very nearly 1:1, tends to indicate the presence of an aromatic nucleus in alkali lignin from corn cobs.

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The Nitration of *o*-Dichlorobenzene

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When *o*-dichlorobenzene is nitrated, theoretically two mononitro isomers may be formed, namely, 2,3-dichloronitrobenzene and 3,4-dichloronitrobenzene. This reaction has been the subject of several investigations. Beilstein and Kurbatow[2] obtained from *o*-dichlorobenzene upon treatment with fuming nitric acid a "half liquid mixture," the solid portion of which melted at 43° after crystallization from alcohol and consisted of 3,4-dichloronitrobenzene. Holleman[3] obtained by the same method a mixture of a solid and a liquid; the solid melted at 43° after several recrystallizations from alcohol. Kipriyanov and Mikhaĭlenko[4] state that *o*-dichlorobenzene forms on nitration a mixture of 2,3- and 3,4-dichloronitrobenzenes, that one part solidifies on standing, and that both the solid and liquid fractions consist for the most part of 3,4-dichloronitrobenzene. McMaster and Magill[5] nitrated *o*-dichlorobenzene with a mixture of sulfuric and nitric acids and obtained a mixture of a liquid and a solid which they believed to be two forms of 3,4-dichloronitrobenzene, both of which changed spontaneously at 22° to an equilibrium mixture containing about half solid and half liquid.

The purpose of the present work was to investigate the "liquid form" obtained by the nitration of *o*-dichlorobenzene, and to determine, if possible, whether two isomers actually were present.

o-Dichlorobenzene[6] was purified by fractionation through a six-foot column. The portion boiling from 179.9 to 180.6° was nitrated according to the method of McMaster and Magill.[5] From 845 g. of *o*-dichlorobenzene 750 g. of a brown oil was obtained which boiled from 189.2 to 189.4° at 100 mm. The product was perfectly clear and homogeneous at 40°; it became cloudy at 35° and solidified to a mass of hard crystals at 15°. A portion of this material was partially frozen, and the resulting slush filtered. By repeating this process several times, 165 g. of a liquid and 200 g. of a solid were obtained having the characteristics given in Table I.

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[2] Beilstein and Kurbatow, *Ann.*, **176**, 41 (1875).

[3] Holleman, *Rec. trav. chim.*, **23**, 357 (1904).

[4] Kipriyanov and Mikhaĭlenko, *Ukrainskiĭ Khem. Zhur.*, **5** Tech. pt., 225–39 (1930); *C. A.*, **25**, 5033 (1931).

[5] McMaster and Magill, THIS JOURNAL, **50**, 3038 (1928).

[6] Generously furnished by the du Pont Company.

TABLE I

PROPERTIES OF THE CRUDE NITRATION PRODUCT OF *o*-DICHLOROBENZENE

Form	Solid	Liquid
Boiling point at 100 mm., °C.	188.5–189.0	188.5–189.0
n_D^{25}	1.5929 (supercooled)	1.5884
Freezing point, °C.	35–40	15–20
State after four months at room temperature	Solid	Liquid

The solid portion melted at 42.5° after crystallization from alcohol, and appeared to be 3,4-dichloronitrobenzene. It is to be noted that neither the solid nor the liquid portion, on prolonged standing, showed any tendency to change state.

The presence of another isomer was suspected in the liquid fraction. Because the separation of 2,3- and 3,4-dichloronitrobenzenes is very difficult due to the proximity of their boiling points,[4] the liquid fraction was reduced to the dichloroanilines whose boiling points differ by 22°. The reduction was carried out with iron and acetic acid as described by Hodgson and Kershaw.[7] 2,3- and 3,4-dichloroanilines were found and identified. It therefore seems logical to conclude that 2,3-dichloronitrobenzene is formed in small amounts when *o*-dichlorobenzene is nitrated, and that the reported behavior of the crude nitration product is due to the presence of this second isomer.

Experimental

Separation and Identification of 2,3- and 3,4-Dichloroanilines.—The product resulting from the reduction of the liquid dichloronitrobenzene was fractionated several times. There were obtained 15 g. of an oil boiling from 175 to 181° at 100 mm. and melting at −10 to −15°, and about 90 g. of a white solid boiling from 181.4 to 182° at 60 mm. and melting after one recrystallization from water at 71°. The constants for 2,3-dichloroaniline and 3,4-dichloroaniline are, respectively: b. p.[3] atm. 250° (est. 180° at 100 mm.), m. p.[3] 24°; b. p. atm.[8] 272° (est. 182° at 60 mm.), m. p. 71.5°.[8] The liquid dichloroaniline was converted to the acetyl derivative with acetic anhydride. After crystallization from benzene, white needles were obtained which melted at 149–156°. Four recrystallizations raised the melting point to 158.5–159.5°, and after an additional crystallization, the compound melted sharply at 159.5°. The melting point of 2,3-dichloroacetanilide is reported as 157°.[3] *Anal.* Calcd. for $C_8H_7ONCl_2$: N, 6.86. Found: N, 6.88. The acetyl derivative was refluxed with 20% sodium hydroxide solution, and a colorless oil freezing at 21–22° was obtained.

A portion of the solid dichloroaniline was converted to the acetyl derivative. After one crystallization from benzene, the white prisms melted at 125.5°. The melting point of 3,4-dichloroacetanilide has been reported as 120.5°.[8]

Summary

It has been shown that when *o*-dichlorobenzene is nitrated, a small amount of 2,3-dichloronitrobenzene is formed along with a much larger amount of 3,4-dichloronitrobenzene.

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(7) Hodgson and Kershaw, *J. Chem. Soc.*, 2922 (1929).

(8) Beilstein and Kurbatow, *Ann.*, **196**, 217 (1879).