_2$: Cl, 10.88. Found: Cl, 10.56.

The *p*-nitrobenzoate was obtained as rhombic crystals from ethanol, m.p. 111-112°.

Anal. Calc'd for $C_{13}H_{11}ClNO_4$: Cl, 10.01. Found: Cl, 10.45.

7-Chloro-1-vinylnaphthalene. Again, the direct potassium acid sulfate dehydration gave principally polymer and only a poor yield (20%) of vinyl compound at low pressure, so the "dehydration-polymerization" procedure at 230-240° under 40 mm. of pressure was used to produce reprecipitated polymer in 75% yield, softening point 190-192°.

Anal. Calc'd for $(C_{12}H_9Cl)_n$: Cl, 18.81. Found: Cl, 18.92.

The monomer was obtained in 68% yield by pyrolysis at 400-450° under 4-5 mm. pressure, b.p. 120-121° (4-5 mm.).

7-Chloro-1-naphthylacetic acid. A mixture of 10 g. of 7-chloro-1-naphthyl methyl ketone, 2.5 g. of sulfur and 6.5 g. of morpholine was boiled gently under reflux for 16 hours. The crude thiomorpholide was hydrolyzed in a mixture of acetic and sulfuric acids and the resulting acid purified from benzene-*n*-hexane to give 6.0-6.5 g. (55-60%) of needles, m.p. 162-163°.

Anal. Calc'd for $C_{12}H_9ClO_2$: Cl, 16.18. Found: Cl, 16.60.

2-(7-Chloro-1-naphthyl)ethanol. A sample of 11 g. (0.05 mole) of the above acid was placed in the thimble of a Soxhlet extractor and a solution of 2.85 g. (0.05 mole) of lithium aluminum hydride in the flask. The mixture was refluxed until all the acid had dissolved. After hydrolysis and washing, the ether layer was evaporated. The residue crystallized from ethanol as needles, 8 g. (75%), m.p. 55-57°.

Anal. Calc'd for $C_{12}H_{11}ClO$: Cl, 17.18. Found: Cl, 17.68.

The *phenylurethan* was recrystallized from ethanol, m.p. 138-139°.

Anal. Calc'd for $C_{13}H_{13}ClNO_2$: Cl, 10.88. Found: Cl, 11.05.

The *p*-nitrobenzoate was also recrystallized from ethanol, m.p. 140-141°.

Anal. Calc'd for $C_{13}H_{11}ClNO_2$: Cl, 10.01. Found: Cl, 10.25.

7-Chloro-1-vinylnaphthalene. Dehydration of the alcohol was accomplished by heating 8 g. with 2.5 g. of potassium hydroxide to 240-250° under 30-40 mm. pressure to yield 3.5 g. (47%) of vinyl compound.

The *dibromide* formed colorless crystals, m.p. 98-99°.

Anal. Calc'd for $C_{12}H_9Br_2Cl$: Halogen, 56.05. Found: Halogen, 55.80.

1-Naphthaldehyde can be prepared satisfactorily by chloromethylation of naphthalene (15) followed by the Sommelet reaction (16, 17). The troublesome separation of naphthalene from its chloromethyl derivative was successfully avoided by carrying out the Sommelet reaction on the crude product prepared according to "Organic Syntheses" (15), relying on the aldehyde-bisulfite addition compound for purification. The crude chloromethylation mixture from 256 g. of naphthalene was dissolved in 400 ml. of boiling glacial acetic acid and treated with 120 g. of urotropine. After cooling, the mixture was poured into 1.5 l. of cold water with good stirring. The crude 1-naphthaldehyde was extracted with 800 ml. of ether which, after washing with 5% sodium bicarbonate and water, was shaken vigorously for half an hour with 400 ml. of 40% sodium bisulfite and 100 ml. of 95% ethanol. The precipitate was washed thoroughly with ether. Addition to 10% sodium carbonate liberated the aldehyde, which was separated by extraction with ether and distilled, b.p. 140-142° (8 mm.); yield, 105-125 g. (34-40%).

5,8-Dichloro-1-naphthaldehyde was prepared by chlorinating 60 g. of 1-naphthaldehyde in 90 ml. of chloroform in the presence of 0.5 g. of ferric chloride at 55-60°. After washing the product in benzene solution, evaporation left a solid which was recrystallized from hexane as pale yellow, short needles, m.p. 136-137°; yield, 55-60 g. (65-70%). Recrystallization from benzene-hexane with charcoal decolorization produced colorless needles of 5,8-dichloronaphthaldehyde, m.p. 139-140°.

Anal. Calc'd for $C_{11}H_6Cl_2O$: Cl, 31.20. Found: Cl, 31.11.

During recrystallization, it was possible to isolate very small amounts of two *by-products*, one, short, yellow needles, m.p. 124–125°, was believed to be the monochloro (5- or 8-?) derivative. The other, a yellow powder, m.p. 235°, gave the proper chlorine analysis for a dichloronaphthoic acid (%Cl: calc'd 29.00; found, 28.66).

The *anil* formed readily on warming the aldehyde with aniline in ethanol. After recrystallization from hexane, it melted at 140–141°. Digestion with methanol raised the melting point to 144.5–145°.

Anal. Calc'd for $C_{17}H_{11}Cl_2N$: C, 68.05; H, 3.66; N, 4.70; Cl, 23.60.

Found: C, 68.17; H, 3.89; N, 4.71; Cl, 23.54.

Digestion of the anil in 10% hydrochloric acid regenerated *aldehyde* which, after recrystallization from methanol, melted at 140–140.5° and gave a 20° depression on mixing with the anil.

The *semicarbazone* separated from ethanol as colorless needles, m.p. 234–235°.

Anal. Calc'd for $C_{12}H_9Cl_2N_3O$: N, 14.90. Found: N, 14.52.

The *oxime* also separated from ethanol as colorless needles, m.p. 199–200°.

Anal. Calc'd for $C_{11}H_8Cl_2NO$: N, 5.96. Found: N, 5.85.

The *structure* of the aldehyde was established by oxidation of a 1-g. sample in pyridine solution by addition of aqueous alkaline potassium permanganate. After boiling for two hours, the solution was filtered and then washed with three portions of chloroform. Acidification of the aqueous layer precipitated 0.75 g. of white solid, m.p. 187–188°, in agreement with that reported for 5,8-dichloronaphthoic acid (18).

(5,8-Dichloro-1-naphthyl)methylcarbinol was prepared from 22.5 g. of the aldehyde by addition to the Grignard reagent prepared in ether from 15.1 g. of methyl iodide and 2.43 g. of magnesium. After hydrolysis, the ether solution was washed with water, 5% sodium bicarbonate, 40% sodium bisulfite and water, dried, and evaporated. The solid residue was recrystallized from cyclohexane to yield 17–18 g. (70–75%) of colorless rhombic crystals, m.p. 107–107.5°.

Anal. Calc'd for $C_{12}H_{10}Cl_2O$: C, 59.75; H, 4.18; Cl, 29.00.

Found: C, 59.70; H, 4.30; Cl, 29.00.

The *p-nitrobenzoate* crystallized from ethanol as yellow plates, m.p. 149–150°.

Anal. Calc'd for $C_{19}H_{13}Cl_2NO_4$: N, 3.59. Found: N, 3.59.

Dehydration-polymerization with potassium bisulfate at 240–250° for three hours under 45 mm. pressure gave a 70% yield of reprecipitated polymer. This was depolymerized by heating at 400–450° under 0.5–1.0 mm. pressure to yield 67–75% of 5,8-dichloro-1-vinylnaphthalene, b.p. 150–152° (2–3 mm.). The *dibromide* crystallized from 80% ethanol as yellow needles, m.p. 92–93°.

Anal. Calc'd for $C_{12}H_8Br_2Cl_2$: Halogen, 60.31. Found: Halogen, 59.58.

The polymer was obtained as a yellow powder, softening point 120–130°.

Anal. Calc'd for $(C_{12}H_8Cl_2)_n$: Cl, 31.84. Found: Cl, 31.51.

β -(5,8-Dichloro-1-naphthyl)acrylic acid was prepared by refluxing 12 g. of the aldehyde, 8 g. of malonic acid, and a few drops of piperidine in 60 ml. of dry pyridine for six hours. After cooling, the mixture was poured into 20% sulfuric acid. The solid was collected and recrystallized from methanol or aqueous ethanol with decolorization, to yield 12.5–13.0 g. (85–90%) of colorless short needles, m.p. 258–259°, with some decomposition.

Anal. Calc'd for $C_{13}H_9Cl_2O_2$: C, 58.50; H, 3.00.

Found: C, 58.55; H, 2.96.

Decarboxylation to the vinyl compound was accomplished by heating to 225° in quinoline containing copper powder and hydroquinone; yield, 45%. Substituting acridine for quinoline raised the yield to 51%.

SUMMARY

4-Chloro-, 5-chloro-, 7-chloro-, and 5,8-dichloro-1-vinylnaphthalenes and a number of intermediates and derivatives have been prepared and characterized.

All four vinyl compounds polymerize readily to hard resins, the 7-chloro polymer having the highest, the 5,8-dichloro the lowest softening point.

NOTRE DAME, INDIANA

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