Methods are given for the preparation of α-bromonaphthalene, α-naphthoic acid, di-α-naphthylketone and di-α-naphthylcarbinol.

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THE POLARITY OF THE CARBON-HALOGEN BOND

I. DEVELOPMENT OF A QUANTITATIVE METHOD FOR THE DETERMINATION OF RELATIVE RATES FOR THE ACID HYDROLYSIS OF POSITIVE HALOGENS

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Recently Nicolet and collaborators[1] have studied the different degrees of polarity that are shown by halogens attached to carbon in the aromatic series. The present investigation was undertaken with a two-fold purpose: to develop a more quantitative method for the determination of the rate of removal of positive halogens and to determine to what extent halogens in halogen naphthols show different degrees of polarity. The reaction which Nicolet has found useful as a preliminary test for positive halogens, that of the action of stannous chloride in acid solution on the organic halide, is one which has been applied in a qualitative way to the removal of halogen atoms from halogen amines and phenols[2] and to a less extent to the removal of bromine from bromo-β-naphthols and bromo-β-naphthylamines.[3] The method described below differs from those referred to in that the hydrolysis was carried out in an oxygen-free atmosphere, and that the amount of halogen removed was determined by titration of the excess stannous chloride solution with standard iodine solution.[4] It is thus considerably more convenient and rapid.

Method of Hydrolysis

The standard solution of stannous chloride was prepared by dissolving 60 g. of $SnCl_2 \cdot 2H_2O$ in 1000 g. of hydrochloric acid (37%) and the solution was diluted to 3700 cc. with 95% alcohol (the alcohol was added to make the organic halides soluble). This solution was stored in an atmosphere of hydrogen to prevent oxidation; after twenty-four hours the oxygen in the gases above the solution had disappeared and the stannous chloride maintained its strength unaltered during the time required to make the hydrolyses. The apparatus used for the storage of the solution and for the titration was

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[1] (a) Nicolet, THIS JOURNAL, **43**, 2081 (1921); (b) Nicolet and Sampey, *ibid.*, **49**, 1796 (1927); (c) Nicolet and Ray, *ibid.*, **49**, 1801 (1927); (d) Nicolet and Sandin, *ibid.*, **49**, 1806 (1927); (e) Nicolet, *ibid.*, **49**, 1810 (1927).

[2] Burton and Kenner, *J. Chem. Soc.*, **121**, 675 (1922).

[3] (a) Franzen, *J. prakt. Chem.*, **101**, 58 (1920); (b) **103**, 352 (1922); (c) Fries, *Ann.*, **334**, 342 (1904).

[4] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York City, **1919**, p. 698.

similar to that described by Thornton.[5] The standardization of the stannous chloride solution against a 0.1 *N* solution of iodine was done in an atmosphere of nitrogen.

Briefly, the procedure as finally adopted in the method of hydrolysis was as follows. A weighed sample of the organic halide was placed in an Erlenmeyer flask and, after sweeping out the air with a stream of nitrogen, an excess of the stannous chloride solution was introduced. The flask was placed under a reflux condenser in a thermostat heated to 70° and the temperature of the thermostat was kept constant within ±0.01°. A layer of oil over the surface of the water in the thermostat prevented evaporation and made it easier to maintain a constant temperature. The solution was kept in an atmosphere of nitrogen at all times and at the end of a definite length of time the flask was removed from the thermostat to a pail of water where it was cooled for one minute. The amount of halogen removed from the organic halide by the hydrolysis was determined by titration of the excess of stannous chloride with 0.1 *N* iodine solution. The calculation of the amount of halogen removed was based on the number of cubic centimeters of stannous chloride solution consumed in the removal of all of the bromine and iodine from the halogen phenols and naphthols; as was expected, it was found that one mole of stannous chloride was required in every case for the complete removal of each atom of bromine or iodine; for example, exactly half a gram of 1-bromo-2-hydroxynaphthalene, when heated until all the bromine was removed, oxidized as much stannous chloride solution as did 43.80 cc. of 0.1 *N* iodine. This would be equivalent to the presence of 0.3504 g. of molecular bromine, but there are only 0.1750 g. of bromine in the 0.5 g. sample used. This is further evidence that the halogen when removed is positive.[1a]

Several sources of error in the hydrolysis were examined. It was possible that some iodine substitution might have taken place during the titration with the standard iodine solution; no evidence of interaction of the iodine solution with the halogenated or unhalogenated phenols and naphthols was found when titrations were made. Care was taken to recrystallize several times all compounds used in order to free them from adsorbed halides and other impurities. A considerable error in the rate measurement was introduced by the method of heating the stannous chloride solution from room temperature to 70° after the introduction of the organic halide. Except in the cases of those compounds which lost their halogen rapidly, this error was found to be less than that caused by the entrance of atmospheric oxygen when attempts were made to introduce the halide into the stannous chloride solution after it had reached a constant temperature of 70°. It was not possible to remove portions of the solution from time to time for titrations without greatly increasing the difficulty of manipulation in keeping out the oxygen of the atmosphere. Efforts were made to keep the error introduced by the method of heating constant by the use of the same volume of stannous chloride solution in all the hydrolyses; in some cases this was not possible because of the insolubility of several of the compounds.[6]

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[5] Thornton, THIS JOURNAL, **43**, 91 (1921).

[6] In the next article it will be seen that the errors in the method of hydrolysis were further reduced by (a) heating the compounds which lose the halogens rapidly in a solution of lower hydrogen-ion concentration, (b) increasing the amount of alcohol for the highly insoluble compounds and (c) introducing the organic halide after the stannous chloride solution has reached 70°.

The results of the hydrolyses are summarized in the following table.

TABLE I

ACID HYDROLYSIS OF HALOGEN PHENOLS AND HALOGEN NAPHTHOLS

Compounds	Weight g.	Time of hydrolysis, min.	Cc. of $SnCl_2$ soln. introduced	Cc. of 0.1 *N* iodine consumed in titrations	G. of halogen removed	Total halogen removed, %
1-Iodo-2-hydroxynaphthalene	0.5	5	20.00	11.20	0.1034	44.01
	.5	5	20.00	11.05	.1043	44.41
1-Bromo-2-hydroxynaphthalene	.5	15	20.00	21.00	.0260	14.85
	.5	15	20.00	21.20	.0252	14.40
1-Bromo-2-methoxynaphthalene	.3	90	20.00	26.90	.0024	2.37
1,6-Dibromo-2-hydroxynaphthalene	.5	60	40.00	47.00	.0320	12.12
	.5	60	40.00	46.80	.0328	12.42
2,4-Dibromo-1-hydroxynaphthalene	.5	60	40.00	49.90	.0204	7.72
	.5	60	40.00	50.10	.0196	7.42
1,4-Dibromo-2,3-dihydroxynaphthalene	.2	10	40.00	44.60	.0416	41.60
	.2	10	40.00	44.60	.0416	41.60
1,4,6,7-Tetrabromo-2,3-dihydroxynaphthalene	.1	10	40.00	50.50	.0180	26.89
	.1	10	40.00	50.58	.0176	26.38
4,6-Di-iodoresorcinol	.3	5	20.00	11.10	.1040	49.55
	.3	5	20.00	11.30	.1028	48.94
4,6-Dibromoresorcinol	.2	60	20.00	25.20	.0092	7.73
	.2	60	20.00	25.00	.0100	8.40
2,5-Dibromohydroquinone	.3	90	20.00	27.45	...	...
4,5-Dibromocatechol	.3	60	20.00	27.40	...	...
1,2-Dimethoxy-4,5-di-iodobenzene	.3	90	20.00	26.80	.0044	2.33
3,4,5,6-Tetrabromocatechol	.3	60	20.00	27.50	...	...
2,4-Dibromophenol	.3	60	20.00	27.45	...	...

Discussion of Table I

The most striking result shown in Table I is the remarkable reactivity of the halogen atoms in halogen naphthols. On the basis of the Lewis definition of a bond, the significance of the fact is that the bonding pair of electrons in the carbon-halogen bond of halogen naphthols is drawn further from the halogen nucleus and nearer the carbon than is the case with halogen phenols. Identification of the organic products of the reaction showed, however, that halogens in the 6 and 7 positions did not respond to the test for positive halogens, for they were not removed even on prolonged heating. 6-Bromo-2-hydroxynaphthalene was isolated after the reduction of the 1,6-dibromo-2-hydroxynaphthalene had gone as far as it would under the experimental conditions, and 6,7-dibromo-2,3-dihydroxynaphthalene was identified after the reduction of the tetra-bromo derivative. These results lend further support to the explanation[1e] for the mechanism of the removal of positive halogens through quinone formation, for Vesely and Jokes[7] have shown that of the six naphthoqui-

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[7] Vesely and Jokes, *Bull. soc. chim.*, **33**, 955(1923).

nones of Willstätter, the two which are the most readily formed possess an intact benzene nucleus.

Preparation of Compounds

In the preparation of the compounds studied in Table I it was found necessary in several cases to modify the procedure as described in the literature. Attempts to prepare 2,3-dihydroxynaphthalene from "R-salt" by the method of Friedländer[8] were so unsuccessful that considerable time was consumed in the development of a satisfactory method of preparation. When the reaction was carried out as described the chief product was β-naphthol. This indicated that the alkali fusion of the "R-salt" had failed to replace the 3-sulfonic acid group by an hydroxyl group and that the subsequent bomb reaction had removed both the 3- and 6-sulfonic acid groups. An increase in the temperature of the fusion resulted in considerable charring; varying the amount of water added to the fusion failed to produce the desired result. A potassium hydroxide fusion was substituted for the sodium hydroxide fusion and the temperature was raised to 300°; no water was added. When this fusion was acidified, much sulfur dioxide was liberated, indicating the removal of a sulfonic acid group. The bomb reaction proved that the 3-sulfonic acid group had been replaced with the hydroxyl group. The conditions under which the bombs were heated were also changed, for after more than twenty trials in which the temperature, the concentration of the sulfuric acid and the time of heating were varied, it was found that there was less charring when the strength of the acid was reduced from one-to-three to a concentration of one-to-four. This made it necessary to increase the time of heating to fourteen hours at 165–175°. The 2,3-dihydroxynaphthalene was brominated according to Fries.[3c] Attempts to prepare an iodo-derivative by direct iodination of the 2,3-dihydroxynaphthalene resulted in the formation of a dark, amorphous mass with the disappearance of little of the iodine.

Armstrong[9] mentions the fact that 1,6-dibromo-2-hydroxynaphthalene can be prepared by bromination of β-naphthol in acetic acid; no details are given. The following procedure gave a yield of 90%: 25 g. of β-naphthol was dissolved in 150 cc. of acetic acid; to the solution was added slowly two moles (55.5 g.) of bromine in 35 cc. of acetic acid. The solution was heated almost to boiling for twenty minutes in order to expel the hydrogen bromide; it was cooled and water was added slowly to precipitate the dibromonaphthol. The solution was filtered and the product dried and recrystallized from hot alcohol.

In following out the procedure of Jackson[10] for the preparation of tetrabromocatechol so much difficulty was experienced in keeping the products in solution during the bromination that a solvent other than chloroform was sought. When the bromination was made in acetic acid, there was no precipitation of the partially brominated products.

Summary

1. A quantitative method is described for the determination of relative rates of acid hydrolysis of positive halogens.
2. The test for positive halogens has been extended to halogen naphthols.
3. Improved methods of preparation are given for several halogen phenols and naphthols.

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[8] Friedländer and Zakrzewski, *Ber.*, **27**, 761 (1894).

[9] Armstrong, *Ber.*, (2) **24**, 705 (1891).

[10] Jackson, *Am. Chem. Jour.*, **26**, 31 (1901).