extent of hydrogen bonding between the constituents of wood and the swelling agent. The observed swelling behavior of the wood is explained in the hypothesis, that the degree of swelling bears a direct relationship to the intensity of hydrogen bonding between the constituents of wood and the swelling agent and that steric hindrance is a controlling influence on the intensity of the hydrogen bonding.

ST. PAUL, MINNESOTA RECEIVED MARCH 5, 1949

[FROM THE CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Removal of Chlorine from Aromatic Nitrochloro Compounds. Preparation of 1,3-Dinitronaphthalene

BY WALTER T. SMITH, JR.

1,3-Dinitronaphthalene has been prepared by various procedures,[1] all of which involve 1-amino-2,4-dinitronaphthalene as an intermediate and the subsequent removal of the amino group by diazotization and reduction. A new method for preparing 1,3-dinitronaphthalene has been discovered which depends on dehalogenation of 1-chloro-2,4-dinitronaphthalene. This intermediate can be prepared easily and in good yield from α-naphthol.[2] The dehalogenation of 1-chloro-2,4-dinitronaphthalene is accomplished by heating it with copper powder in molten benzoic acid at 150–200°. The hydrogen which replaces the chlorine apparently comes from the carboxyl group of the benzoic acid. From this reaction mixture 1,3-dinitronaphthalene can be isolated in 74% yield.

Other acids of suitable boiling point can be substituted for benzoic acid. When the reaction is carried out in *n*-caproic acid (b. p. 205°) the yield of 1,3-dinitronaphthalene is somewhat lower (73% crude).

This use of an organic acid and copper as a means of removing chlorine from aromatic nitrochloro compounds explains Ullmann's isolation of 3,5-dinitrobenzoic acid in unspecified yield when 2-chloro-3,5-dinitrobenzoic acid was heated with copper in phenol.[3] During the present work a 77% yield of the copper salt of 3,5-dinitrobenzoic acid was obtained when 4-chloro-3,5-dinitrobenzoic acid was heated with copper in nitrobenzene. That the carboxyl group need not be in the same molecule as the chlorine is shown by our preparation of 1,3-dinitronaphthalene and by other reactions cited below. Rindl[4] also observed the formation of an appreciable amount of 1,3-dinitronaphthalene as a by-product in the preparation of $2,4,2',4'$-tetranitro-α,α'-binaphthyl. In this case the source of the hydrogen which replaces the chlorine is not known. It is suggested that the hydrogen may have come from traces of water in the nitrobenzene in which the reaction was carried out. This would be in keeping with reports in the literature that when picryl chloride and copper are heated in toluene hexanitrobiphenyl is obtained[5] whereas when the same reagents are heated in alcohol[6] trinitrobenzene is formed. In the present work 1,3,5-trinitrobenzene was obtained in only 20% yield by the action of copper on picryl chloride in boiling nitrobenzene containing an equivalent of benzoic acid.

In order to learn more about the generality of the reaction, the removal of chlorine from chloronitrobenzenes was also studied. 2,4-Dinitrochlorobenzene gave a 52% yield of 1,3-dinitrobenzene. *o*-Chloronitrobenzene gave a 59% yield of nitrobenzene. The *meta*-isomer gave at best only a small amount of nitrobenzene. With the *para*-isomer there was no evidence of the formation of nitrobenzene. The inactivity of the chlorine *para* to the nitro group is in keeping with the results of Ullmann[5] who found that although *o*-chloronitrobenzene gave a 60% yield of *o,o'*-dinitrobiphenyl, *p*-chloronitrobenzene gave unsatisfactory yields of the corresponding biphenyl and it was necessary to use the iodo compound in order to obtain comparable yields.

Experimental

1,3-Dinitronaphthalene.—To a hand-stirred mixture of 7 g. (0.057 mole) of benzoic acid and 5 g. (0.02 mole) of 1-chloro-2,4-dinitronaphthalene in a 50-ml. beaker was added 5 g. of copper powder (Baker and Adamson, fine powder) in several portions over a period of five minutes (temp. at 150–200°). After the melt solidified, the beaker was placed in 100 ml. of 10% sodium bicarbonate solution and the melt was digested until it was completely broken up and no effervescence was evident. The liquid suspension was filtered through a Soxhlet thimble. The material in the thimble was then extracted in a Soxhlet extractor with 100 ml. of acetone until no more color was extracted. Upon cooling and filtering the extract there was obtained 1.6 g. of 1,3-dinitronaphthalene, m. p. 145–146° (cor.). From the filtrate there was obtained 2.1 g. of material which after recrystallization from 35 ml. of aqueous pyridine weighed 1.9 g., m. p. 145–146° (cor.); total yield 3.2 g. (74%).

In another run *n*-caproic acid was substituted for benzoic acid. The product was isolated after removing

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(1) See for example, Hodgson, Birtwell and Marsden, *J. Chem. Soc.*, 112 (1944).

(2) Morgan and Evens, *J. Chem. Soc.*, **115**, 1128 (1919); Ullmann and Bruck, *Ber.*, **41**, 932 (1908).

(3) Ullmann and Engi, *Ann.*, **366**, 88 (1909).

(4) Rindl, *J. Chem. Soc.*, **103**, 1917 (1913).

(5) Ullmann and Bielecki, *Ber.*, **34**, 2177 (1901).

(6) Meyer, German Patent 234,726 (*Chem. Zentr.*, **82**, I, 1767 (1911)).

the caproic acid by steam distillation from acid solution and removing any dinitronaphthol by digestion with sodium carbonate solution. There was obtained 3.1 g. (73%) of crude product melting at 95–110°.

3,5-Dinitrobenzoic Acid from 4-Chloro-3,5-dinitrobenzoic Acid.—To a gently boiling solution of 6 g. (0.024 mole) of 4-chloro-3,5-dinitrobenzoic acid in 40 ml. of nitrobenzene was added 5 g. of copper powder in several portions. After all the copper had been added, the reaction mixture was heated for fifteen minutes and then filtered while hot. The insoluble material was washed with a few milliliters of petroleum ether (b. p. 60–70°). The filtrate and washings were combined and cooled. The brick-red solid which formed was removed by filtration and washed with petroleum ether. It weighed 4.5 g. Treatment with dilute hydrochloric acid and extraction with ethyl acetate gave 3,5-dinitrobenzoic acid, m. p. 197–200° (uncor.); identified by mixed m. p. with authentic sample and by preparation of the methyl ester, m. p. 106–107° (lit. 107°).

Dehalogenation of Chloronitrobenzenes: *o*-**Chloronitrobenzene.**—To a molten mixture of 14 g. (0.11 mole) of benzoic acid and 6.3 g. (0.04 mole) of *o*-chloronitrobenzene (at 150–200°) was added 10 g. of copper powder in several portions over a period of five minutes. The mixture was allowed to solidify, and was then taken up in 50 ml. of 20% sodium carbonate solution. The alkaline mixture was steam distilled until the distillate was of a clear yellow color. From the distillate there was separated 2.4 ml. (2.9 g. or 59%) of nitrobenzene, m. p. 3.5–4.5°.

m-**Chloronitrobenzene.**—The procedure was carried out substituting *m*-chloronitrobenzene for the ortho-isomer. The steam distillate contained 5.4 g. of oily solid which after melting starts to solidify at about 36°. *m*-Chloronitrobenzene containing 17% nitrobenzene starts to solidify at 34°. Assuming that the product obtained from the steam distillate was a mixture of *m*-chloronitrobenzene and nitrobenzene, less than 17% of nitrobenzene was formed in the reaction.

p-**Chloronitrobenzene.**—The procedure for *o*-isomer was repeated using *p*-chloronitrobenzene. From the steam distillate there was obtained 4.3 g. of *p*-chloronitrobenzene.

2,4-Dinitrochlorobenzene.—To a molten mixture of 14 g. (0.11 mole) of benzoic acid and 8.1 g. (0.04 mole) of 2,4-dinitrochlorobenzene (Eastman Kodak Co. practical grade) was added 10 g. of copper powder in several portions over a period of five minutes. Temperature of melt was 150–180° until about one-half of the copper had been added, at which point the reaction became quite vigorous. Heating was stopped but temperature rose to 235°. The remainder of the copper was added while temperature was above 200°. The mixture was cooled, treated with 50 ml. of 20% sodium carbonate solution and steam distilled to give 3.5 g. (52%) of 1,3-dinitrobenzene, m. p. 87–88°.

1,3,5-Trinitrobenzene.—To a gently boiling solution of 3 g. (0.025 mole) of benzoic acid and 6 g. (0.024 mole) of picryl chloride in 40 ml. of nitrobenzene was added 4.3 g. of copper powder in several small portions. The solution was heated for ten minutes after all the copper had been added, then filtered while warm and taken up in 80 ml. of ethyl acetate. The ethyl acetate solution was treated first with 10% hydrochloric acid and then with 10% sodium hydroxide solution to convert copper benzoate to benzoic acid and then to sodium benzoate. The resulting mixture was steam distilled. The insoluble material in the steam distillation residue was removed by filtration, taken up in acetone, treated with activated carbon and diluted with water to give 1 g. (20%) of 1,3,5-trinitrobenzene, m. p. 120–121°; mixed melting point with an authentic sample 120–121°, with picryl chloride *ca.* 100°.

Summary

Aromatic nitrochloro compounds containing a nitro group ortho to the chlorine undergo dechlorination when heated with copper powder and an organic acid at 150–200°. A new synthesis of 1,3-dinitronaphthalene is described.

IOWA CITY, IOWA RECEIVED MARCH 28, 1949

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Derivatives of Thianaphthene. II[1]

BY F. F. BLICKE AND DON G. SHEETS[2]

During the continuation of our studies of preparative procedures for thianaphthene derivatives, and their use for the synthesis of products of possible therapeutic value, we found that 2-hydroxymethylthianaphthene was obtained in 99% yield by reduction of thianaphthene-2-carboxylic acid[3] with lithium aluminum hydride, and in 56% yield by interaction of 2-thianaphthenyl sodium[3] and formaldehyde. The 2-hydroxymethyl derivative reacted with thionyl chloride to form the 2-chloromethyl compound which, in turn, was converted by potassium cyanide into 2-cyanomethylthianaphthene. Thianaphthene-2-acetic acid[4] was obtained in 93% yield by hydrolysis of the 2-cyanomethyl derivative.

2-Thianaphthenylmethyl benzoate was prepared by interaction of 2-chloromethylthianaphthene and sodium benzoate, and also by reaction between 2-hydroxymethylthianaphthene and benzoyl chloride.

In order to obtain N,N-dimethyl-N′-phenyl-N′-(2-thianaphthenylmethyl)-ethylenediamine, N,N-dimethyl-N′-phenylethylenediamine[5] was allowed to react with sodamide and then with 2-chloromethylthianaphthene. N,N-Dimethyl-N′-(2-pyridyl)-N′-(2-thianaphthenylmethyl)-ethylenediamine was prepared in an analogous manner from N,N-dimethyl-N′-(2-pyridyl)-ethylenediamine[6] and 2-chloromethylthianaphthene.

Reduction of thianaphthene-3-carboxylic acid[7] with lithium aluminum hydride produced 3-

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[1] This paper represents part of a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Monsanto Chemical Company Fellow.

[3] Schönberg, Petersen and Kaltschmitt, *Ber.*, **66**, 233 (1933).

[4] Blicke and Sheets, THIS JOURNAL, **70**, 3768 (1948).

[5] Leonard and Solmssen, *ibid.*, **70**, 2066 (1948).

[6] Huttrer, Djerassi, Beears, Mayer and Scholz, *ibid.*, **68**, 2001 (1946).

[7] Komppa and Weckman, *J. prakt. Chem.*, **138**, 109 (1933).