diately but decolorized slowly as the flask was warmed up after the second pumping. (A similar solution took about 4 to 6 hours to decolorize before pumping and filling with nitrogen.) After four cycles of cooling, pumping, warming and pressuring with nitrogen, the flask was warmed to room temperature and the two solutions mixed rapidly. The resulting solution decolorized in *ca.* 15 seconds. The original concentrations in this experiment were 0.0294 M for iodine and 0.0547 M for mercurial. Another 5.0-ml. aliquot of the iodine solution was added to the above mixture (to give a slight excess of iodine) and the degassing procedure repeated. After 12 hours, the entire solution was poured into 200 ml. of 0.1 N sodium thiosulfate. The white precipitate which separated was filtered on a weighed, sintered glass crucible and dried to constant weight over sodium hydroxide pellets to yield 0.192 g. (88.4%) of 4-iodocamphane, m.p. 128°, mixed m.p. with authentic 4-iodocamphane, 127.8–128.6°.

The method for measuring the rate of this reaction was exactly that described by Keller,[10] except that the titration was carried out in water instead of methanol and starch was used as an indicator.

Reaction of 4-Camphylmercuric Iodide with Iodine and Excess Iodide.—The method of rate measurement in this reaction was similar to that described by Keller.[10] The solvent composition and iodide concentration were changed, and the titration was carried out by draining the aliquot into approximately 40 ml. of water containing a known amount of sodium thiosulfate and back-titrating with iodine, using starch as described by Kolthoff and Sandell.[21]

For the rate measurements at low iodine concentration, the end-point in the thiosulfate titration of the iodine was determined by the electrometric method developed by Foulk and Bawden[22] and modified by Boyer.[23] This titration was not affected by the presence of mercuric iodide, 4-camphylmercuric iodide or dioxane.

The product of the action of iodine and lithium iodide on 4-camphylmercuric iodide was obtained from a reaction solution after 15 half-lives by pouring the solution into excess sodium thiosulfate, and isolating the product in exactly the same way as for the radical reaction. The 4-iodocamphane, m.p. 127.7–128.2°, mixed m.p. with pure 4-iodocamphane, 127.8–128.6°, was obtained in 70% yield.

Reaction of Di-4-camphylmercury with Acetic Acid.—The method of measuring the rate of acetolysis of di-4-camphylmercury both with and without added perchloric acid was identical with that employed for dineophylmercury.[7b] The titration of acetolysis reaction mixtures containing dicamphylmercury with hydrogen bromide in glacial acetic acid gave end-points which were stable for only *ca.* two seconds even in the presence of hydroquinone.

After the 0.0106 M dicamphylmercury solution was held for 10 half-lives, 40 ml. was added to a solution of 5 g. of lithium chloride in 10 ml. of water, and the resulting solution was diluted to 125 ml. with water. The white solid was filtered off, dried over sodium hydroxide pellets, and recrystallized from about 5 ml. of an acetone–petroleum ether mixture at −80°. The large crystals obtained (55.4 mg., 37%) melted at 254–255.5°.

Reaction of Di-4-camphylmercury with Mercuric Chloride.—J. T. Baker analyzed mercuric chloride (0.0816 g., 0.000301 mole), dried at 110° for 12 hours, and 0.1432 g. (0.000314 mole) of di-4-camphylmercury were dissolved in 3.1 ml. of ether. After *ca.* 7 hours at room temperature, large crystals were observed. The mixture was allowed to stand for 48 hours and cooled to 0°. The crystals were filtered off and air-dried to yield 0.141 g. of material, m.p. 255–256°, mixed m.p. with authentic 4-camphylmercuric chloride, 254.5–256.5°. An additional 0.053 g., m.p. 255–256°, was obtained by evaporating the filtrate to dryness and recrystallizing the solid from petroleum ether–ethyl acetate. The total yield was 0.197 g. (87%).

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[21] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 620.

[22] C. W. Foulk and A. T. Bawden, THIS JOURNAL, **48**, 2045 (1926).

[23] M. H. Boyer, Thesis, U. C. L. A., 1951.

[CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON]

A Reinvestigation of the Role of Phenylsulfamic Acid in the Formation of Aminobenzenesulfonic Acids

BY GABRIELLO ILLUMINATI[1]

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The tendency of phenylsulfamic acid to rearrange to anilinesulfonic acids has been investigated in connection with a debated problem concerning the mechanism of sulfonation of aniline. The main results we have established can be summarized as follows: (1) Bamberger and Kunz's rearrangement of phenylsulfamic acid to orthanilic acid in cold glacial acetic acid has been disproved with the aid of a large number of experiments under varying conditions. (2) Rearrangement can be performed in dry dioxane at 100° and the product of the reaction was found to consist essentially of sulfanilic acid. (3) Phenylsulfamic acid proved to be a side-product, not an intermediate, in the reaction of β-phenylhydroxylamine with sulfur dioxide leading to orthanilic acid. These results show that phenylsulfamic acid has no tendency to rearrange to orthanilic acid under a variety of experimental conditions and remove the only piece of evidence for Bamberger's postulation that orthanilic acid is an intermediate in the course of sulfonation of aniline.

Bamberger's early theory on the mechanism of sulfonation of aniline with sulfuric acid involves an *ortho*-rearrangement of the supposedly intermediate phenylsulfamic acid, followed by rearrangement of the orthanilic acid thus formed to sulfanilic acid at a higher temperature.[2–5] Evidence for the tendency of phenylsulfamic acid to rearrange to orthanilic acid in cold glacial acetic acid was claimed by Bamberger and Kunz. However, in the course of a discussion on the subject by Hughes and Ingold,[6] from which the present work originated, the reaction appeared never to have been confirmed. Previous reports on the *para*-rearrangement of phenylsulfamic acid have dealt with thermal reactions of the corresponding salts in the solid state.[2,7] Also, the free acid is quite unstable in aqueous acidic media[8] and can be quantitatively cleaved into aniline and sulfuric acid under very mild conditions.[9]

The reaction of β-phenylhydroxylamine with sul-

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[1] On leave from the Department of General Chemistry, University of Rome, Italy.

[2] E. Bamberger and E. Hindermann, *Ber.*, **30**, 654 (1897).

[3] E. Bamberger and J. Kunz, *ibid.*, **30**, 2274 (1897).

[4] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 247.

[5] E. R. Alexander, THIS JOURNAL, **69**, 1599 (1947).

[6] E. D. Hughes and C. K. Ingold, *Quart. Revs.*, **6**, 51 (1952); see also C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 628–631.

[7] A. Seyewets and Bloch, *Bull. soc. chim.*, [4] **1**, 320 (1907).

[8] C. D. Hurd and N. Kharasch, THIS JOURNAL, **69**, 2113 (1947).

[9] W. H. Hunter and M. M. Sprung, *ibid.*, **53**, 1443 (1931).

fur dioxide in ethyl alcohol to give orthanilic acid and phenylsulfamic acid[2,3] has also been considered in support of an *ortho*-rearrangement of phenylsulfamic acid. The object of the present work was to ascertain the tendency of phenylsulfamic acid to rearrange under suitable conditions; thus we have reinvestigated (1) the Bamberger and Kunz reaction and (2) the β-phenylhydroxylamine reaction with sulfur dioxide.

Results

Phenylsulfamic Acid with Non-aqueous Solvents.—In contrast to Bamberger and Kunz's early report, we have been unable to obtain any rearrangement on mixing phenylsulfamic acid with glacial acetic acid, at 0 to 45°, in the presence of amounts of sulfuric acid varying over a wide concentration range. The sulfamic acid was cleaved to a varying extent, depending on acid concentration, time and temperature, by some solvolytic process analogous to the well known hydrolysis by aqueous acidic solutions. No anilinesulfonic acid was detected at the end of any experiment. All attempted rearrangements were quantitatively followed by gravimetric determination of the sulfate ion; this measured only the amount of the unrearranged phenylsulfamic acid, as any product of rearrangement would not be hydrolyzed under the conditions used for the analysis.

When in contact with dry dioxane, which was not likely to promote any solvolysis even at higher temperature, phenylsulfamic acid was found to rearrange to anilinesulfonic acids to the extent of 22%, at 100° in 55 hr. The rearranged product was identified as sulfanilic acid. Although no attempt was made to carry out a complete product analysis, our results show that sulfanilic acid is the main, if not exclusive, product of the reaction. Identical conditions in dioxane proved to be unsuitable to either the sulfonation of aniline or the rearrangement of orthanilic acid to sulfanilic acid.

Role of Phenylsulfamic Acid in the β-Phenylhydroxylamine Reaction with Sulfur Dioxide.—The reaction of β-phenylhydroxylamine with sulfur dioxide to give orthanilic acid in 60% aqueous alcohol was first described by Bretschneider,[10] but independently discovered by Bamberger and Hindermann. Although full experimental details on the conditions of the reaction were not given by either group, the latter authors reported the formation of phenylsulfamic acid as accompanying that of orthanilic acid. We have found that the formation of orthanilic acid is only part of a complex reaction which β-phenylhydroxylamine undergoes with sulfur dioxide in absolute ethyl alcohol, the yield with respect to this product never being higher than 33%. Addition of water decreased the yield, which was 10 to 20% in 60% ethyl alcohol and negligible in water; addition of sulfuric acid had no effect on the formation of orthanilic acid in absolute alcohol. We must note that the orthanilic acid was identified satisfactorily by qualitative procedures (see Experimental Part) but that a complete product analysis was not carried out in the crude orthanilic acid fraction. The nature and composition of the other products seem to depend largely on the solvent. Besides the occurrence of unidentified products, aniline in various amounts was found under all conditions reported in the present work. However, the main result concerning these side-reactions was the identification of small amounts of phenylsulfamic acid from the experiments in 60% ethyl alcohol, thus confirming the report by Bamberger and Hindermann.

Phenylsulfamic acid, however, appeared to result from a side-reaction and not to be an intermediate product in the formation of orthanilic acid, because, starting from phenylsulfamic acid under the same conditions used for the reaction of β-phenylhydroxylamine with sulfur dioxide in 60% alcohol, no orthanilic acid could be isolated. Also, the observed effect of water on the yield of orthanilic acid is inconsistent with an alternative mechanism, proposed by Bamberger and Rising,[11] involving the participation of water in the attack of β-phenylhydroxylamine by sulfur dioxide.

Discussion

Bamberger's hypothesis that the sulfonation of aniline involves orthanilic acid as an intermediate has already been questioned by Suter,[4] because of the absence of any appreciable amount of this compound from the product obtained by the sulfonation of aniline with oleum at 0°. Our unexpected results showing the non-rearrangement of phenylsulfamic acid in acetic acid disprove the only available experimental evidence claimed by Bamberger in support of his view. Such results also show that a rearrangement of the sulfamic acid is indeed possible under conditions not suitable to either the rearrangement of orthanilic acid or the sulfonation of aniline sulfate, but that great care as to the nature of the medium must be taken in drawing any conclusions regarding the course of the reaction in sulfuric acid. Thus, while acetic acid was found unable to effect any rearrangement, dry dioxane allowed some rearrangement to occur at a relatively high temperature (100°). Also, the rearrangement product was essentially sulfanilic acid. Therefore, as far as the mechanism of sulfonation of aniline in sulfuric acid is concerned, *if* any phenylsulfamic acid is formed during the process, sulfanilic acid would be the most likely isomer as a result of migration of the SO_3H group from side-chain to nucleus.

All rearrangements previously reported in the literature have dealt with reactions of the salts of phenylsulfamic acid, even though hydrated,[12] in the solid state and at temperatures quite a bit higher than the reaction herein reported in dioxane. This may indicate that the rearrangement in dioxane occurs under conditions approaching those allowing the free phenylsulfamic acid to exist. A rearrangement under the latter conditions has never been reported; in dioxane, acid–base interaction with the solvent must be taken into account.

The possible scheme proposed by Hughes and Ingold[6] for an *ortho*-migration of the SO_3H group in phenylsulfamic acid is

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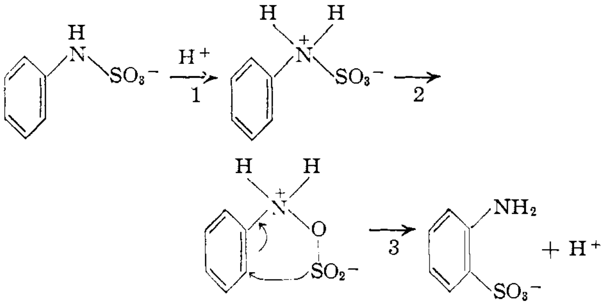
[10] W. Bretschneider, *J. prakt. Chem.*, **55**, 285 (1897).

[11] E. Bamberger and A. Rising, *Ber.*, **34**, 241 (1901).

[12] E. R. Alexander, THIS JOURNAL, **70**, 1274 (1948).



A

Such a scheme involves a sulfitoamine (A) which is also a possible intermediate in the β-phenylhydroxylamine reaction. Phenylsulfamic acid can be supposed to be formed by reversal of step 2. But since no rearrangement was observed starting from phenylsulfamic acid under the conditions suitable for the reaction of the hydroxylamine, phenylsulfamic acid apparently takes no part in the formation of orthanilic acid. Accordingly, the latter reaction was found to be unaffected by the addition of sulfuric acid, in contrast to step 1. In the above sequence, it is interesting to note that, although step 2 is disproved by experiment, step 3 remains to be verified and is still a possible route to orthanilic acid from β-phenylhydroxylamine by an intramolecular rearrangement.

Experimental

Attempted Rearrangement under Bamberger and Kunz Conditions.—Potassium phenylsulfamate was prepared by two methods[13,14] and was purified by recrystallization from 90% ethyl alcohol. In the attempt to reproduce the rearrangement reported by Bamberger and Kunz,[3] we have carried out a large number of experiments with various concentrations of sulfuric acid in acetic acid by adopting the following general procedure.

A weighed amount of finely powdered potassium phenylsulfamate (*ca.* 1 g.) was thoroughly mixed with a solution of a weighed amount of 98% sulfuric acid in 2.5 ml. of glacial acetic acid. The resulting slurry was kept in a refrigerator for 80 hr. After this time, it was dissolved in water and the solution thus formed was made slightly alkaline with potassium hydroxide, transferred to a volumetric flask and finally diluted to the mark. Aliquots of this solution were used for both the determination of the total non-rearranged material and the estimation of the extent of cleavage of the sulfamic acid by the medium. In the first case an aliquot was treated with distilled water, the resulting solution was made acid with hydrochloric acid and then boiled for ten minutes. On the hydrolyzate thus obtained sulfate ion analysis was carried out in the conventional manner. This procedure proved to be reliable; under the same conditions authentic samples of anilinesulfonic acids did not undergo any hydrolysis. In a series of experiments, involving various relative concentrations of sulfuric acid in the range of 0 to 4.85 moles per mole of the potassium sulfamate, the amount of the sulfate ion recovered by analysis appeared to be equivalent to the amount of the starting sulfamate, thus showing that no rearrangement had occurred. The same results were obtained from experiments at 45°.

For the estimation of the extent of cleavage of phenylsulfamic acid by the medium, an approximate analysis of the sulfate ion was carried out with aliquots of the alkaline stock solution without acidification. After the barium sulfate precipitate was collected in a Gooch crucible, it was washed once with dilute hydrochloric acid to remove any trace of barium carbonate. The extent of cleavage resulted to be 1.27% in the absence of sulfuric acid at 0°, 27.9% in the presence of 0.78 mole of sulfuric acid per mole of potassium phenylsulfamate at the same temperature and 87.2% in the absence of sulfuric acid at 45°.

Rearrangement in Dioxane.—A solution of 4.66 g. of sulfuric acid (0.047 mole) in 100 ml. of dry dioxane was mixed with 10.11 g. of potassium phenylsulfamate (0.048 mole) in a glass-stoppered flask and kept in a thermostat at 100° for 55 hr. After cooling, the mixture was filtered and the collected white solid was treated with hot absolute alcohol, filtered and finally crystallized once from hot water. The fine, colorless needles were collected and washed with cold ethyl alcohol. The yield was 1.85 g. of anilinesulfonic acid. At 80° there was observed only 3.4% rearrangement after 24 hr., and at room temperature no rearrangement at all occurred in 9 weeks.

For the identification of the anilinesulfonic acids, the procedure of Allen and Frame[15] was used. We found that if pure samples of either sulfanilic or orthanilic acids are converted by this procedure to the corresponding chlorobenzenesulfonamide derivative, the crude derivative can be effectively purified by treatment with charcoal and one crystallization from the aqueous solution. The authentic *o*- and *p*-chlorobenzenesulfonamide derivatives thus obtained melted at 186–188° and 142–144°, respectively. The over-all loss of material in the preparation of these derivatives was about 40–50% by weight.

From the product of the rearrangement in dioxane a derivative, m.p. 142–144°, was obtained with the same general procedure and results just described in the case in which the starting material was pure sulfanilic acid. A mixed melting point gave no depression with an authentic specimen of *p*-chlorobenzenesulfonamide and a 15° depression with an authentic specimen of *o*-chlorobenzenesulfonamide.

Experiments carried out under the conditions described above for the rearrangement of phenylsulfamic acid in dioxane showed that neither orthanilic acid nor aniline and aniline sulfate underwent any change. For orthanilic acid, this was shown by comparing the chlorobenzenesulfonamide derivative from the material obtained at the end of the experiment with an authentic sample of *o*-chlorobenzenesulfonamide, m.p. 186–188°. A mixed melting point was not depressed. In the case of aniline or aniline sulfate, none of the anilinesulfonic acids could be detected and the starting materials were recovered unchanged.

Reaction of β-Phenylhydroxylamine with Sulfur Dioxide in Alcohol.—β-Phenylhydroxylamine was prepared by the method reported in reference 16 and purified by recrystallization from petroleum ether, b.p. 60–80°. In the experiments described below, freshly prepared material was always used because the compound decomposes on standing.

The following is a general description of the experiments carried out in absolute alcohol. Through a solution of 5.45 g. of β-phenylhydroxylamine (0.05 mole) in 60–80 ml. of absolute ethyl alcohol, dry sulfur dioxide was passed for 1 to 4 hr. with stirring. A crystalline solid was gradually formed and the mixture became dark green. Then the flask was stoppered and allowed to stand for one to three days. The mixture was filtered and the collected solid was crystallized once from water. The chlorobenzenesulfonamide derivative obtained from these crystals melted at 186–188° and proved, by mixed melting point determination, to be identical with a pure sample of *o*-chlorobenzenesulfonamide (see preceding section for details on the general identification procedure). The yield of the crude product ranged from 30.8 to 33.0%. In one experiment, involving the addition of sulfuric acid in a molar ratio 1:1 with respect to the hydroxylamine, the yield was 32.4%. The mother liquor from the filtration of orthanilic acid was evaporated to dryness to give a solid which was found to be impure aniline sulfate.

In 60% alcohol the reaction led to lower yields of orthanilic acid (10.6 to 21.3%) and to more complex side-reactions. In one experiment, starting from 25.1 g. of β-phenylhydroxylamine, the mother liquor from the filtration of orthanilic acid was worked up as follows. After alkalinization with potassium hydroxide, the liquid was steam distilled. The distillate contained aniline and an unidentified oil. The residue from the distillation was acidified with hydrochloric acid and yielded, on evaporation, a brown solid which was extracted several times with hot absolute alcohol until it

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(13) W. Traube, *Ber.*, **23**, 1653 (1890).

(14) P. Baumgarten, *ibid.*, **59**, 1166 (1926).

(15) C. F. H. Allen and G. F. Frame, *J. Org. Chem.*, **7**, 15 (1942).

(16) O. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 445.

became light tan. Then the solid was extracted twice with hot 90–95% alcohol and, at the end, consisted of inorganic material only. From the absolute alcohol extracts, on evaporation, 7 g. of a very dark-colored substance was obtained, which was very soluble in water and strongly acidic. Its neutral equivalent was about 310, but from these data and the analyses, the substance could not be identified with any pure and simple compound known. From the 90–95% alcohol extracts, on cooling, a small amount (0.5 g.) of crystals separated, which was recrystallized from 90% alcohol and identified as potassium phenylsulfamate. The differential extraction was made possible by the fact that the latter compound is only sparingly soluble in absolute alcohol.

The identification of potassium phenylsulfamate was based on elementary analysis and on comparison with the following properties of an authentic specimen of the salt. (1) The salt is readily soluble in cold water and the resulting solution is neutral. (2) The aqueous neutral solution gives no test for the sulfate ion. If such a solution is made acid and heated up to boiling, addition of the barium chloride reagent yields an abundant precipitate of barium sulfate. (3) On making the aqueous solution of the salt alkaline with a sodium hydroxide solution, no hydrolysis occurs even after prolonged boiling. However, if the solution of the salt is first made acid with hydrochloric acid and boiled for a short time and, then, is made alkaline, aniline is liberated. (4) The compound crystallizes from ethanol or aqueous ethanol in the form of shiny plates. The solubility in hot absolute ethanol is very low.

Attempted Rearrangement in 60% Ethyl Alcohol in the Presence of Sulfur Dioxide.—A solution of 9 g. of potassium phenylsulfamate in 310 ml. of 60% aqueous alcohol, in the presence of 4.2 g. of 100% sulfuric acid, was made up by dissolving the sulfamate in water, adding a dilute sulfuric acid solution and, successively, the calculated amount of ethyl alcohol. Through this solution dry sulfur dioxide was passed at room temperature for 7 hr., then the reaction flask was stoppered and let stand overnight. On filtration the liquid was separated from some inorganic material, then made alkaline with potassium hydroxide and evaporated on a steam-bath. The residue was extracted with small portions of hot 90% alcohol and the extracts, on cooling, yielded 2.2 g. of unchanged phenylsulfamate. The residue left behind and the mother liquors were recombined, made acid, heated to boiling, then made alkaline and evaporated again. Any anilinesulfonic acid would be expected to be found in the residue as a salt, but such a residue proved to be inorganic material only. Any aniline formed during the reaction or further treatments of the reaction mixture was eliminated in the evaporations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Molecular Association of Diarylformamidines. II. Effects of O- and P-Methyl Groups

BY ROYSTON M. ROBERTS

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Cryoscopic molecular weight determinations have been performed on benzene solutions of N,N′-di-*o*-tolylformamidine, N,N′-di-*p*-tolylformamidine, N-phenyl-N′-*o*-tolylformamidine and N-phenyl-N′-mesitylformamidine. All are associated except the first. The association factors of these compounds are compared with those of N,N′-diphenylformamidine, N,N′-di-*o*-chlorophenylformamidine and N,N′-di-*p*-chlorophenylformamidine. Steric and electronic effects of the substituents on the aromatic rings are discussed.

In an earlier paper[1] it was shown by cryoscopic measurements that molecules of N,N′-diphenylformamidine and N,N′-di-*p*-chlorophenylformamidine are associated in benzene solution, and that the degree of association is a function of the concentration of the solution. N,N′-Di-*o*-chlorophenylformamidine was found not to be associated under similar circumstances. The lack of association of this *o*-substituted compound was correlated with the fact that ethyl malonate reacts more slowly with N,N′-diarylformamidines which contain *o*-methyl and chloro substituents than with those which contain *meta, para* or no substituents.[1] Since both methyl and chloro substituents in the *o*-position decrease the rate of this reaction, it appears that the similar steric properties of the substituents are more important than the different electronic properties. It seemed interesting to investigate the effect of introducing *o*- and *p*-methyl groups into the N,N′-diphenylformamidine molecule upon the ability of these molecules to associate in benzene solution.

To this end the following compounds have been synthesized and their apparent molecular weights have been determined in benzene solution at the freezing point: N,N′-di-*o*-tolylformamidine, N,N′-di-*p*-tolylformamidine, N-phenyl-N′-*o*-tolylformamidine and N-phenyl-N′-mesitylformamidine. In Table I are given the apparent molecular weights of these four compounds at different concentrations. All but the first are associated, and the degree of association increases with the concentration of the solutions.

Some interesting observations can be made if the data on these compounds and those on the unsubstituted and chloro-substituted compounds described in the earlier paper are converted into units allowing direct comparison. This may be done by expressing the concentration of the solutions in molality and by dividing apparent molecular weight values by formula weights to give the association factor, α. The data on all seven compounds studied thus far are plotted in these units in Fig. 1.

It may be seen that the presence of two *p*-chlorine atoms does not greatly affect the degree of association; the curve for N,N′-di-*p*-chlorophenylformamidine (II) lies only slightly below that of N,N′-diphenylformamidine (I). However, replacement of the two *p*-hydrogens of N,N′-diphenylformamidine by methyl groups significantly increases the degree of association (III). These results are in

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[1] R. M. Roberts, THIS JOURNAL, **72**, 3608 (1950).