

**ON
CHLORIMIDOQUINONES. A
DISSERTATION,
DEPARTMENT OF CHEMISTRY**

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On chlorimidoquinones. A dissertation, department of chemistry by Lemuel Charles Raiford

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LEMUEL CHARLES RAIFORD

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On Chlorimidoquinones.

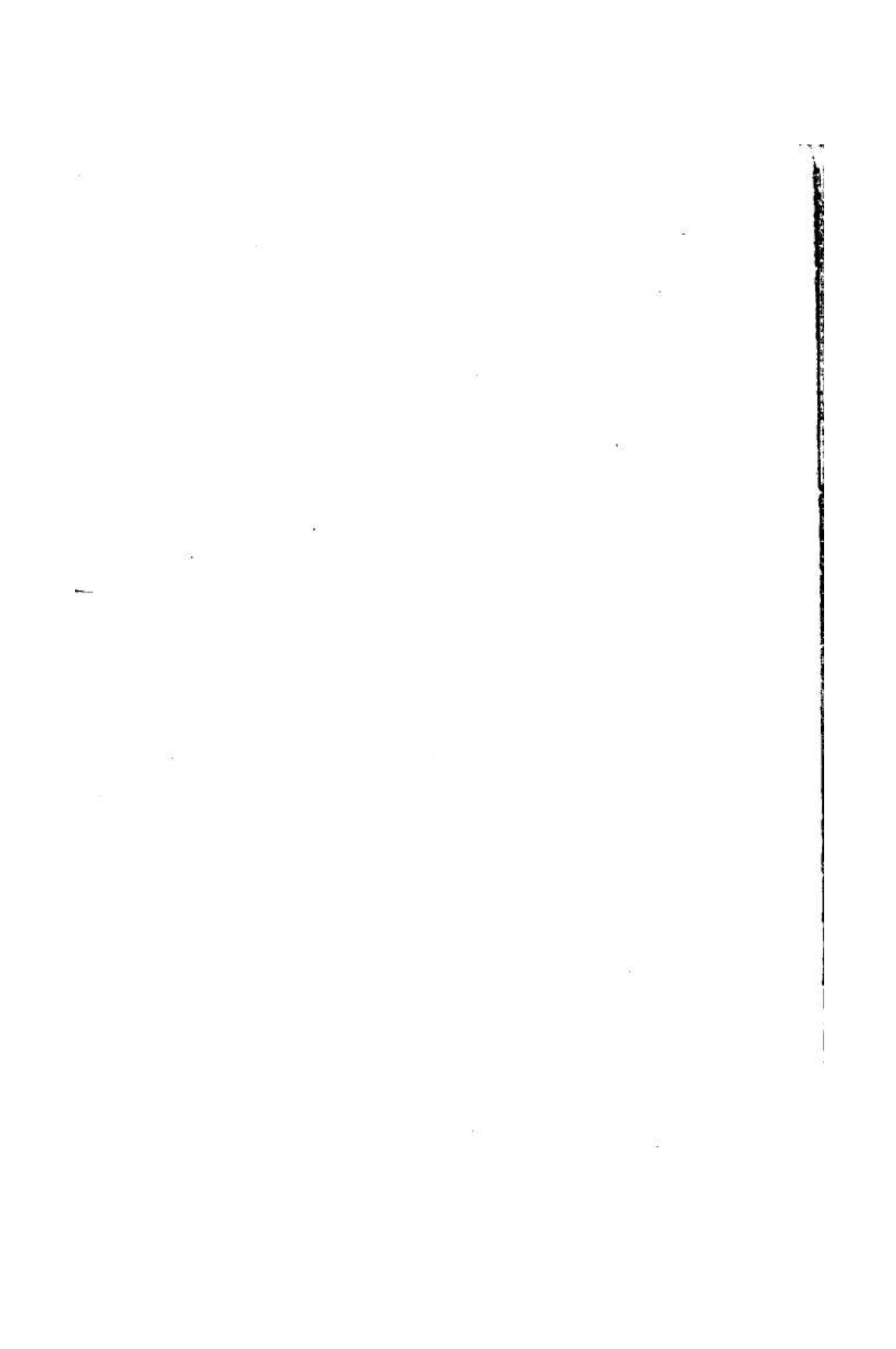
A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE
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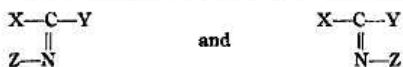
By LEMUEL CHARLES RAIFORD.

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On Chlorimidoquinones.

In 1890 Hantzsch and Werner¹ formulated the theory that the isomerism of nitrogen compounds of the same composition and structure which contain a doubly bound nitrogen atom is of the same nature as the stereoisomeric ethylene derivatives, like maleic and fumaric acids. In accordance with the theory we should have the two configurations



The objections of Victor Meyer² that the differences between the isomeric benziloximes and dioximes might depend on peculiarities of the hydroxylamine molecule were met by Hantzsch³ by the preparation of stereoisomeric phenylhydrazones of anisylphenylketone; but he was unable to extend⁴ the proof beyond these two closely related groups of compounds, the oximes and the hydrazones, his efforts to prepare stereoisomers in which Z in the above formula is represented by such simple radicals as CH₃, C₂H₅, etc., being un-

¹ Ber. d. chem. Ges., 23, 11 and 1243 (1890).

² *Ibid.*, 18, 503 (1883); 21, 784, 3510 (1888).

³ *Ibid.*, 24, 3525 (1891).

⁴ Hantzsch: "Stereochemie" p. 141.

successful. The first representatives of such stereoisomers, other than oximes and hydrazones, were prepared in 1903 by Stieglitz and Earle¹ in the form of a pair of stereoisomeric chlorimido esters in which *Z* in the configuration given is represented by a single chlorine atom. Stieglitz and Hale² prepared a second pair of stereoisomers in 1904, and Hilpert,³ working with Stieglitz in 1907, added five pairs of such compounds to the list. The type is now characterized on a broad and firm basis.⁴

In order to investigate the question of the occurrence of stereoisomeric chlorimides in classes of compounds other than the acid esters, Professor Stieglitz suggested to me to determine whether stereoisomerism can be observed in the case of chlorimidoquinones, comparable with that of the quinone oximes, discussed and investigated by Kehrman.⁵ Although six chlorimidoquinones whose structure would admit of the occurrence of such stereoisomerism were prepared and studied, and though the structure was varied to cover all the possible types, instances of stereoisomerism were not observed, not even in the case of the chlorimide of 2-chlor-5-methylquinone, whose oxime, according to Kehrman,⁶ has the most favorable structure for the occurrence and persistence of this form of stereoisomerism. Stieglitz and Hale found that the labile form of stereoisomeric chlorimidonitrobenzoates is very readily converted into the stable form by the action of chlorine and Hilpert confirmed this observation for the chlorimido esters which he studied. Whether the failure to obtain stereoisomeric chlorimidoquinones is due to the fact that chlorine was present in the solution in which the chlorimides were prepared, and that the method of preparation⁷ necessarily involved a much greater time of contact of the reagents with the material than in the case of the preparation of the chlor-

¹ Am. Chem. J., **26**, 399 (1903); **40**, 37 (1908).

² Unpublished reports.

³ Am. Chem. J., **40**, 150 (1908).

⁴ Stereoisomeric chlorimido ketones have recently been prepared by Stieglitz and Peterson.

⁵ Ann. Chem. (Liebig), **278**, 27 (1894); **303**, 1 (1898).

⁶ *Loc. cit.*

⁷ The oxidation of *p*-aminophenols with hypochlorous acid in acid solution.

imido esters, or whether one of the two possible forms is so much the more stable that it is obtained exclusively, it is impossible, of course, to say. It is quite a common experience that cases of stereoisomerism theoretically possible are not readily realizable by our preparation methods.

In the study of the chlorimidoquinones for this work a number of interesting new observations were made on compounds of the phenol and quinone series, and, in particular, some incorrect statements and uncertain points given in the literature on the preparation and structure of such compounds were noted and corrected. All our conclusions were carefully verified by experimental work. In the following paper the most interesting of the observations made are reported.

1. 4-Chlorimido-2-bromquinone

The starting point in the preparation of this compound was 4-nitrophenol, which was first brominated according to the method of Brunk¹ and Körner.² The resulting brom compound was purified by crystallization of its barium salt, from which, by subsequent treatment with hydrochloric acid, the free phenol was obtained. The latter was finally crystallized from water, from which it separated out in colorless needles that melt at 112°.³ It was further identified by the preparation of its reduction products, the corresponding amine and its hydrochloride.

Hydrochloride of 2-Brom-4-aminophenol.—2-Brom-4-nitrophenol was dissolved in the smallest possible quantity of hot alcohol (1 gram to 1 cc.) and to the hot solution was added one-fourth more than the calculated amount of stannous chloride, dissolved in concentrated hydrochloric acid (1 gram to 1 cc.). During this time the flask was shaken and the mixture kept hot in order to prevent the immediate separation of crystals. Next, one volume of concentrated hydrochloric acid was added and the solution set aside to cool. Crystals of the amino hydrochloride soon separated

¹ Z. Chem., 1887, 204.

² *Ibid.*, 1888, 323.

³ The statement of Brunk that 2-brom-4-nitrophenol melts at 102° is probably a misprint. Meldola and Streetfield (J. Chem. Soc., 73, 681 (1898)) prepared this compound by nitrating *o*-bromphenol, and they found 112° as the melting point.

out. These were filtered off and recrystallized as follows: The crude material was dissolved in warm water and the solution filtered through paper, after which one volume of concentrated hydrochloric acid was added to the filtrate. Upon standing, slightly yellowish crystals of the amino hydrochloride, free from tin compounds, were deposited.

The hydrochloride thus obtained is readily soluble in water containing a trace of acid, in alcohol, and in a solution of sodium hydroxide. When heated to 225° the compound begins to blacken, but does not melt. A sample dried *in vacuo* over potassium hydroxide for 72 hours was analyzed for halogen and gave the following results:

0.2913 gram substance gave 0.4311 gram AgHal.

	Calculated for $C_6H_7ONClBr$	Found
Halogen	51.42	51.56

2-Brom-4-aminophenol.—The free amine was easily obtained by treatment of a water solution of the hydrochloride described above with ammonium carbonate solution. The precipitated amine was filtered off at once, and dried on a clay plate. In this condition it melted at 164° and was very nearly pure. The compound is soluble in alcohol, chloroform, ether, and a solution of sodium hydroxide, but much less soluble in benzene. It is best crystallized from the last-named liquid, from which it separates in needles having a faintly brownish color and melting at 165° . Analysis for bromine gave the following figures:

0.2450 gram substance gave 0.2474 gram AgBr.

	Calculated for C_6H_6ONBr	Found
Br	42.54	42.97

4-Chlorimido-2-bromquinone, $O : C_6H_4Br : NCl$.—A portion of the hydrochloride of 2-brom-4-aminophenol, weighing 5 grams, was dissolved in 75 cc. of water to which a trace of hydrochloric acid had been added, and the resulting solution cooled to about 0° . This liquid was then allowed to flow slowly from a tap funnel into acidulated (hydrochloric acid) solu-

tion of sodium hypochlorite¹ which had been cooled to 0°, and in which pieces of ice were floating. The flask containing the hypochlorite was kept surrounded by a mixture of ice and water, and was shaken continuously while the amino hydrochloride was being added. A yellow solid, having the characteristic odor of a chlorimidoquinone, was promptly precipitated, and after standing for a few minutes was filtered off and washed several times with cold water.

When dried on a clay plate the chlorimide began to darken after 24 hours, a change that goes on more rapidly as the temperature rises. The crude product did not have a characteristic melting point, but decomposed suddenly, after softening, when heated above 60°. The compound is soluble in alcohol, ether and chloroform, but less readily so in ligroin. It is best crystallized from the low-boiling (40°-60°) fraction of the latter liquid, because the heat required to saturate the higher boiling fractions to a sufficient degree to give a satisfactory yield of crystals will decompose the chlorimide. Attempts to fractionate² the compound gave negative results. The purest product obtainable decomposed, without melting, when heated to 60°, as already indicated.

For analysis, the method employed by Stieglitz and Earle³ in the determination of halogen in their chlorimido esters, consisting in the liberation of iodine from hydrogen iodide, was first tried; but concordant results could not be obtained, because not only the chlorimide group but the quinone ring, too, oxidizes the hydrogen iodide. Halogen was determined, in this and all other compounds described in this paper, by the Carius method.

0.3460 gram substance gave 0.5233 gram AgHal.

	Calculated for C ₁₂ H ₉ ONClBr	Found
Halogen	52.36	52.71

II. 4-Chlorimido-2-chlor-6-bromquinone

This chlorimidoquinone was prepared in accordance with

¹ Graebe: Ber. d. chem. Ges., 35, 43 and 2753 (1902).

² Hilpert: Loc. cit.

³ Am. Chem. J., 30, 402 (1903).