TABLE III

FREQUENCY NUMBERS OF BANDS IN ALCOHOLIC ALKALINE SOLUTIONS OF HYDROXYHYDROQUINOLPHTHALEIN

Ratio to KOH							
1:2	1975	2039	2165	2330	3018	3657	4125
1:4	1965				2911	3612	4093
1:23	1962				2950	3600	4092
1:87	1911				2995	3558	3987
1:100	1855				2900	3450	3950

Summary

1. Data and curves are presented on the absorption spectra of various phthalein derivatives of pyrogallol, hydroxyhydroquinol and phloroglucinol. Correlations are drawn with data previously obtained for phthaleins of the mono- and dihydroxybenzenes.

2. The effect on the chemical properties and absorption spectra of the phthaleins, due to the introduction of hydroxyl groups, is discussed.

3. Gallein, which is colored in both the solid state and in neutral solution, is shown to be primarily lactoid in structure, but probably in equilibrium with a small amount of the quinoid modification.

4. The unusual behavior of hydroxyhydroquinolphthalein in weakly alkaline solutions both as regards its absorption and fluorescence is described and a possible explanation is advanced.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

THE PREPARATION OF AMINONAPHTHOLS

BY WILSON F. BROWN, JOHN C. HEBDEN AND JAMES R. WITHROW

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1-Amino-7-naphthol and 1-amino-6-naphthol were needed for work in progress. An investigation was therefore conducted for the preparation of these compounds by caustic fusion of the respective α-naphthylaminesulfonic acids.

Among other things, the results indicated that 1-amino-6-naphthol could be prepared from α-naphthylamine-6-sulfonic acid by caustic soda fusion. The melting point of the picrate of 1-amino-6-naphthol was not the same as that given in the literature. Further, 1-amino-7-naphthol was prepared in good yield (average of 58%) by caustic soda fusion of α-naphthylamine-7-sulfonic acid.

Literature

The Cassella Company[1] gave an example of the preparation of 1-amino-7-naphthol by caustic fusion from α-naphthylamine-7-sulfonic acid. In

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[1] German patent 69,458; *Friedländer*, **3**, 476 (1890).

the first part an autoclave is used and in the second part an open kettle. They do not mention the 1-amino-6-naphthol.

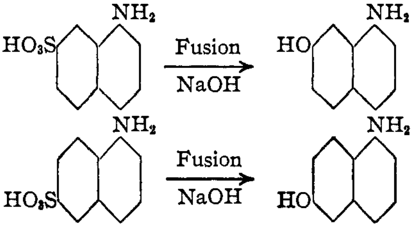
Kehrmann and Engelke[2] described the purification of crude 1-amino-7-naphthol and gave the melting point of the purified product as 205–207°. They also described the preparation of the mono-acetyl compound of 1-amino-7-naphthol.

1-Amino-6-naphthol was prepared by nitration of naphthalene, according to Friedländer,[3] and subsequent partial reduction.

Franz Sachs[4] gave a method for the production of 1-amino-6-naphthol in his patent on the preparation of aminonaphthols by the action of sodamide on naphthol sulfonic acids. He stated that the melting point of the 1-amino-6-naphthol was 185°.

Nowhere in the literature was there found a process for the preparation of 1-amino-6-naphthol by fusion of α-naphthylamine-6-sulfonic acid with caustic soda. A method was devised, therefore, based on the illustration of the Cassella patent for the 1,7-compound.

The reactions involved in the preparation of the 1-amino-7-naphthol and 1-amino-6-naphthol were anticipated to be the following



Experimental

Preparation of Aminonaphthols.—The Cassella illustration for the 1,7-compound was investigated but failed to work. When the temperature of the fusion was raised from 265 to 305°, however, good results were obtained. The method finally adopted consisted in melting caustic soda, with the addition of a small quantity of water, and then adding the α-naphthylaminesulfonic acid gradually to avoid foaming. When all of the α-naphthylaminesulfonic acid was in, the melt was heated to 265–275° for one hour, then to 305° for five minutes and finally cooled to 200°. The aminonaphthol was isolated by diluting the melt with water, neutralizing with hydrochloric acid, boiling, filtering and adding soda solution until no more precipitation could be obtained.

Preparation of 1-Amino-6-Naphthol.—In preparing to make the 1-amino-6-naphthol the method selected was that given by the Cassella Company[1] for making 1-amino-7-naphthol. This method was followed as to proportions but here also it was found necessary to heat to approximately 305° in order to complete the reaction when an open pot was used. The isolation of the final product presented no difficulties. The yield of 1-amino-6-naphthol was consistently good and even better than the 1,7. There was some loss of aminonaphthol, however, by volatilization.

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[2] Kehrmann and Engelke, *Ber.*, **42**, 351 (1909).

[3] Friedländer, *Ber.*, **25**, 2079 (1892); **29**, 1979 (1896); **39**, 3016 (1906).

[4] German patent 173,522; *Friedländer*, **8**, 172 (1905–1907).

Acetylation of 1-Amino-6-naphthol.—The method of Kehrmann and Engelke[5] for the preparation of the acetyl compound of 1-amino-7-naphthol was followed in attempting to prepare the acetyl compound of 1-amino-6-naphthol. One part of 1-amino-6-naphthol was mixed with three parts of acetic anhydride, the mixture becoming slightly warm. It was warmed on the hot-plate for a few minutes, filtered and the mass washed with water. The residue was extracted with boiling dilute ethyl alcohol (1:1) and filtered. The filtrate was allowed to cool and the precipitate that came out was filtered and dried in air. On testing, the substance melted gradually, starting at 195° and continuing up to 220°. The mono-acetyl and di-acetyl compounds are said to melt at 218 and 186°, respectively.[6]

TABLE I

1-AMINO-7-NAPHTHOL

Experiment no.	27	28	32	91	92	93	94	95
Sulfonic acid used, g.	20	40	40	252	252	252	252	252
Yield of base, g.	7.3	5.0	12.0	71.0	42.0	58.0	144.0	76.0
Yield of hydrochloride, g.	..	..	..	38.0	95.0	78.0	...	...
Yield calcd. as base, g.	..	..	..	101.9	119.3	121.4	...	...
Yield based on sulfonic, %	51.2	17.5	42.0	56.7	66.3	67.6	80.1	42.3

Variation in yield due mainly to volatilization of aminonaphthol from open pot.

TABLE II

1-AMINO-6-NAPHTHOL

Experiment no.	29	30	33	67	68	69	70	96	97
Sulfonic acid used, g.	40	40	40	252	252	252	252	252	252
Yield of base, g.	24.4	20.2	22.7	151.0	58.0	96.0	42.0	105.0	53.0
Yield of hydrochloride, g.	..	..	..	...	...	...	...	57.0	116.0
Yield calcd. as base, g.	..	..	..	...	...	...	...	151.4	147.4
Yield based on sulfonic, g.	85.6	70.8	79.6	84.0	32.3	53.4	23.4	84.2	82.0

Variation in yield due mainly to volatilization of aminonaphthol from open pot.

Purification of 1-Amino-6-Naphthol.—The 1-amino-6-naphthol was purified in two ways. (A) The 1-amino-6-naphthol was extracted with 7.5% hydrochloric acid, filtered and ammonium hydroxide added to the filtrate just to alkalinity. Three crops of precipitates were obtained, the third of which was crystalline and gave a melting point of 186.8°, corrected. (B) The 1-amino-6-naphthol was purified by repeated recrystallization from boiling water. The melting point of the purified product was found to be 190.6° corrected. As previously mentioned, Sachs gave the melting point as 185° but did not state whether it was corrected or not.

Identification of 1-Amino-6-Naphthol.—The picrate of 1-amino-6-naphthol was prepared several times and a melting point of 170°, corrected, obtained. This is not in accord with the value given by Sachs,[4] who states that the picrate of 5,2-amino-naphthol (1-amino-6-naphthol) melts at 185° (as he states for the parent substance also). The hydrochloride was prepared by adding an excess of hydrochloric acid to the melt during neutralization and cooling the solution to room temperature. The 1-amino-6-naphthol hydrochloride separated in glistening, dark red crystals, whereas the hydrochloride of 1-amino-7-naphthol is gray. References to these two hydrochlorides are not found in the literature.

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[5] Ref. 2, p. 351.

[6] German patent 173,522; *Friedländer*, **8**, 172 (1905–1907).

Conclusions

1. The 1-amino-7-naphthol was prepared in good yield and of good quality from α-naphthylamine-7-sulfonic acid by caustic soda fusion, at much higher temperatures than were given by Cassella and was isolated both as the base and as the hydrochloride.
2. The 1-amino-6-naphthol was prepared in good yield and of good quality from α-naphthylamine-6-sulfonic acid, by caustic soda fusion, and was isolated both as the base and as the hydrochloride.
3. Acetylation of the 1-amino-6-naphthol was unsuccessful.
4. The melting point of the picrate of 1-amino-6-naphthol was found to be 170°, corrected, as against 185° as given by Sachs.

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[CONTRIBUTION FROM THE ROCKEFELLER PHYSICAL AND BAKER CHEMICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF SOME HALOGENATED FLUORESCEINS[1]

BY R. C. GIBBS AND C. V. SHAPIRO[2]

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In previous investigations on the absorption spectra of resorcinolbenzein,[3a] fluorescein[3b] and sulfonefluorescein[3c] in various solvents, the effect of introducing acid groups, carboxyl and sulfoxyl, into the benzein was studied. It was shown that in the presence of the highly dissociated sulfonic acid group an inner salt was formed with the basic, quinoid oxygen atom. Dibromosulfonefluorescein[3c] also exhibited the inner salt configuration, but the bands in its absorption spectra were shifted toward longer wave lengths relative to those of sulfonefluorescein, as the result of the addition of two bromine atoms.

Data are now presented for di- and tetrabromofluorescein (eosin), in which the bromine atoms are attached to the phenol residues, and for tetrachlorofluorescein, in which the chlorine replaces the hydrogen atoms of the phthalic acid residue. It is known from the work of B. Cohen[4] on indicators of the sulfonephthalein class that halogen substitution in the phenolic residues results in an increase in the apparent dissociation constant of the phenolic hydrions. Although his data on the halogen derivatives give

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[1] The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–1928.

[3] (a) Orndorff, Gibbs and Shapiro, THIS JOURNAL, **48**, 1327 (1926); (b) *ibid.*, **50**, 819 (1928); (c) Gibbs and Shapiro, *ibid.*, **50**, 1755 (1928).

[4] B. Cohen, *Public Health Reports*, **41**, 3053 (1926).