[Contribution from the Chemistry Department of the University of Kansas]

The Schmidt Reaction Applied to Aldehydes and Epoxides[1]

By William E. McEwen, Walter E. Conrad[2] and Calvin A. VanderWerf

Reaction of benzaldehyde with hydrazoic acid in the presence of a low concentration of sulfuric acid affords mainly benzonitrile together with a small yield of formanilide. With an increased amount of sulfuric acid, formanilide becomes the major product and benzonitrile the minor product. This behavior also holds true for *p*-tolualdehyde and *p*-chlorobenzaldehyde. Anisaldehyde and *p*-nitrobenzaldehyde, on the other hand, give the nitrile as the main product even at the higher sulfuric acid concentration. An interpretation of these results is offered. The acid-catalyzed reaction of styrene oxide with hydrazoic acid to give aniline, and the S_N2 type of reaction of styrene oxide with the azide ion to give a product, $C_8H_9N_3O$, which affords β-phenyl-β-aminoethanol on hydrogenolysis are also described.

As early as 1926 Schmidt[3] observed that the action of hydrazoic acid on benzaldehyde in the presence of sulfuric acid produced both benzonitrile and formanilide; he reported further that the yields of benzonitrile and formanilide shifted from 70% and 13% to 5% and 50%, respectively, when the molar ratio of sulfuric acid to benzaldehyde was changed from 0.72 to 5.4. Apparently this curious shift in the relative percentages of reaction products with change in sulfuric acid concentration has escaped further investigation and is as yet completely unexplained. In an attempt to investigate the generality of this type of shift in the predominant products of the reaction and to obtain evidence for a mechanism which would explain it, we have repeated Schmidt's work on benzaldehyde[4] and have studied four additional aldehydes. The results as obtained in at least duplicate runs in every case are summarized in Table I.

Table I

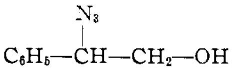
The Schmidt Reaction of Aldehydes

Aldehyde	Ratio of sulfuric acid to aldehyde	Yield, %[a] Nitrile	Formanilide
Benzaldehyde	0.72	32	14
	5.4	10	59
p-Methoxybenzaldehyde	0.72	86	0
	5.4	64	0
p-Chlorobenzaldehyde	0.72	55	12
	5.4	15	48
p-Nitrobenzaldehyde	0.72	72	2
	5.4	46	23
p-Methylbenzaldehyde	0.72	50	6
	5.4	13	43

[a] Yields are based on unrecovered aldehyde and include yields of hydrolysis products as well as of unhydrolyzed nitrile and amide. In every case, the amount of nitrogen evolved during the course of reaction was equal to or greater than that indicated stoichiometrically for the yield of products reported.

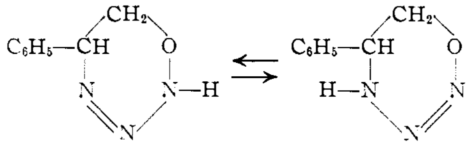
Since the reactions of epoxides are in many respects similar to those of aldehydes, the reaction of hydrazoic acid with styrene oxide was studied in the hope that additional light might be shed on the mechanism of the reactions with aldehydes. In the high concentration of sulfuric acid usually employed in the Schmidt reaction only tarry materials were formed. Similarly treatment of styrene oxide with hydrazoic acid in the presence of thionyl chloride, zinc chloride and trichloroacetic acid gave no isolable product. With anhydrous stannic chloride a 17% yield of aniline and a low yield of a mixture of neutral nitrogen containing compounds, which were not separated or identified, were obtained.

The reaction in aqueous dioxane of styrene oxide with sodium azide, however, gave a good yield of nitrogenous product, $C_8H_9N_3O$. This product, which will be the subject of a future communication, is either β-phenyl-β-azidoethanol (I) or 5-phenyl-5,6-dihydro-1,2,3,4-oxatriazine (II) as shown by its hydrogenolysis to β-phenyl-β-aminoethanol (III) in high yield.

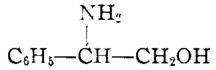


$C_6H_5—\overset{N_3}{\overset{|}{C}}H—CH_2—OH$

I



II



$C_6H_5—\overset{NH_2}{\overset{|}{C}}H—CH_2OH$

III

Experimental[5]

Reactions of Benzaldehyde with Hydrazoic Acid. A. At Low Sulfuric Acid Concentration.—To a stirred mixture of 450 ml. of benzene and 46.7 g. (0.72 mole) of sodium azide, 31.9 ml. (0.58 mole) of concentrated sulfuric acid was added dropwise while the temperature was maintained at 10–15°. Then 30.3 ml. (0.3 mole) of benzaldehyde was added dropwise at the same temperature. Stirring was continued at room temperature until the evolution of gas had ceased (several hours). Excess ice was then added, the two layers were separated, the aqueous layer was extracted with ether and the ether extracts were added to the benzene layer. The aqueous layer, made alkaline and extracted with ether, yielded no aniline. The combined benzene layer and ether extracts were extracted with a 10% solution of sodium hydroxide and then stirred for an hour with excess 40% sodium bisulfite solution. Hydrolysis of the precipitated bisulfite addition product led to the recovery of 8.9 g. (28%) of benzaldehyde. Distillation of the organic layer *in vacuo* gave 8.0 g. (26% based on total amount of benzaldehyde) of benzonitrile and 4.1 g. (11.3%) of formanilide.

B. At High Sulfuric Acid Concentration.—The procedure was the same as that described above except that 110 ml.

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[1] Abstracted from the Ph.D. thesis of Walter E. Conrad, July, 1951. A summary of this work was presented at the XIIth International Congress of Pure and Applied Chemistry, New York, Sept. 10–14, 1951.

[2] Stanolind Fellow, 1949-1950.

[3] K. F. Schmidt, German Patent 427,858, April 20, 1926.

[4] Whereas Schmidt[1] used hydrazoic acid and sulfuric acid in his reactions, we generated the hydrazoic acid *in situ* by the use of sodium azide. Thus, in our reactions the effective catalyst at the low sulfuric acid concentration was sodium bisulfate.

[5] All melting points are corrected, boiling points are uncorrected. Analyses are by Oakwold Laboratories, Alexandria, Virginia.

(2.0 moles) of concentrated sulfuric acid was used. Treatment of the aqueous layer gave 4.2 g. (15%) of aniline which was further characterized as benzanilide. No benzaldehyde could be recovered from the organic layer; distillation yielded 3.1 g. (10%) of benzonitrile and 16.0 g. (44%) of formanilide.

Reaction of *p*-Methoxybenzaldehyde with Hydrazoic Acid. A. At Low Sulfuric Acid Concentration.—The procedure was the same as that for benzaldehyde except that the reaction mixture was stirred for 12 hours at room temperature. Upon addition of ice a precipitate was obtained which upon refluxing with 8 *N* hydrochloric acid for one hour gave an 8% yield (based on anisaldehyde) of anisic acid. Distillation of the organic layer *in vacuo* gave 31.6 g. (78%) of anisonitrile, further characterized as the acid and phenacyl anisate.

B. At High Sulfuric Acid Concentration.—This reaction was complete in three hours, the reaction mixture being kept at 45° during the last hour. Upon addition of ice 33.0 g. of precipitate was obtained which, upon recrystallization from alcohol–water afforded 9.0 g. (22%) of pure anisamide, further characterized as the acid. The remaining solid on hydrolysis with sodium hydroxide solution gave 6.8 g. (15%) of anisic acid. Distillation of the organic layer gave 9.8 g. (25%) of anisonitrile. No anisidine was recoverable from the aqueous solution.

In a series of runs with *p*-methoxybenzaldehyde it was found that the total molar yield of combined anisonitrile and anisamide remained essentially constant, although the exact percentages of each varied considerably, depending upon the conditions, especially the reaction temperature and the isolation procedure. It appears probable—in view of the known ease of acid-catalyzed hydrolysis of anisonitrile—that all of the amide isolated resulted from such hydrolysis.

Reaction of *p*-Chlorobenzaldehyde with Hydrazoic Acid. A. At Low Sulfuric Acid Concentration.—Heating on the steam-bath was necessary in order to bring the reaction to completion. Upon addition of ice, a precipitate of *p*-chloroanilinium sulfate, from which 8.4% of *p*-chloroaniline was recovered, came down. Inasmuch as the nitrile could not be separated cleanly from the formanilide by distillation the crude mixture was hydrolyzed by means of 10 *N* hydrochloric acid. The yield of *p*-chlorobenzoic acid thus obtained was 55%, that of *p*-chloroaniline, also characterized as the acetyl derivative, 4%.

B. At High Sulfuric Acid Concentration.—The reaction was brought to completion by final heating for two hours at 40°. The precipitate formed upon addition of ice yielded no amine but gave 0.8 g. (1.8%) of *p*-chlorobenzoic acid upon acid hydrolysis. Crystallization from aqueous alcohol of the basic fraction obtained when the aqueous layer was made alkaline gave 6.1 g. (16%) of pure *p*-chloroaniline. From the organic layer 4.3 g. of *p*-chlorobenzaldehyde was recovered and there were isolated after hydrolysis 5.7 g. (13.5%) of *p*-chlorobenzoic acid and 10.5 g. (27%) of *p*-chloroaniline.

Reaction of *p*-Nitrobenzaldehyde with Hydrazoic Acid. A. At Low Sulfuric Acid Concentration.—One-half of the usual molar quantities of all reactants was used in this experiment. Nitrogen was evolved in good yield at room temperature. The organic layer yielded 4.6 g. (22%) of recovered *p*-nitrobenzaldehyde. Upon removal of most of the benzene and steam distillation 12.0 g. (54%) of pure *p*-nitrobenzonitrile, also characterized as the acid, was isolated from the distillate; hydrolysis of the crude material remaining in the mother liquor yielded 0.6 g. (2%) of *p*-nitrobenzoic acid. From the residue remaining after the steam distillation 0.3 g. (1.5%) of *p*-nitroaniline was isolated and characterized as the acetyl derivative.

B. At High Sulfuric Acid Concentration.—Again only half of the usual molar quantities of reactants was used. A quantitative yield of gas was obtained as soon as all the aldehyde had been added, even below room temperature. Addition of ice caused the formation of a precipitate which was combined with the acid extract of the benzene layer. Crystallization of the liberated amine from alcohol–water afforded 4.7 g. (23%) of *p*-nitroaniline. Steam distillation of the residue from the benzene layer yielded 10.3 g. (46%) of *p*-nitrobenzonitrile. No *p*-nitrobenzaldehyde could be recovered.

Reaction of *p*-Methylbenzaldehyde with Hydrazoic Acid. A. At Low Sulfuric Acid Concentration.—One-third of the usual molar quantities of reactants was used. Nearly the theoretical yield of nitrogen was evolved at room temperature. After recovery of 0.75 g. (6.2%) of *p*-methylbenzaldehyde by means of bisulfite, distillation of the organic layer *in vacuo* afforded 5.0 g. (44%) of *p*-methylbenzonitrile. The distillation residue was hydrolyzed by refluxing with 6 *N* hydrochloric acid for four hours. The amine which resulted was benzoylated affording 1.1 g. (5.3%) of N-benzoyl-*p*-toluidine. The neutral fraction from the acid hydrolysis was refluxed with 10% sodium hydroxide solution and 0.35 g. (2.6%) of *p*-toluic acid was isolated.

B. At High Sulfuric Acid Concentration.—One-third the usual molar quantities of reactants was used. The aqueous layer yielded some amine which was converted to 0.35 g. (1.7%) of N-benzoyl-*p*-toluidine. No *p*-methylbenzaldehyde could be recovered. Distillation of the organic layer *in vacuo* afforded 1.3 g. (11%) of *p*-methylbenzonitrile and 5.6 g. (41.4%) of *p*-methylformanilide. A small amount of intermediate distillate gave 0.28 g. (2%) of *p*-toluic acid on alkaline hydrolysis.

Effect of Concentrated Sulfuric Acid on Benzamide.—A solution of 0.50 g. of benzamide in 2.0 ml. of sulfuric acid was allowed to stand overnight at room temperature and then maintained at 33° for one hour. No benzonitrile could be detected, and 0.35 g. (70%) of benzamide was recovered on dilution of the acid solution.

Reaction of Styrene Oxide with Hydrazoic Acid.—A solution of 0.26 mole of hydrazoic acid and 26 ml. of anhydrous stannic chloride (0.22 mole) in 350 ml. of benzene was stirred at 20° while 25 ml. (0.22 mole) of styrene oxide was added dropwise. The reaction was allowed to proceed at room temperature until the evolution of gas was complete (several hours). Ice was then added in excess. The aqueous layer was made alkaline with 50% sodium hydroxide solution and distilled into hydrochloric acid. Evaporation of the solution now afforded 4.8 g. (17%) of aniline hydrochloride. The organic layer gave a few grams of a mixture of nitrogenous products which distilled at 75–125° (3 mm.) and a trace of 2,5-diphenyldioxane, m.p. 175°.[6]

Several variations of the reaction procedure and method of isolation were tried. Traces of crystalline materials were usually isolated but in no case was the yield of identifiable products greater than in the run described.

Reaction of Styrene Oxide with Sodium Azide.—To a refluxing solution of 100 g. of styrene oxide in 1300 ml. of dioxane a solution of 68 g. of sodium azide in 175 ml. of water was added dropwise. Refluxing was continued for 20 hours after which the two layers were separated. The dioxane layer on distillation gave 95 g. of crude material boiling at 130–139° (5 mm.). On careful redistillation of this fraction 90 g. (63%) of a product, b.p. 105–107° (1 mm.), was obtained.

Anal. Calcd. for $C_8H_9ON_3$: C, 58.9; H, 5.56; N, 25.8. Found: C, 58.4, 58.6; H, 6.21, 6.11; N, 26.2, 26.2.

This compound is insoluble in water, hydrochloric acid and sodium hydroxide solution. It can be recovered unchanged after refluxing for three hours with 3 *N* hydrochloric acid containing 50% dioxane or for half an hour with 5% sodium hydroxide in 50% alcohol. On warming with concentrated hydrochloric acid or with acetic anhydride containing 20% concentrated sulfuric acid, decomposition occurs with evolution of nitrogen. The compound can be distilled at 159–160° (21 mm.) with little decomposition.

The 3,5-dinitrobenzoyl derivative crystallized from ethyl acetate or an ethyl acetate–ligroin mixture in the form of light yellow needles, m.p. 137.4–138.2°.

Anal. Calcd. for $C_{15}H_{11}O_6N_5$: C, 50.4; H, 3.11; N, 19.6. Found: C, 50.3, 50.5; H, 3.07, 3.13; N, 19.8, 19.9.

Reduction of the Compound $C_8H_9ON_3$.—Hydrogenation of 16.3 g. (0.1 mole) of the compound $C_8H_9ON_3$, in 50 ml. of ethanol at three atmospheres in the presence of 0.1 g. of platinum oxide proceeded without any drop in pressure. After hydrogenation for 24 hours the solution was filtered and distilled. The yield of β-amino-β-phenylethanol (III), b.p. 115–126° (3 mm.), was 11.1 g. (81%). This compound is a difficultly crystallizable oil, which, on standing in air, forms a solid, probably a carbonate, m.p. 104–109°. Adkins and Pavlic[7] reported a b.p. of 101–104° (2 mm.) and a m.p.

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[6] L. A. Bryan, W. M. Smedley and R. K. Summerbell, THIS JOURNAL, **72**, 2206 (1950), reported 173° for the *trans* form.

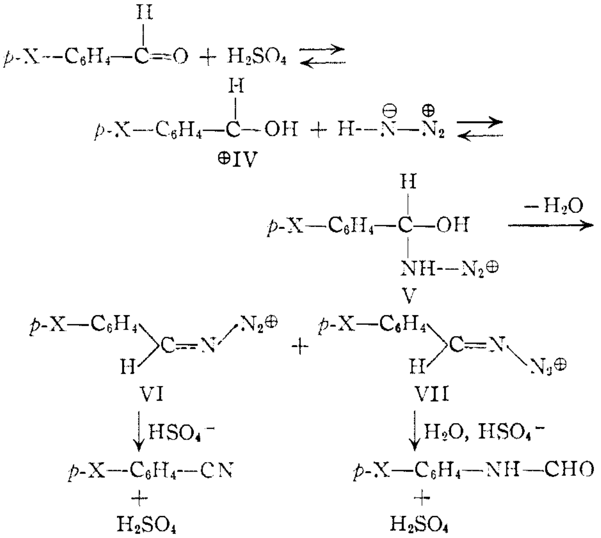
[7] H. Adkins and A. A. Pavlic, *ibid.*, **69**, 3039 (1947).

of 108–111° but they probably confused the m.p. of the latter with that of the carbonate. The compound was also characterized as the diacetate, m.p. 104–105° (reported,[8] 103°) and the picrate, m.p. 205–206° (reported,[9,10] 208–210° and 207°).

Discussion

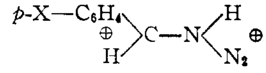
From the point of view of a mechanism study the most striking feature of the Schmidt reaction of aldehydes is the apparently fairly general increase in the ratio of formamide to nitrile formation that occurs on increasing the amount of sulfuric acid used to catalyze the reaction. In this discussion we intend to superimpose on the currently most attractive mechanism for the Schmidt reaction of ketones[11,12,13] some proposals which are capable of explaining the interesting catalytic effect in the aldehyde reactions.

It seems entirely reasonable to assume that the aldehyde reactions should possess many of the mechanistic features of the ketone reactions and the following proposal embraces these features. The aldehyde reacts with sulfuric acid to form the conjugate acid IV. This combines with hydrazoic acid to give the complex V which then undergoes dehydration to the *syn* and *anti* isomers VI and VII. The species VI affords the nitrile by the *trans* elimination of a proton and a molecule of nitrogen while VII yields the formanilide by a *trans* migration of the aryl group accompanied or followed by the addition of a molecule of water.



To explain the overturn in the ratio of products on varying the concentration of sulfuric acid the following extensions of the argument are necessary: (1) The free energy of VII is lower than that of VI (steric influence).[14] (2) The rate of formation of VI is greater than the rate of formation of VII. (3) Interconversion between VI and VII can occur, subject to acid catalysis.[15]

(4) When the reaction is catalyzed by a small amount of sulfuric acid (effectively sodium bisulfate in our reactions) the rate of nitrile formation from VI exceeds the rate of interconversion of VI and VII. Hence the major product is the nitrile. (5) At the high concentration of sulfuric acid the rate of interconversion of VI and VII exceeds the rate of conversion of VI to the nitrile. Hence the bulk of VI is converted to the more stable VII, and the formanilide becomes the major product, *i.e.*, as the acid concentration is increased the overall rate leading from V to the formanilide *via* VI and VII, respectively, begins to compete favorably with the more direct route from V to the nitrile *via* VI. In this connection the behavior of anisaldehyde is somewhat anomalous. Although the yield of anisonitrile is decreased on going from the lower to the higher concentration of sulfuric acid the nitrile is nevertheless obtained in 64% yield even at the higher concentration. This difficulty can be resolved by attributing to the strongly electron-donating *p*-methoxyl group the ability to accelerate the conversion of VI ($X = CH_3O$) to the nitrile. This seems reasonable in that the elimination reaction represents a net transfer of electron density away from the *p*-anisyl group. Hence, even at the higher concentration of sulfuric acid the rate of isomerization of VI to VII does not exceed the rate of conversion of VI to the nitrile and the nitrile remains the major product. Also the behavior of *p*-nitrobenzaldehyde requires some comment. In this case it can be assumed that both the conversion of VI to the nitrile and the interconversion of VI and VII are retarded by the powerful electron-withdrawing nitro group. The latter statement would have particular validity if the interconversion of VI and VII proceeded *via* the conjugate acid, VIII. Although it would be impossible to predict where a balance in these effects would lie, the facts suggest that deceleration of interconversion between VI and VII outweighs deceleration of nitrile formation in the case where the substituent is a para nitro group[16]; hence the nitrile remains the major product even at the high sulfuric acid concentration. More work is required to establish these hypotheses and to evaluate other possibilities.[17]



VIII

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(8) H. Reihlen, L. Knopfle and W. Sapper, *Ann.*, **534**, 247 (1938).

(9) G. Ovakimian, M. Kuna and P. A. Levene., *J. Biol. Chem.*, **135**, 91 (1940).

(10) S. Gabriel and J. Colman, *Ber.*, **47**, 1866 (1916).

(11) P. A. S. Smith, THIS JOURNAL, **70**, 320 (1948).

(12) P. A. S. Smith and B. Ashby, *ibid.*, **72**, 2503 (1950).

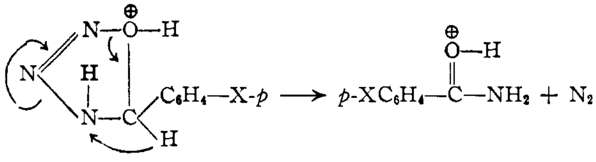
(13) P. A. S. Smith and J. P. Horwitz, *ibid.*, **72**, 3718 (1950).

(14) In the case of alkyl phenyl ketones, the observed migration ratios undergo a progressive change from preferred phenyl migration to preferred alkyl migration with increasing branching on the α-position of the alkyl groups.[13] This strongly suggests that the more stable intermediate in each case has the larger group *trans* to the N_2 group.

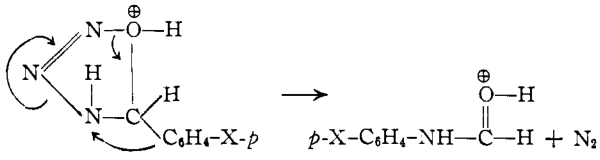
(15) Compare the work of C. R. Hauser and G. Vermilion, THIS JOURNAL, **63**, 1224 (1941), on the acid-catalyzed conversion of benzoyl-*syn*- to benzoyl-*anti*-benzaldoxime.

(16) A possible objection to this interpretation is the fact that the reaction of *p*-nitrobenzaldehyde in the high concentration of sulfuric acid appeared to be the fastest of the ten reactions studied. If one of the earlier steps in the reaction, the formation of the adduct V, for example, were the over-all rate-determining step, however, this apparent discrepancy would conceivably be resolved.

(17) An alternate mechanism for the Schmidt reactions involving 1,2 shifts within the rings of IX and X (formed by cyclization of V), accompanied by ring opening (see curved arrows in the drawings below) can be rejected on the grounds that benzamides are not generally isolated in these reactions and are not dehydrated to nitriles in concentrated sulfuric acid at temperatures ranging from 0-50° (see the experimental section).



IX



X

From the theoretical standpoint, the point of attack of the azide ion on styrene oxide is of considerable interest. Attack at the secondary carbon of styrene oxide is clearly indicated. Considering the fact that as a linear structure the azide ion probably possesses only relatively small steric requirements, this fact is in line with the observations of other investigators[18] on the position of attack of less bulky anions on styrene oxide. Additional work on this interesting epoxide reaction is now in progress in these laboratories.

[18] See D. Swern, G. N. Billen and H. B. Knight, THIS JOURNAL, **71**, 1152 (1949); C. C. Guss, *ibid.*, **71**, 3460 (1949).

LAWRENCE, KANSAS RECEIVED AUGUST 8, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

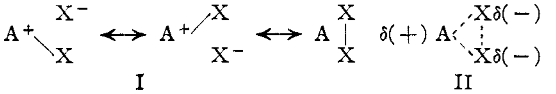
The Interaction of Bromine with Substituted Tetraphenylethylenes[1]

BY ROBERT E. BUCKLES AND NORMAN A. MEINHARDT

The electrical conductivities of methylene chloride solutions containing bromine and various substituted tetraphenylethylenes have been measured. A comparison has been made with the conductivity of tetrabutylammonium iodide in the same solvent. Tetraphenylethylenes with methoxyl or dimethylamino groups in at least two of the para positions gave highly colored solutions, which had molar conductances of the same order of magnitude as the ionic ammonium salt. Tetraphenylethylenes substituted with halogen or phenyl groups in the para positions had lower molar conductances on interaction with bromine, but the complexes formed still showed definite ionic character. Lowering the temperature in most cases increased the conductance of the solutions. This behavior roughly paralleled the qualitative observation of the amount of complex present based on changes in color.

Some sort of ionic complex formed by the interaction of an aromatic compound or an olefin with a halogen is generally considered as an intermediate in aromatic substitution or olefin addition reactions.[2] Several recent studies have yielded conclusive spectrophotometric evidence that certain simple aromatic compounds form 1:1 complexes with iodine,[3] bromine[4] and iodine chloride.[5] Possible structures for such complexes as well as those formed by halogens with oxygen-containing solvents known to give brown solutions with iodine have been extensively discussed recently.[6]

The general structure of the complex appears to involve the aromatic ring (or the oxygen or nitrogen of the "brown" solvents) as a source of electrons—a base according to the generalized concept—for bonding to the halogen which is somewhat electron deficient, *i.e.*, acidic. The two halogen atoms can be represented in equivalent positions with respect to the aromatic compound as in the resonance hybrid (I) or the partial bond structure (II) in which A is a complexing compound



I II

Analogous to I and II are III and IV in which the halogen atoms have assumed non-equivalent positions

$$\underset{\text{III}}{A^+\text{—}XX^- \longleftrightarrow A\ X\text{—}X} \qquad \underset{\text{IV}}{A\delta(+)\text{----}X\text{----}X\delta(-)}$$

A third possibility is that the complex formation involves a heteropolar dissociation of the halogen. In the relatively non-polar solvents usually used for the preparation of such complexes the ions formed would be expected to be associated as ion pairs, triple ions and higher ion aggregates.[7]

$$AX^+ + X^- \rightleftarrows AX^+X^-, \text{ etc.}$$

Such a complex in the case of the action of iodine on pyridine has been shown to be ionic by electrical conductance,[8] to involve the PyI^+ ion by comparison of its absorption spectrum with those of other PyI^+ salts,[9] and to be formed by a rapid equilibrium from iodine and pyridine by the rapid exchange of radioactive iodine with various PyI^+ salts in pyridine.[10]

In the case of the more complex aromatic–olefin systems of highly arylated ethylenes evidence for ionic complexes with halogens has been presented.[11] A number of such compounds both substituted tetraphenylethylenes[11a] and substituted *unsym*-diphenylethylenes,[11b,c] interacted with halogen to give highly colored, salt-like solids containing varying amounts of halogen depending on the nature of the ethylene and the identity of the halogen. The structures suggested[11] for the salt-like complexes were stable carbonium ions associ-

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[1] From the Ph.D. Thesis of Norman A. Meinhardt.

[2] C. C. Price, "Mechanisms of Reactions of Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, Chap. 2.

[3] J. H. Hildebrand and H. A. Benesi, THIS JOURNAL, **70**, 2382 (1948); **71**, 2703 (1949).

[4] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950).

[5] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

[6] R. S. Mulliken, *ibid.*, **72**, 600 (1950).

[7] R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

[8] L. F. Audrieth and E. J. Birr, THIS JOURNAL, **55**, 668 (1933).

[9] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **73**, 88 (1951).

[10] J. Kleinberg, *ibid.*, **73**, 1865 (1951).

[11] (a) R. Wizinger and J. Fontaine, *Ber.*, **60**, 1377 (1927); (b) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 132 (1928); (c) P. Pfeiffer and P. Schneider, *J. prakt. Chem.*, **129**, 129 (1931).