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TOMMY LYLE TOLBERT

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APPROVED BY

[redacted]

[redacted]

Ernest Bryson

D. V. Colbert

John B. Bruce

DISSERTATION COMMITTEE

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CHAPTER I

INTRODUCTION

An imine can best be described as an organic compound which contains a double bonded nitrogen atom attached to a carbon atom; the hydrogen of the imine nitrogen may or may not be replaced. The unsubstituted secondary imines (ketimines) have been very thoroughly studied, and a considerable number of substituted aldimines (primary or terminal imines) and ketimines have been prepared and characterized. The unsubstituted aldimines, however, are a group of compounds which are so reactive and difficult to obtain pure that they have remained relatively untouched. This lack of attention is not due to unimportance or rarity, for these imines are intermediates in some of organic chemistry's well known reactions, but simply due to difficulties in isolation and purification from the mixtures in which they are formed.

Using as a basis of analogy the reactions of ketimines, it should be possible to characterize aldimines by the ease with which they are hydrolysed to the aldehyde; by their basic character as shown by the formation of salts; by the replacement of hydrogen to form N-substituted derivatives, and by their unsaturation as shown by their

hydrogenation to amines. Support of this supposition comes from the reported properties of the terminal imines which have been prepared. Unfortunately, this evidence is somewhat weak, since only four unsubstituted aldimines are reported and even these have been only partially characterized.

The long but sparse history of these compounds begins in 1840 with the report of E. Ettling (1) of the preparation of salicylaldimine as a part of a metal complex, which would today be termed a chelate. Since that time a great deal of research has been done on this type of complex, but the aldimines, as such, have never been isolated.

A. Reychler (2) obtained a compound which he believed to be acetaldimine in 1884 by the dehydration of an α-hydroxy ethylamine-silver nitrate complex. A trimer of this compound was reportedly obtained by A. Delepine (3) in 1889 by reacting the appropriate aldehyde with ammonia and dehydrating at room temperature and aspirator pressure. Although a stable, isolated imine was not obtained, the picrate derivative was reported. H. H. Strain (4) in 1932 was successful in obtaining this trimer by a similar method and claimed to have isolated the monomer by dry distillation of the trimer and chilling the vapors. The reactions proving the monomer, however, were chiefly those of an aldehyde.

The hydrochloride of benzaldimine was prepared in 1896 by M. Busch (5). This was accomplished by the reaction of hydrobenzamide, ethanol, and hydrogen chloride to give the imine hydrochloride and ethyl benzacetal. The reactions reported for the salt are those to be expected from an imine hydrochloride. This salt was again reported in 1925 by V. Grignard and R. Escourrou (6). An attempt to isolate benzald-

imine formed from the catalytic hydrogenation of the nitrile had been unsuccessful due to the imine's instability, but they did report the hydrochloride of the imine. However, the physical constants differed markedly from those reported by Busch. Some physical constants had been obtained for the unstable imine itself, and the work was reported again by Escourrou (7) in 1929. H. H. Strain (8), in 1930, working with liquid ammonia in an attempt to prepare ammino bases analogous to those of water, obtained hydrobenzamide from the reaction of benzaldehyde and liquid ammonia; this reacted further with ammonia to give a crystallizable oil. This substance was believed to be benzaldimine; however, some of the reactions which Strain reports are unlike those expected from an imine.

Phenylacetaldimine had been prepared in the previously mentioned hydrogenations carried out by Grignard and Escourrou (6, 7). This imine proved to be relatively stable and a fairly complete set of physical constants was determined.

By use of Willstätter's platinum black in anhydrous ethanol, E. D. Kohler and N. L. Drake (9) in 1923 were successful in reducing the corresponding nitro compound to diphenylacetaldimine. This compound proved to be a solid, and although it was quite reactive, some physical constants were determined and derivatives prepared.

In the most recent reported work on aldimines the hydrochloride of α-methoxy acetaldimine was prepared by reaction of ethanol, acetonitrile, dichloroethane, and hydrogen chloride. The report was made by A. I. Gravin (10) in 1943.

It is surprising that, in the 118 years of active organic

synthesis since the first report of an aldimine type compound, these substances whose molecular form is well known among organic chemists have not been prepared and characterized. Such a problem is challenging and is particularly interesting when one has a background in ketimine chemistry; for this reason the preparation and characterization of aldimines were chosen as the subjects of this dissertation.

Of the three methods of approach to the synthesis which seemed most feasible, hydrogenation of nitriles, modification of an aldehyde synthesis of the Gattermann type, or modification of the Stephen aldehyde synthesis, the last seemed best. The choice was made due to the large amount of work which has been done using the reaction for aldehyde preparation, thus making data on yields, stability of the intermediates, etc., plentiful, and due to the ease of handling to which the reaction seemed to lend itself.

The Stephen reaction can be said to consist of three steps: preparation of anhydrous stannous halide, use of this salt in reduction and complex formation with an appropriate nitrile, and hydrolysis of this complex to the aldehyde. The reaction can be generalized and written:

$$RC{\equiv}N + SnX_2 \xrightarrow[\text{dry ether}]{HX} [R\text{-}CH{=}NH\cdot HX]_2\, SnX_4 \xrightarrow{HOH} R\text{-}CH{=}O + \text{Salts}$$

Although there has been controversy over yields and relative value of this reaction, the yields are good except in certain cases of strong steric and/or inductive effects, and the method is, generally speaking, reliable.

Modification of this reaction to produce aldimines rather than aldehydes would require only a nonaqueous rather than aqueous

decomposition of the stable aldimine hydrohalide-stannic halide intermediate. Such a decomposition would leave the imine group intact and it then would be only a problem of isolation and purification. Since the initial preparation of the intermediate is all important to the success of the later steps, as much as possible should be known about complex formation in the Stephen reaction. For this reason and in order to get an idea of the applicability and breadth of the reaction, the work of Stephen and later workers was reviewed carefully.

In 1925 Henry Stephen (11) reported his new method of aldehyde preparation. The method was to convert a nitrile into an aldehyde by the addition of an ether solution of the nitrile to a solution of stannous chloride in ether saturated with hydrogen chloride. The nitrile, combining with a molecule of hydrogen chloride, forms an imido chloride which is then reduced to the imine by the stannous chloride. The imine hydrochloride, formed immediately, yields aldehyde on hydrolysis.

$$RCN + HCl \longrightarrow RC(Cl)=NH$$

$$RC(Cl)=NH + SnCl_2 + 2HCl \longrightarrow RCH=NH\cdot HCl + SnCl_4$$

$$RCH=NH\cdot HCl + H_2O \longrightarrow RCHO + NH_4Cl$$

Stephen reported that, upon reduction of the nitrile, the resulting aldimine precipitated as an aldimine hydrochloride-stannic chloride complex of the form: $(RCH=NH\cdot HCl)_2SnCl_4$. The original report implied that the yields of aldehyde in most cases were very nearly quantitative, but gave few actual yields. Subsequent studies of the method have shown that in certain cases quantitative yields are obtained, but, that in many cases, the yields are considerably less than one would expect

from Stephen's report.

In the earlier work using this reaction, the precipitation of the aldimine stannichloride was taken as a measure of completeness of the reaction. Lieber (12), however, has shown that, by varying the conditions of the reaction, at least two different complexes can be obtained, one of which is ether soluble. It has been further shown by Knight and Zook (13) that the precipitate obtained may not be the pure aldimine complex as was previously supposed, but rather a mixture of the complex and the products of a side reaction between the imine and nitrile. This reaction can be postulated as occurring in three steps: reaction of the imine with two successive molecules of nitrile, and, if water is present, reaction with two molecules of water.

$$[RCH{=}NH_2]^+Cl^- \xrightarrow{R'CN} [R'C{=}NCH(NH_2)R]^+Cl^-$$

$$[R'C{=}NCH(NH_2)R]^+Cl^- \xrightarrow{R'CN} [R'\overset{+}{C}{=}NCHRN{=}\overset{+}{C}R'] \, 2Cl^-$$

$$[R'\overset{+}{C}{=}NCHRN{=}\overset{+}{C}R'] \, 2Cl^- \xrightarrow{2H_2O} (R'CONH_2)CHR + 2HCl$$

Since yields are often calculated from the amount of precipitated complex it is not surprising that variations in yield have been reported.

In a study of the kinetics of this reaction, Turner (14) has shown that the rate (another controversial point) of the reaction depends on the concentrations of all three reactants, nitrile, stannous chloride, and hydrogen chloride. It was shown that precipitation of the aldimine stannichloride is the accelerating factor and often the factor driving the reaction to completion. Removing the imine from the reaction zone also serves to hinder the secondary reaction mentioned above. Turner was also able to show some surprising effects on reaction rate by

substitution on an aromatic nucleus. This work tends to support the first step in a mechanism proposed by Meerwein (15) which was the formation of a nitrilium salt from the nitrile and chlorostannous acid:

$$R\text{-}CN + H_2SnCl_4 \longrightarrow [R\text{-}C{\equiv}NH]^+ HSnCl_4$$

Yields obtained from the Stephen reaction vary widely, depending on the structure of the nitrile used. Acetonitrile and n-propionitrile give poor yields, however, the yield from normal aliphatic nitriles increases markedly with chain length. When unsaturation is introduced into the chain of a phenyl substituted aliphatic nitrile, the yield falls off sharply and continues to decrease with increase in the number of double bonds in the chain. As an example, $C_6H_5CH{=}CHCN$, $C_6H_5CH{=}CHCH{=}CHCN$, and $C_6H_5CH{=}CHCH{=}CHCH{=}CHCN$ give yields of 40%, 10%, and a trace respectively. On the other hand, an aldehyde can not be obtained by this method from the unsubstituted aliphatic α,β unsaturated nitrile, 2 nonenoic nitrile. Good to excellent yields of aldehyde are obtained from most aromatic nitriles. Exceptions in which the yield of an aromatic aldehyde is low can not be explained entirely by steric or inductive effects but seem to be caused by a combination of the two. Relatively few heterocyclic aldehydes have been prepared by the Stephen method; the yields of those which have been prepared by this method, however, are generally good. In some cases modification of the reaction to better fit the properties of the product has led to successful preparation of difficultly prepared aldehydes.

Modifications of the Stephen method have been tried by a number of workers. Wittig and Hartman (16) obtained much higher yields in certain cases by the use of stannous bromide and hydrogen bromide.

In the instance of the unsaturated compounds mentioned above, the yield of $C_6H_5CH{=}CHCN$ increased 25% and the yield of $C_6H_5CH{=}CHCH{=}CHCN$ increased 40% with this variation. Slotta and Kether (17) were also successful in modifying the Stephen procedure, employing stannous chloride preparations containing 1.4 to 1.5% water. They had observed that absolutely anhydrous stannous chloride did not dissolve in hydrogen chloride saturated ether, while a trace of water made it completely soluble; yields of 80% to 90% aldehyde were obtained.

Excess hydrogen chloride and a temperature elevation of 30-40°C above room temperature increased yields in certain cases and leads to an increased reaction rate in all cases. No correlation has been found between the solvent used, the yield obtained, and the type nitrile, but, in preparing certain aldehydes, dioxane (18) has been used to a greater advantage. Stephen (19), himself, has recently suggested the use of ethyl formate or ethyl acetate as a solvent to obtain slightly improved yields. The increased yields in these solvents may be due only to the effect of the higher reflux temperature of the solvent. Wittig and Hartmann (16) did some preliminary work on the effect of replacing stannous chloride with chromous, vanadous, or titanous chloride; all were found ineffective. A modification which makes little change in yield but which is important for a few studies was developed by Turner (14). Desiring to study the kinetics of the Stephen reaction, he wished to accomplish the reduction of the nitrile in such a way that the aldimine stannichloride would not precipitate or, at least, would be slow in precipitating and, more important, he wanted the system to be homogeneous before nitrile addition. Both

aims were achieved when the stannous chloride-hydrogen chloride saturated ether reduction mixture was replaced by a mixture of stannous chloride dihydrate, ether and acetyl chloride.

Table I gives a partial list of aldehydes prepared by the Stephen method.

Having accepted the challenge of the preparation and characterization of unsubstituted aldimines and with an approach to the synthesis in mind, it was felt that the problem would best be solved in three steps. Initially a method of preparation and isolation would have to be developed, the compounds then would be characterized as completely as possible by chemical and instrumental means, and finally, a comparison of steric and inductive effects in the new imines would be made. The results of this work are described and discussed in the following chapters.

TABLE I

ALDEHYDES WHICH HAVE BEEN PREPARED BY THE STEPHEN REACTION

Aliphatics	Yield	Reference
Acetaldehyde	30%	14
n-Propanal	23%	14
n-Butanal	53%	14
n-Pentanal	61%	14
s-Butanal	25%	14
2,2 Dimethyl propanal	22%	14
α (β' -Phenoxyethyl) valeraldehyde	38%	20
n-Octanal	quant.*	11
n-Dodecenal	88%	12,13
n-Tetradecanal	quant.*	11
n-Hexadecanal	quant.*	11
n-Octadecanal	quant.*	11
Isocapraldehyde	31%	21
β -Hydroxypropional	0	21
γ -Phenoxy α- methylbutyraldehyde	46,51%	22,23
γ -Phthalimido α- methylbutyraldehyde	54%	23
γ -Phthalimido-butyraldehyde	74%	24
γ -Phenoxybutyraldehyde	79%	25
5-Phenylpentadienal	50%	16
Cinnamylaldehyde	65,40%	16,26,27

TABLE I (Continued)

Phenylacetaldehyde	quant.*, 33%	11,21
β -Phenylpropionaldehyde	quant.*	11
p -Chlorophenylacetaldehyde	quant.*	11
p -Tolylacetaldehyde	quant.*	11
β -Phenylpropional	quant.*	11
Cinnamylideneacetaldehyde	10, 50%	16,26
Malonaldehyde tetraethylacetal	35%	28

Aromatics	Yield	Reference
α -Naphthaldehyde	quant.*, 20,7%	19,21,24
β -Naphthaldehyde	91%	21,29
2,7-Naphthalenedicarboxaldehyde	24.3%	30
Benzaldehyde	97%	11,16,21,27
o-Chlorobenzaldehyde	quant.*	11
m-Chlorobenzaldehyde	53%	31
p-Chlorobenzaldehyde	quant.*	11
o-Tolualdehyde	quant.*, 9%	11,21,24
m-Tolualdehyde	50%	31
p-Tolualdehyde	quant.*, 30,70%	11,19,21
p-Methoxybenzaldehyde	15%	19
m-Trifluoromethylbenzaldehyde	0	32
p-Trifluoromethylbenzaldehyde	26%	33
p-Bromobenzaldehyde	62%	31
p-Iodobenzaldehyde	56,70%	31

TABLE I (Continued)

3-Fluoro-4-methoxybenzaldehyde	63%	34
3-Acetyl-6-methoxybenzaldehyde	39%	35
3,4,5-Trimethoxybenzaldehyde	quant.*, 10-20%	11,36
3-Carbomethoxybenzaldehyde	84%	17
4-Carbomethoxybenzaldehyde	90%	17
3-Carbethoxybenzaldehyde	86%	36
4-Carbethoxybenzaldehyde	86%	17
3-β-Chlorocarbethoxybenzaldehyde	74%	17
4-β-Chlorocarbethoxybenzaldehyde	75%	17
4-(3',5'-Diiodo-4'-methoxyphenoxy) benzaldehyde	55%	37
3,5-Diiodo-4-(2'-methoxyphenoxy) benzaldehyde	55%	38
3,5-Diiodo-4-(3'-methoxyphenoxy) benzaldehyde	75%	39
3,5-Dichloro-4-(4'-methoxyphenoxy) benzaldehyde	75%	40
3,5-Dibromo-4-(4'-methoxyphenoxy) benzaldehyde	80-85%	40
3,5-Diiodo-4-(4'-methoxyphenoxy) benzaldehyde	70-100%	41
3,5-Diiodo-4-(3'fluoro-4'-methoxyphenoxy) benzaldehyde	68%	42
3,5-Diiodo-4-(3',5'-difluoro-4'-methoxyphenoxy) benzaldehyde	72%	42
p-Sulfamylbenzaldehyde	0	43
p-Methylsulfonylbenzaldehyde	68%	44
p-Phenylsulfonylbenzaldehyde	82%	43
4-(4'-Methylphenylthio) benzaldehyde	81%	44
4-(4'-Ethoxyphenylthio) benzaldehyde	82%	44

TABLE I (Continued)

3,5-Diiodo-4-(4'-methoxyphenylthio) benzaldehyde	66%	45
2-Hydroxy-4-methoxybenzaldehyde	good	46
4-Hydroxy-2-methoxybenzaldehyde	good	46
p-Methyl-p'-aldehydo diphenylsulfide	81%	44
p-Ethoxy-p'-aldehydo diphenylsulfide	good	44

Heterocyclics	Yield	Reference
Nicotinaldehyde thiosemicarbazone	83%	45
4-Ethoxymethyl-2-hydroxy-6-methylpyridine-3-carboxaldehyde thiosemicarbazone	10%	45
2-Benzyloxazole-4-carboxaldehyde	88%	47
4-Methylthiazole-5-carboxaldehyde	40%	48

*Yield reported by Henry Stephen

CHAPTER II

EXPERIMENTAL

This chapter is devoted to the preparation of aldimines and their intermediates. The next chapter, Chapter III, will deal with the work carried out which is related but not directly connected to imine synthesis.

Preparation of Stannous Chloride. Stannous chloride dihydrate as obtained commercially usually contained several impurities, the principle one being stannic oxy-chloride. These impurities were most conveniently removed and the salt dehydrated to the pure, anhydrous stannous chloride by the method of H. Stephen (49). The dihydrate was treated with twice the molar volume of acetic anhydride and, after the reaction had subsided, the mixture was cooled. This treatment dehydrated the salt and, since the impurities present were soluble in acetic acid, filtration and thorough washing with anhydrous diethyl ether yielded the pure, dry, halide. The resulting salt was white, finely powdered, and slightly hydroscopic.

Of the methods tried, the salt seemed to keep best under a slight vacuum and in the dark. It remained unchanged for several months under these conditions. If this precaution was not observed, darkening of the salt occurred within a few days.

Preparation of Stannous Bromide. The stannous bromide which was used was prepared by a modification of the method of Wittig and Hartman (16). The bromide was prepared in solution by the reaction of metallic tin and aqueous hydrogen bromide. Water was then gradually distilled from the system until only the molten salt remained at a temperature of 400 to 450°C. The bromide which Wittig and Hartman used was obtained by distilling this mixture at 620°C and collecting the bromide distillate. However, since reactants of high purity were used, it was felt that distillation of the molten reaction mixture was unnecessary. The mixture was poured into a porcelain dish and allowed to cool slowly in a desiccator. On cooling, a dense mass of silver-gray, very large crystals were obtained; after being powdered these were kept in a sealed bottle and in the dark.

Nitriles. Whenever possible, the nitriles needed were obtained commercially. The nitriles obtained in this manner were benzonitrile, phenylacetonitrile, diphenyacetonitrile, o-, m-, and p-tolunitrile, p-aminobenzonitrile, o-, and p-chlorobenzonitrile, 2-cyanopyridine, α-naphthylacetonitrile and α-naphthonitrile. Each of these was purified either by distillation or recrystallization before use.

Preparation of p-Nitrobenzonitrile. This compound was obtained in 90% yield following the procedure developed by C. S. Miller (50). The general method was the transamidation of p-nitrobenzoic acid, followed by dehydration with phosphorous pentachloride.

The compound was also prepared by a modified Sandmeyer reaction. Using the preparation of 2,4 dinitrobenzonitrile by F. R. Storrie (51) as an analogy, the nitrile was prepared using 0.13 moles of potassium

nickelocyanide, 0.12 moles of nitrous acid, and 0.1 moles of p-nitroaniline in a standard Sandmeyer reaction. The potassium nickelocyanide was prepared by mixing a solution of 35 grams of potassium cyanide in 150 ml. of water with a solution of 28.6 grams of nickelous chloride hexahydrate in 50 ml. of water, and cooling the resulting mixture. The yield obtained after recrystallization from acetone was 70%.

Preparation of N-Acetyl p-Aminobenzonitrile. This compound was prepared in 97% yield by treating p-aminobenzonitrile in anhydrous diethyl ether with an excess of acetic anhydride. The product melted at 199 - 200°C.

Preparation of p-Cyanobenzoic Acid. The method of E. P. Valby and H. J. Lucas (52) was followed with only one modification. The general synthesis was a Sandmeyer reaction involving a cuprous chloride-sodium cyanide mixture reacting with diazotized p-aminobenzoic acid. The only change in the procedure was to use, in addition to the theoretical quantity of cuprous chloride, 0.1 mole of cupric sulfate in forming the reactant mixture with sodium cyanide. The result of this variation in procedure is a yield of 82% nitrile (m.p. 216°C) rather than the 45% yield reported. Recrystallization from water resulted in an overall yield of 75% of product melting at 219°C. Analysis based on percent nitrogen by the semimicro Dumas method showed: theoretical, 9.52% N; found 9.65% N.

Preparation of p-Cyanobenzaldehyde. Reaction between p-cyanobenzylbromide and the sodium salt of 2-nitropropane resulted in a 67% yield of this nitrile. The method was developed by H. B. Hass and M. L. Bender (53).

Preparation of Salicylnitrile. The preparation of this nitrile involved the dehydration of salicylaldoxime with acetic anhydride. Following the method of E. Beckmann (54), a 74% yield was obtained.

An attempt was also made to prepare this compound by the dry distillation of a mixture of salicylamide and phosphorous pentoxide. Less than 3% of the nitrile was obtained by this method.

Preparation of o- and p-Trichloromethylbenzonitrile. An 85% yield of o-trichloromethylbenzonitrile was obtained when dry, gaseous chlorine was bubbled into a mixture of one mole of o-tolunitrile and five grams of phosphorous pentachloride at 180°C. After 70 hours, the theoretical quantity of chlorine had been taken up, as shown by the increase in weight of the mixture. The flow of gas was stopped and the mixture was vacuum distilled. The nitrile distilled at 146°C and 0.15 mm. pressure. Final purification was by recrystallization from hot, absolute ethanol.

The melting point shown by this nitrile, 96.5°C, was 1.5°C higher than that previously reported for the compound (55, 56). Analysis of the nitrile by the semimicro Dumas method showed a nitrogen content of 6.32%. o-Trichloromethylbenzonitrile contains 6.34% nitrogen.

p-Trichloromethylbenzonitrile was prepared by bubbling dry, gaseous chlorine into p-tolunitrile at 180°C and under strong light. The light source was a 200 watt, unfrosted, incandescent light bulb held 0.5 inches from the wall of the reaction vessel. The flow of gas was stopped after 40 hours and the mixture was vacuum distilled. The nitrile distillate, after recrystallization from hot, anhydrous ethanol,

represented only 11% of the quantity theoretically possible. The nitrile melted at 209°C. Analysis of the compound by the semimicro Dumas method showed a nitrogen content of 6.39%. p-Trichloromethylbenzonitrile contains 6.34% nitrogen. Hydrolysis of the prepared nitrile produced a compound having a neutralization equivalent of 167; terephthalic acid, the hydrolysis product of p-trichloromethylbenzonitrile, has a neutralization equivalent of 166.

Preparation of 3-Cyanopyridine. A yield of 60% was obtained when this compound was prepared by the dehydration of nicotinamide with phosphorous pentachloride. The amide was thoroughly mixed with a 30% molar excess of the chloride and the reaction initiated by heating the mixture to 50°C. After the initial reaction had subsided, the temperature of the system was gradually raised to 200°C and held there until nothing else distilled. The mixture was then cooled and pyridine (three times the molar amount of PCl_5 used) was slowly added with stirring. The system was again cooled to room temperature and water (twice the molar amount of PCl_5) was added slowly. The nitrile was removed from the mixture by filtration and was thoroughly washed with water. Final purification was by vacuum distillation. The compound melted at 50°C.

Preparation of the Nitrile-Stannic Halide Complexes. There are two general methods by which these complexes can be prepared. The most recent method, developed by Turner (14), gives a homogeneous system which is ideal for kinetic studies of the complex formation but which is somewhat inconvenient for preparative work. This procedure was discussed in Chapter I. The original method of Stephen (11) is still the

more widely used and is, for most purposes, the better of the two. In the system produced by the older procedure the complex which is formed is insoluble, and so may be isolated. It was often very convenient to isolate the stable, solid complex, therefore the Stephen procedure was used throughout this study.

The complex was formed by addition of a nitrile to a mixture of diethyl ether and stannous halide which had been previously saturated with the corresponding hydrogen halide. Conveniently, the ether, salt, and gas formed a liquid complex, so one could be sure of a hydrogen halide saturated system as soon as solid was no longer present in the mixture. At this point the system was composed of a clear, colorless, upper, ethereal layer and a clear, pale yellow, immiscible, lower layer of stannous complex. The nitrile was added with stirring to this two phase mixture; immediate, though not vigorous, reaction was usually apparent. However, even though some reaction did occur on mixing, initial precipitation required from three to ninety-six hours. Once the initial precipitate had formed, the solid accumulated rapidly and was usually completely precipitated within eighteen hours. There was some evidence that resaturation of the mixture after several hours with the appropriate hydrogen halide would push the reaction nearer completion than it would have otherwise gone. For this reason all of the complex mixtures were resaturated with the halide gas at twelve hour intervals until reaction seemed complete.

All of the complexes prepared were stable, crystalline solids. There was no difficulty in filtering, washing, and drying the precipitates, and no change was apparent when they were stored for long periods

of time, if they were dry, under a slight vacuum, and in the dark. Some decomposition of the complexes occurred if they were not completely dried when stored, or if they were stored in colorless bottles and left in the light.

The amount of solid precipitated in the preparation of many of the complexes was near the theoretical amount of complex. However, several workers in the field have shown that the precipitate which forms may not be pure complex, while others have shown that precipitation is not necessarily a criterion of the extent of the reaction. For these reasons all of the yields reported are based only on the amount of starting nitrile and the amount of purified imine actually obtained.

Solvents Used. A variety of solvents were tested for use during the decomposition of the nitrile-stannic halide complex. Among the characteristics of a solvent ideal for this purpose are that it be non-reactive, readily available, easily handled and, most important, that it dissolve imine without dissolving the nitrile complex or tin salts. The compounds tested were: diethyl ether, pyridine, acetone, dimethyl formamide, ethyl formate, and 1,4 dioxane.

Diethyl ether proved to be the most useful of these and was used exclusively. It was available, non-reactive, had a low boiling point, and could be handled with ease. The nitrile-stannic halide complex was insoluble in ether and could be completely freed of the ethereal stannous complex by thorough washing with ether; and yet, when the nitrile complex was decomposed, the imine produced was completely soluble while the residual tin containing products were not. The solvent

was obtained as commercial "anhydrous diethyl ether" and was not treated before use. In the many cases where the ether was reused, if the reaction involved a gas such as ammonia or hydrogen halide, care was taken to use the reclaimed ether only in a reaction of the type from which it had come.

Pyridine, as a weak base, acted not only as a solvent for the imine but also as a very mild decomposition reagent of the nitrile complex. Even with this mild reactivity for the complex, no definite advantage was found in its use.

Acetone proved to be an excellent solvent for imine; some solution of imine occurred even from unreacted complexes, probably due to the solubility of the complexes in the solvent. This solubility of the reaction salts in acetone, however, prevented its use. Although several attempts were made using it as a solvent, no way was found to adequately control salt as well as imine solution in acetone.

Dimethyl formamide seemed to be a fairly good solvent for the purpose, but was not used due to its cost and lack of availability.

Ethyl formate, a superior solvent when the complex was to be hydrolysed to the aldehyde, was not usable here. This was due to its reactivity with strong bases to give the amide. As an example, when an attempt was made to decompose a complex by treatment with ammonia with ethyl formate as the solvent, the complex was not effected but a fine yield of formamide was obtained.

1,4 Dioxane offered no apparent advantages over diethyl ether and was more expensive and less available; consequently it was not used.

Methods of Complex Decomposition. Using the nitrile-stannic

halide complexes of benzaldimine, phenylacetaldimine, diphenylacetaldimine, and p-tolualdimine a variety of decomposition methods were tested in an effort to find one which would be general for aldimine preparation. In each case anhydrous diethyl ether was used as the solvent. The results of these tests are summarized in Table II.

Ammonia did not seem to be a strong enough base for complete complex decomposition. In the case of benzaldimine, some reaction with the complex did occur, but the equilibrium was far to the side of the complex. The reagent was useful however when the intermediate was not isolated from the system, but was decomposed immediately after precipitation. In this case the large excess of hydrogen halide in the system was first removed by reaction with anhydrous ammonia; the complex could then be decomposed with a minimum of reagent.

Triethylamine was the best and most general reagent found for the nitrile-stannic halide decomposition. By its use benzaldimine could be isolated in nearly quantitative yields and fairly complete decomposition of the other intermediates could be shown in every case tried. In many of these preparations, because of the reactivity of the imine, it was necessary to measure the completeness of decomposition on the basis of indirect evidence. In these instances the amount of polymer formed or the amount of aldehyde which could be formed by hydrolysis of either the imine or complex residue mixture was taken as a measure of the extent of the decomposition. The only disadvantage found with the use of triethylamine was that since it was an amine, it reacted very similarly to an imine. Although in some procedures this complicated separation of the two compounds after the imine was generated, it was not a

TABLE II

COMPARISON OF AGENTS FOR ALDIMINE COMPLEX DECOMPOSITION

Agents Used For Complex Decomposition	Complexes Tested*	Results
Ammonia	B	3% yield of imine
	P	Only a trace of imine freed from the complex
Triethylamine	B	Near quant. yield
	P	Good yield of imine polymer
	dP	Good yield of imine polymer
	pT	5-10% yield of imine
Tributylamine	B	Good yield but azeotrope formed with the imine
	P	Good yield but azeotrope formed with the imine
Sodium Methoxide	B	Some imine freed but residue hard to handle
Sodium Ethoxide	B	Complex decomposition incomplete
Pyridine	B	Complex decomposition incomplete
Diethylamine	B	Complex decomposition incomplete
Ethylenediamine	P	Good yield of imine polymer
	pT	5-10% yield of imine
Dimethylformamide	B	Complex decomposition incomplete
Hydrogen Sulfide	B	Decomposition slow and incomplete
Silver Acetate	B	Good yield and easily handled residue
Sodium Acetate	B	Yield very good
	pT	Yield of polymer good
Sodium Iodide	B	Decomposition occurs but imine difficult to isolate

TABLE II (Continued)

Heat and Vacuum	B	Poor yield
	P	No imine obtained

*Symbols: B - benzaldimine complex
P - phenylacetaldimine complex
dP - diphenylacetaldimine complex
pT - p-tolualdimine complex

major problem, since separation by distillation was usually relatively easy.

In some ways the use of tributylamine had definite advantages over use of the triethyl compound; the reaction was slower and more easily manageable and the salt residue was more crystalline. However, purification could not be so easily accomplished by distillation since this amine boiled 124°C higher than triethylamine and, most important, since it formed azeotropes with the two imines on whose complexes it was tried.

Sodium methoxide reacted vigorously with the stannic complexes and some imine was released, but the residue formed was so difficult to handle that the method showed no obvious advantages. Sodium ethoxide also reacted vigorously, but the imine which was generated was still combined with a tin containing compound. This new imine complex, or compound, was so reactive and impure that the method was abandoned.

Diethylamine reacted very vigorously with a complex of this type and continued to react until a 5 to 6 times molar quantity had been added. The reaction was very hot, a flammable gas was given off, and the solid complex increased in volume by a factor of two to three. Only a trace of imine was freed.

Ethylenediamine was tried in an attempt to replace the imine in the stannic complex. The ability of this amine to form stable complexes coupled with its basic properties made the compound seem ideal for the purpose. While some imine was obtained, the greater part of the stannic complex only added ethylenediamine rather than undergoing a replacement reaction with it. A large volume of flammable gas was

given off in this reaction.

Imine could be generated fairly effectively by suspending the complex in rapidly stirred dry ether and bubbling in dry hydrogen sulfide. The primary difficulties here were that the decomposition was slow, requiring resaturation with hydrogen sulfide over several days, and was likely to be incomplete.

A similar method of attack and a much better one was the use of silver acetate. This salt was readily soluble in dry ether, reacted rapidly, and gave an easily filterable, voluminous residue. The yields of imine were very good, approaching those obtained from the use of triethylamine. Unfortunately, five to six molar proportions of silver salt per molar amount of complex were required for the reaction.

Anhydrous sodium acetate was an effective agent for the decomposition of the stannic complex and gave a decomposition residue which was easily handled. The yields obtained were nearly as good as the ones produced using the triethylamine. However, some agent introduced by this salt seemed to aid polymer formation and so made purification by distillation more difficult. The polymers obtained when this salt had been used had a wine-red color not present in those produced from imine obtained by other methods.

An attempt was made to use sodium iodide in the same way that sodium acetate had been used. The method was extremely unsatisfactory. Although complex decomposition occurred, it was not possible to isolate any imine because of the mixture which was formed with it.

Some complex decomposition occurred when the intermediate was suspended in a high boiling liquid, such as mineral oil, under a pressure

of one millimeter or less and was heated until something distilled. If heating was slow and the mixture was stirred during heating, some imine was obtained, but was always impure due to codistillation of tin containing compounds. The method was relatively awkward and slow, and the yields were very low.

Benzaldimine. This compound was prepared by decomposing a benzonitrile-stannic chloride complex under anhydrous conditions. The complex was formed by saturating an anhydrous diethyl ether solution of stannous chloride with hydrogen chloride and adding benzonitrile. The molar amount of nitrile added was one-third the molar amount of salt used. After 6.5 hours 50% of the theoretical quantity of the intermediate had precipitated. It was found that by saturating the system with hydrogen chloride about six hours after addition of the nitrile it was possible to isolate a 90% yield of the dry, ether washed, complex.

Decomposition of the intermediate by a number of methods was possible. A yield of 70% or over of imine was isolated when the dry complex was placed in ether and decomposed by triethylamine, tributylamine, silver acetate, sodium acetate, or hydrogen sulfide. When the complex was not isolated but decomposed immediately in the same system, a yield of 93.9% was obtained. In this case the excess hydrogen halide was reacted with ammonia before decomposition of the complex with triethylamine was carried out. The molar amount of triethylamine used was five times that of the nitrile. Since on hydrolysis the decomposition residue gave positive tests for aldehyde, it may be possible by modifying this procedure to obtain an even higher percent of imine from

the reaction.

The physical constants obtained for benzaldimine are shown in Table III and the infra-red spectrum in Spectrum I. Using these physical constants in the Lorentz-Lorenz formula of molar refraction a deviation of only 0.63% from the value given by the sum of molar refractive equivalents was obtained. The refractive equivalent value for the double bonded nitrogen is not presented in most tables; the value obtained by P. L. Pickard and coworkers (57), 3.129, was used for this calculation. The derivatives of benzaldimine which were prepared are shown in Table IV.

Since the physical constants of the compound differed somewhat from those given by previous workers, a very careful analysis of the product imine was made. Determination of the degree of alkalinity was made by the method of Iddings (58); this involved nonaqueous potentiometric titration of the imine in glacial acetic acid by perchloric acid in glacial acetic acid. The equivalent weight of the imine by this method was 105; benzaldimine would show an equivalent weight of 105. The percent nitrogen in the compound was determined by the semimicro Dumas method. This analysis showed nitrogen content to be 13.48%; theoretical nitrogen content of benzaldimine is 13.46%.

It had been observed that on long standing or when subjected to excessive heat a benzaldimine sample would become faintly colored and show a change in refractive index. A short but interesting study was made to determine what the change was and how it could be promoted. When the colored substance was isolated it proved to be a sticky, brown polymer-like material which formed a glass-like substance with further

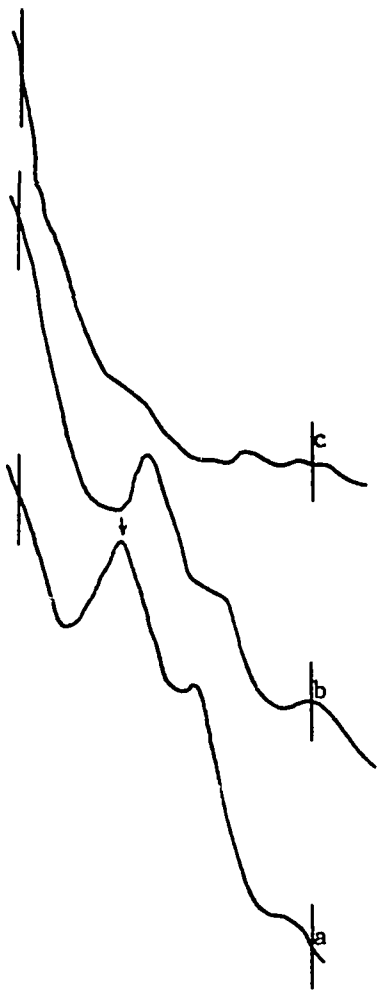
heating. On the assumption that this material was a polymer, a comparison of infra-red spectra was made. The samples compared were purified imine, imine which had been held at its boiling point at atmospheric pressure for one minute, and imine to which a very tiny particle of free radical former, benzoyl peroxide, had been added at room temperature and which had then been heated and held at its boiling point at atmospheric pressure for one minute. After four hours at room temperature the purified imine was unchanged, the heated imine was still clear but pale brown in color, and the imine treated with both peroxide and heat was clear but dark brown in color. The spectra of the three samples taken at this time were super-imposable except for the four portions of the spectrum which are shown in Figure I. The variations in these spectral portions seemed to show that the reaction of the two treated samples was of the same type and differed only in degree. These spectra proved nothing, but were perhaps indications of a free radical mechanism of imine polymerization.

Phenylacetaldimine. Nonaqueous decomposition of a phenylacetonitrile-stannic chloride complex produced a solution of this aldimine. The complex was formed by reacting a diethyl ether solution of stannous chloride saturated with hydrogen chloride with phenylacetonitrile. When the molar amount of nitrile was one-third the molar amount of the salt used, it was possible to isolate 79.8% of the theoretical amount of the complex. No difficulty was encountered in decomposing this nitrile complex, as shown by hydrolysis of the decomposition residue, but, although many attempts have been made to isolate the imine, none has been obtained in pure form. The presence of the

FIGURE I

COMPARISON OF INFRA-RED ABSORPTION SPECTRA OF

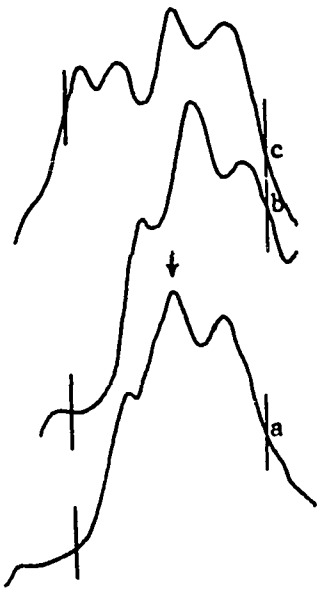
BENZALDIMINE AND ITS POLYMERS



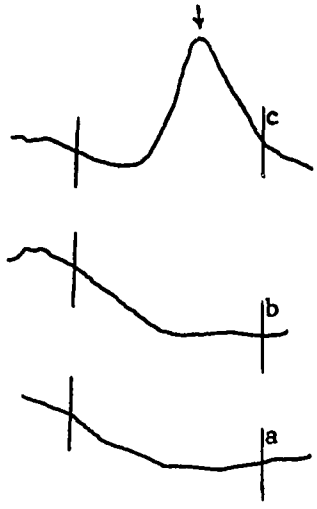
Section 1. Peak at 3.33 , =N-H Stretching vibration

Section 2. Peak at 5.84 , -C=N- Stretching vibration

FIGURE I (Continued)



Section 3. Peak at 8.47



Section 4. Peak at 11.85 , may be the peroxide O-O stretching vibration

All other portions of the spectra were superimposable. The entire spectrum of benzaldimine is shown in Figure II.

a - pure benzaldimine
b - benzaldimine treated with heat
c - benzaldimine treated with free radical contributor and heat

imine in solution has been shown by the preparation of a number of derivatives. These are given in Table IV. However, as soon as the compound was concentrated, it began to polymerize. It was possible to distill a fraction of the aldimine before it all polymerized, but even this fraction showed evidences of polymer formation within an hour. The physical constants obtained from this fraction immediately after distillation are shown in Table III. Although it is possible that small amounts of impurities were entrained in the collection of the fraction, these constants probably are those of the pure imine. Yield of this compound, if calculated on the weight of polymer obtained, would be 70% or better.

The ease of polymerization of phenylacetaldimine, even at room temperature, is not surprising. Due to the volatility of tin compounds, even a carefully distilled fraction of the imine might easily have contained a trace of tin salt, an excellent polymerization agent. Another and probably more important factor is the similarity of structure between phenylacetaldimine and styrylamine. It seems likely that there would be some equilibrium between the tautomers, expecially since the amine is the conjugated form. Any tendency toward such an equilibrium would explain polymerization of the entire sample.

The polymer which was formed was a translucent, brown, easily fractured, glass-like material which was soluble in many organic solvents. Refluxing the material in an acidified aqueous medium resulted in a near quantitative yield of the aldehyde; refluxing in non-aqueous solvents changed the form of the polymer (often to large crystals), but no imine was obtained.

In an attempt to reduce polymerization a trace of hydroquinone was added before distillation of a phenylacetaldimine mixture. Polymerization was less rapid than without the hydroquinone, but did occur. However, the form of the polymer which resulted was changed; this polymer was a dark brown viscous liquid which would not crystallize.

Diphenylacetaldimine. The complex from which this compound was obtained was prepared by reaction of an ether solution of stannous chloride saturated with hydrogen chloride with diphenylacetonitrile. The ratio of stannous salt to nitrile was 3:1. Following precipitation of the complex the free hydrogen halide was removed from the system by sweeping with anhydrous ammonia. The complex was decomposed with triethylamine. The molar quantity of amine was twice that of nitrile used. After recrystallization from anhydrous methanol a 6% yield of the imine was obtained. The decomposition of the complex was shown to be incomplete by the amount of aldehyde obtained from the hydrolysis of the decomposition residue. Had a larger amount of triethylamine been used, a much larger amount of imine might well have been freed.

o-Tolualdimine. The o-tolunitrile stannibromide complex of this aldimine precipitated from the reaction mixture very slowly. After initial addition of the nitrile to the ethereal stannous bromide mixture the solution was saturated with hydrogen bromide at 24 hour intervals, but only 30% of the theoretical amount of complex had precipitated after eight days. This failure to precipitate did not indicate a failure to react, however, for when the filtrate of the complex mixture was reduced in volume by distillation a large amount of impure complex was obtained. Decomposition of this complex with a

four times excess of triethylamine resulted in the isolation of 11.2% of the theoretical quantity of imine monomer. Final purification of the monomer was accomplished by formation and isolation of the imine hydrochloride followed by regeneration of the imine with liquid ammonia. If the polymeric material isolated is considered to represent an equal weight of monomer, overall yield for the reaction was 21.3%.

The physical constants of the monomer are presented in Table III, while those of the derivatives prepared are in Table IV. These constants used in the Lorentz-Lorenz equation for molar refraction give a variation from the theoretical value of summed refractive equivalents of only 0.45%. Spectrum II shows the infra-red spectrum of this compound.

Analysis of the prepared o-tolualdimine for nitrogen content by the semimicro Dumas method showed the compound to contain 11.84% nitrogen. o-Tolualdimine theoretically contains 11.76% nitrogen. Analysis for total alkalinity showed a molecular weight of 120; that of o-tolualdimine is 119.

m-Tolualdimine. The complex of this imine was isolated in 98% yield. It was formed from an ether solution of stannous chloride saturated with hydrogen chloride and one-third of this molar amount of m-tolunitrile. Although several decomposition agents such as diethyl and triethylamine were used, no way was found to decompose the complex and isolate the imine. The decomposition step was easy, but polymerization prevented isolation of the product.

The derivatives of the complex which were prepared are listed in Table IV.

p-Tolualdimine. This aldimine was prepared both from a stannic chloride and stannic bromide complex. In each case the molar amount of halide used was three times the molar amount of the nitrile used. The bromide complex was the only one isolated; a 70% yield was obtained. Decomposition of the complexes by triethylamine (five times the molar amount of nitrile used) was fairly complete, but isolation of the imine was difficult. Polymerization occurred easily. The aldimine was isolated in only 8.4% yield, but has been isolated as a derivative in 25% yield. If the weight of the polymer is considered as weight of pure imine, the yield would be 70% or more.

The physical constants of p-tolualdimine are given in Table III and the derivatives prepared are listed in Table IV. Using these physical constants in the Lorentz-Lorenz equation for molar refraction, a variation of only 1.22% from the summed refractive equivalents is observed. The infra-red absorption spectrum is shown in Spectrum III.

Analysis of p-tolualdimine for nitrogen content by the semi-micro Dumas method showed 11.88% nitrogen. p-Tolualdimine contains 11.76% nitrogen.

The polymer which the imine formed was a soft, sticky, brown semi-solid which hydrolysed to give a high yield of p-tolualdehyde. In non-aqueous solvents no imine was obtained on refluxing, but a change of form was often noted. Anhydrous methanol as the reflux solvent led to the formation of large well formed octahedral crystals.

p-Nitrobenzaldimine. When p-nitrobenzonitrile was added to an ether solution of stannous bromide saturated with hydrogen bromide, reaction was immediate and vigorous. A large amount of yellow solid

was quickly precipitated. When this solid complex was decomposed with triethylamine, a very good yield of p-aminobenzonitrile was obtained. Only a trace of imine was present. This preparation was repeated several times varying conditions in an attempt to obtain the imine; only the p-amino compound resulted.

p-Aminobenzaldimine. An ether solution of stannous bromide saturated with hydrogen bromide reacted vigorously with p-aminobenzonitrile. Precipitation of a complex was immediate but neither imine nor aldehyde were obtained from attempted decomposition of the compound. Evidently a complex had formed with the amino nitrogen which in some way deactivated or protected the nitrile group.

N-Acetyl p-Aminobenzaldimine. N-Acetyl p-aminobenzonitrile was treated in the same way as the unsubstituted nitrile, and with about the same results. Although precipitation was not as quick, this solid, like the unsubstituted complex, seemed to have the nitrile group still intact. No method was found to treat or decompose the complex in such a way as to yield either imine or aldehyde.

o-Chlorobenzaldimine. Addition of o-chlorobenzonitrile to an ethereal solution of stannous bromide saturated with hydrogen bromide produced immediate reaction; precipitation began after only three hours. The mixture was saturated with hydrogen bromide at 24 hour intervals for seven days; 72% of the theoretical amount of complex had precipitated by this time. Decomposition of the complex with triethylamine resulted in the isolation of 21.8% of the theoretical amount of imine. No polymer was obtained.

Physical constants of the imine and its derivatives are listed

in Tables III and IV respectively. A variation of only 0.03% from the theoretical value of summed refractive equivalents is given by use of these constants in the Lorentz-Lorenz equation for molar refraction. The infra-red spectrum is shown in Spectrum IV.

Analysis of the imine for total alkalinity by the method of Iddings showed an equivalent weight of 139; the equivalent weight of o-chlorobenzaldimine is 139.5. Nitrogen analysis by the semimicro Dumas method showed a nitrogen content of 10.07%. Nitrogen content of o-chlorobenzaldimine is 10.03%.

p-Chlorobenzaldimine. The stable intermediate of this compound was formed by reaction of p-chlorobenzonitrile with an ether solution of stannous bromide saturated with hydrogen bromide. The molar amount of nitrile used was one-third the molar concentration of the stannous salt. A 99% yield of the complex was obtained when the complex mixture was regularly saturated with hydrogen bromide over a period of ten days.

Following decomposition of the complex the imine was isolated as the hydrochloride in 72% yield. The solid imine was regenerated from this salt by the action of liquid ammonia. Final purification was by sublimation.

The physical constants of this aldimine are given in Table III and the infra-red spectrum in Spectrum V. The derivatives which were prepared are listed in Table IV.

Analyses for the percent nitrogen of the compound by the semimicro Dumas method showed a content of 10.00%. Nitrogen content of p-chlorobenzaldimine is 10.03%. The equivalent weight determined by

the non-aqueous titration method of Iddings is 140. The equivalent weight of p-chlorobenzaldimine is 139.5.

2- and 3-Aldiminopyridine. Addition of 2-cyanopyridine to an ethereal solution of stannous bromide saturated with hydrogen bromide resulted in a vigorous reaction and immediate precipitation of a yellow, crystalline solid. The weight of the solid an hour after the addition of the nitrile was greater than the theoretical amount of nitrile stannibromide complex which could have been formed. Saturation with hydrogen bromide of an ethereal mixture of this solid at regular intervals over a period of four days made no apparent change. Neither aldehyde nor imine was obtained from the yellow substance in any but trace amounts. It seemed probable that this nitrile had been complexed by the reaction mixture without affecting the cyano group in much the same way as the p-aminobenzonitrile previously described.

There was no significant difference between the reaction of the 2- and 3-cyanopyridines when treated in this way. Although a careful study was not made, on hydrolysis the 3-cyano complex seemed to yield slightly larger amounts of aldehyde than did the 2-cyano complex. This quantity of aldehyde was still too small, however, to justify further work.

p-Aldiminobenzoic Acid. The intermediate complex of this aldimine formed from reaction of p-cyanobenzoic acid and a hydrogen bromide saturated diethyl ether solution of stannous bromide was obtained in 95% yield. The ratio of salt to nitrile used was 3:1; the mixture was saturated with hydrogen bromide at 24 hour intervals for three days before filtration of the complex. Decomposition of the

complex was accomplished with a four times excess of triethylamine; the yield of imine monomer obtained was 26.6%. No polymer was isolated.

The physical constants of the monomer are shown in Table III, those of the derivatives of the monomer in Table IV, and the infra-red spectrum in Spectrum VI. Use of these physical constants in the Lorentz-Lorenz equation for molar refraction shows a deviation of 1.72% from the value obtained by summing the refractive equivalents of the molecular parts. The experimental value for the refraction was 41.2, while the theoretical one was 40.51. The difference between the two is small and the percent variation compares favorably with other work, but even this small variation has a possible, and reasonable, explanation. If the addition of a carboxyl group to the benzaldimine molecule at the para position is considered an extension of conjugation in the molecule, and it normally is, then an optical exaltation would be predicted by theory (59). Since the variation between values is an exaltation, the experimental value seems to be vindicated.

Analysis by the semimicro method of Dumas showed the imine monomer to contain 9.40% nitrogen. p-Aldiminobenzoic acid contains 9.39% nitrogen. Attempts to obtain an equivalent weight by the determination of relative alkalinity of the compound were unsuccessful.

p-Aldiminobenzaldehyde. The intermediate complex of this imine was prepared using a nitrile to salt ratio of 3:1. Only 0.1 mole of the nitrile was available for use, consequently the amount of solid precipitating from the reaction mixture was not great. Four days after addition of the nitrile, triethylamine was added to the mixture

until decomposition was complete. The amount of amine used in the composition was three times the amount of nitrile used in complex formation. No aldimine was isolated. However, it was possible to prepare derivatives of terephthalaldehyde from the decomposition filtrate. These derivatives are presented in Table IV.

It is surprising that at least some aldimine was not isolated. The reason seemed to be a failure in complex formation. Infra-red spectra of the decomposition filtrate showed the presence of a relatively large amount of nitrile.

∝ -Naphthaldimine. Addition of 0.1 moles of ∝ -naphthonitrile to 0.3 moles of ethereal stannous bromide complex resulted in immediate reaction, but precipitation did not occur for three days. The complexes of all the other imines prepared were white or pale yellow, but that of ∝-naphthaldimine was a bright medium green. The complex mixture was saturated daily with hydrogen bromide but after six days only 15.4% of the theoretical amount of the complex had precipitated. The entire reaction mixture along with the precipitated solid was subjected to decomposition by triethylamine. The imine was isolated in 49.5% yield.

Nitrogen analysis by the semimicro Dumas method showed a nitrogen content of 9.01%. ∝ -Naphthaldimine contains 9.03% nitrogen. Physical constants of the compound are shown in Table III. The derivatives which were prepared are listed in Table IV.

∝ -Naphthylacetaldimine. A molar ratio of ∝ -naphthylacetonitrile to ethereal stannous complex of 1:3 was used in forming the stannic complex of this aldimine. The mixture was saturated daily

with anhydrous hydrogen bromide, but after eight days only 1.3% of the theoretical quantity of the yellow complex had precipitated. Decomposition of the stannic complex was accomplished by addition of an excess of triethylamine to the complex reaction mixture. The imine was isolated from the decomposition filtrate as the hydrochloride, and, after thorough washing of the salt with diethyl ether, was regenerated with liquid ammonia. A yield of 23% was obtained.

The physical constants of α-naphthylacetaldimine are given in Table III and the derivatives prepared are listed in Table IV. The infra-red spectrum is shown in Spectrum VII. Analysis of the aldimine for nitrogen content by the semimicro Dumas method showed 8.33% nitrogen. α-Naphthylacetaldimine contains 8.28% nitrogen.

o-Trichloromethylbenzaldimine. Although a 3:1 mixture of stannous complex and o-trichloromethylbenzonitrile had been saturated daily with hydrogen bromide, no stannic complex had precipitated after five days. This mixture was treated with an excess of triethylamine and the decomposition products were very thoroughly washed with dry ether. When the decomposition filtrate was reduced in volume, a large amount of dark brown, imine containing material was obtained. After distillation of this substance, the aldimine fraction was further purified by preparation and isolation of the imine hydrochloride. The imine was regenerated with liquid ammonia. A yield of 44% was obtained.

The physical constants of o-trichloromethylbenzaldimine are given in Table III. The derivatives of the imine and its hydrolysis product are given in Table IV. The infra-red spectrum of the compound is given in Spectrum VIII.

Analysis by the semimicro Dumas method showed a nitrogen content for the prepared aldimine of 5.87%. Determination of the total alkalinity for the compound by the method of Iddings showed an equivalent weight of 220. o-Trichloromethylbenzaldimine contains 5.84% nitrogen and has an equivalent weight of 222.5.

p-Trichloromethylbenzaldimine. p-Trichloromethylbenzonitrile was insoluble in diethyl ether, but, on addition of the compound to three times its molar quantity of ethereal stannous bromide complex, solution was immediate. Reaction was not vigorous but precipitation occurred within 15 minutes of the addition of the nitrile. On isolation four hours after initial precipitation the yellow precipitate weighed twice the theoretical amount of the complex. Decomposition of this solid with triethylamine resulted in the isolation of about 1% of the theoretical amount of aldimine. This small yield was not due to lack of decomposition agent for a three times molar excess of amine was used initially on decomposition. After the small amount of imine resulting became apparent, further decomposition of the initial decomposition precipitate was attempted with no effect. A possible explanation for this small yield may be the insolubility of the imine in diethyl ether. Since p-trichloromethylbenzonitrile is very insoluble in diethyl ether, one would not expect the imine to be very soluble in this solvent. Tests with the isolated imine support this conclusion. It seems possible that more of the aldimine was formed in the reaction mixture but was simply not removed by the solvent.

Insufficient quantities of the compound were prepared to make analysis possible. The melting point of the compound is shown in

Table III and those of its derivatives are shown in Table IV.

Preparation of Derivatives. As a step in the identification and characterization of the aldimines a series of derivatives were prepared. These were of two types. One group was prepared from the imine itself; the other was of the hydrolysis product, the corresponding aldehyde, of the imine. These derivatives are listed in Table IV.

Four imine derivatives were prepared; these were the hydrochlorides, benzenesulfonamides, oxalates, and phenylthioureas.

The imine hydrochlorides were prepared by mixing equal volumes of ether saturated with hydrogen chloride and a dilute ethereal imine solution. Precipitation was immediate. The precipitates were thoroughly washed with anhydrous ether and dried under vacuum.

The benzenesulfonamide derivatives were prepared by mixing equal parts of benzenesulfonyl chloride and a 1:1 solution of absolute ethanol and imine, and warming the mixture. The mixture was cooled after five minutes to 0°C, and a 10% sodium hydroxide solution was added slowly and with shaking until reaction ceased. The derivatives were recrystallized from ethanol.

Oximides were prepared by boiling a 2:1 mixture of ethyl oxalate and imine for two minutes. The product was recrystallized from ethanol.

In preparing the phenylthiourea derivatives equal parts of phenyl isothiocyanate and imine were mixed, and the mixture was boiled for two minutes. The mixture was then cooled to 0°C, filtered, and washed with ligroin and 50% ethanol. Recrystallization was from 95% ethanol.

TABLE III

PHYSICAL CONSTANTS OF THE PREPARED ALDIMINES

Imine	M.P. °C	B.P. °C/mm	d_4^{20}	n_D^{20}
Benzaldimine		58/4	0.9799	1.5259
Phenylacetaldimine		212/731		1.5251
Diphenylacetaldimine	129			
o-Tolualdimine		192/734	0.9586	1.5212
p-Tolualdimine		35/1.1	1.002	1.5358
o-Chlorobenzaldimine		177/733	1.1912	1.5589
p-Chlorobenzaldimine	48			
p-Aldiminobenzoic Acid		182/733	1.0505	1.4927
∝ -Naphthaldimine	37	267/734		
∝ -Naphthylacetaldimine	85	115/728		
o-Trichloromethylbenzaldimine	112	208/728		
p-Trichloromethylbenzaldimine	135			

Because of the ease of hydrolysis of aldimines, hydrolysis of the imine prior to the preparation of an aldehyde derivative was not necessary. The aldimines were simply mixed with aqueous solutions of the reagents as if they had been already hydrolysed to the aldehyde. The aldehyde derivatives which were prepared are the 2,4 dinitrophenylhydrazones, the semicarbazones, and the oximes. These were prepared according to the directions on derivative preparation in Shriner and Fuson's "Identification of Organic Compounds" (60).

Infra-red Spectra. In recording the infra-red spectra of the aldimines two instruments were used. Spectra I - VIII were recorded on a Perkin-Elmer Infracord Spectrophotometer. This instrument has the advantage of being quick and easy to use and records the absorption spectrum in a space only 9.5 inches in length. Although this short recording space lessens the resolution of the spectrum, the recorded spectrum is much easier to handle and resolution is still sufficient for all but quantitative spectral studies. In the benzaldimine polymerization study previously described greater resolution of the absorption spectra was desirable in order that any change in the reaction mixtures would be easily apparent. For this reason these spectra were recorded using a Perkin-Elmer Infra-red Spectrometer, model 12c. Only the four points of variation in the spectra of the reaction mixtures are shown in Figure I because the spectral recordings are 4.5 feet in length. The entire benzaldimine spectrum is shown in Spectrum I.

The spectrum of p-tolualdimine, Spectrum III, was recorded from a carbon tetrachloride solution of the imine. All other spectra

TABLE IV

DERIVATIVES OF THE PREPARED ALDIMINES

Imine	Derivatives* (M.P.°C)						
	A	B	C	D	E	F	G
Benzaldimine	235-6	203	222	35			
Phenylacetaldimine	110	173	153-4		84-86		
Diphenylacetaldimine				120			
o-Tolualdimine	193	239	212				225d
m-Tolualdimine	194		203-5		200	200	
p-Tolualdimine	234		233			212d	
o-Chlorobenzaldimine	206	111	226				
p-Chlorobenzaldimine	264d	226	230			149	
o-Trichloromethylbenzaldimine	111	194					212
p-Trichloromethylbenzaldimine	112	172		209			
p-Aldiminobenzoic Acid	287d	237	199	209			
p-Aldehydobenzaldimine	278d			155			
α -Naphthaldimine		195	221	98			292
α -Naphthylacetaldimine		65	208	118-9			223

* A - 2,4 Dinitrophenylhydrazone
B - Hydrochloride
C - Semicarbazone
D - Oxime
E - Benzenesulfonamide
F - Oximide
G - Phenylthiourea
d - with decomposition

were recorded using the pure aldimine.

It has been reported (61) that the characteristic absorption bands of the imine group, the -C=N-, and =N-H absorption bands, fall in the ranges 5.7 - 5.8μ and 3.3 - 3.5μ respectively when recorded from secondary imines. It is of interest that only a very small shift from the ketimine absorption bands is shown by the aldimine spectra. This shift is in the direction of 3μ.

FIGURE II

SPECTRUM I - INFRA-RED ABSORPTION SPECTRUM OF BENZALDIMINE

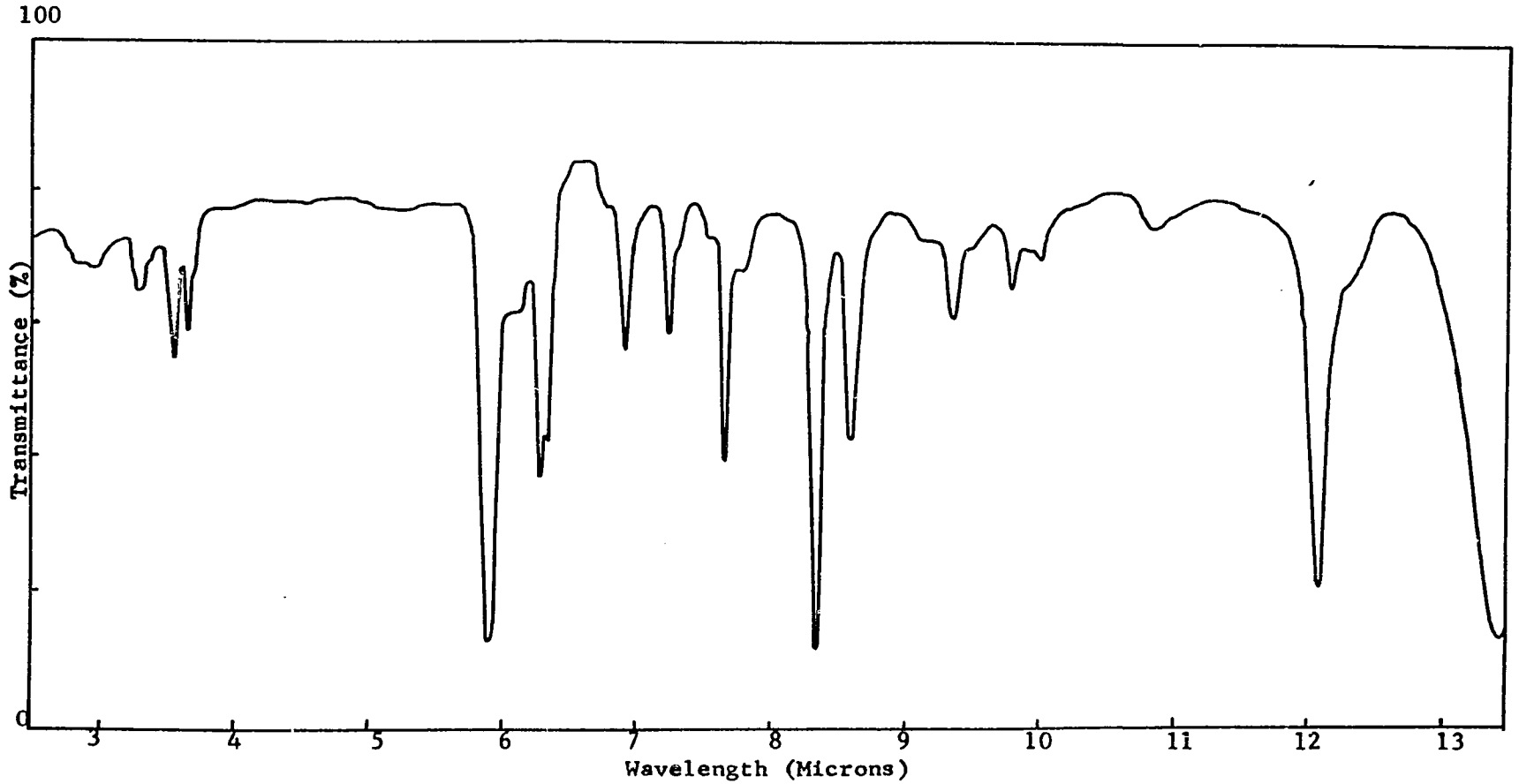


FIGURE III

SPECTRUM II - INFRA-RED ABSORPTION SPECTRUM OF o-TOLUALDIMINE

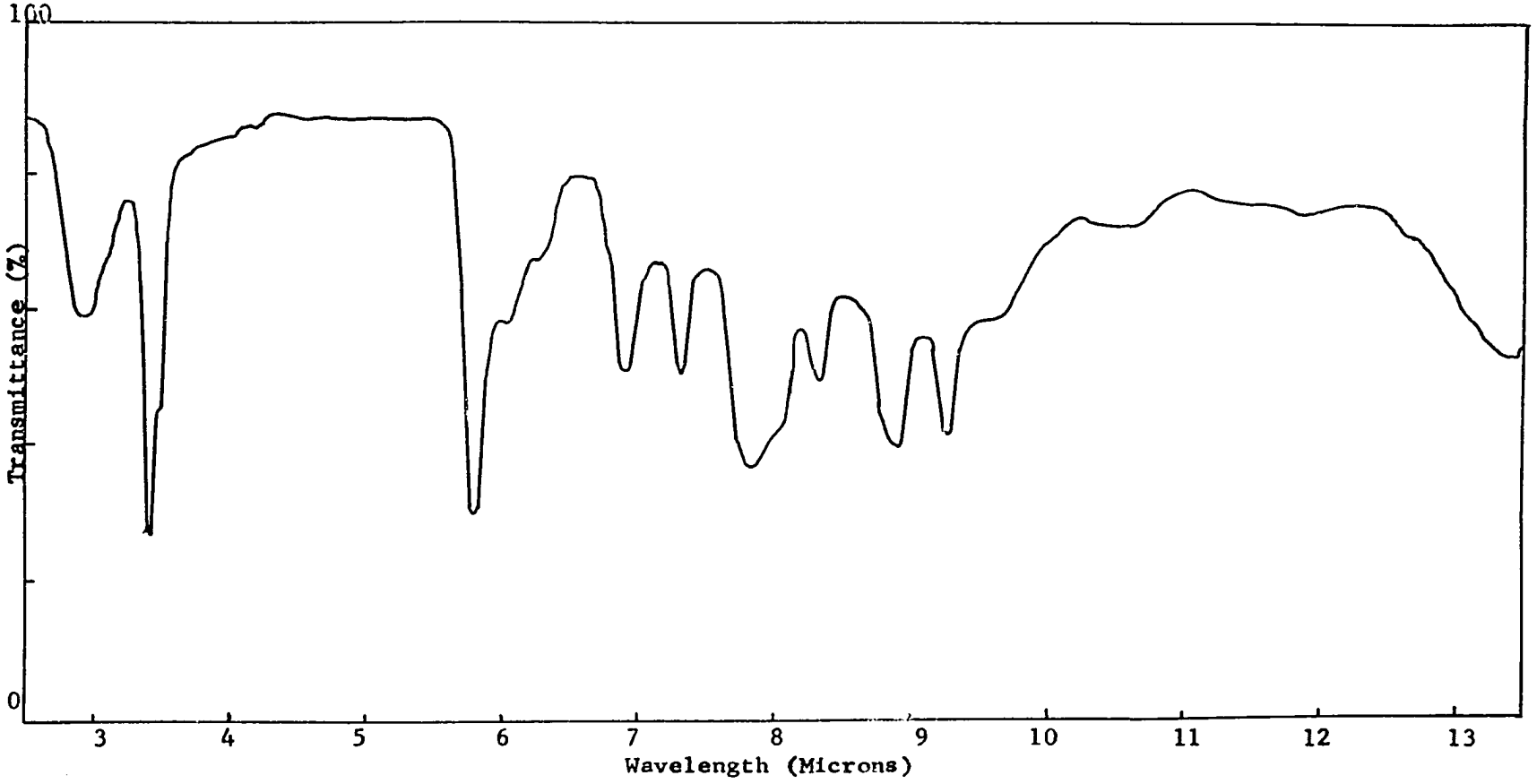


FIGURE IV

SPECTRUM III - INFRA-RED ABSORPTION SPECTRUM OF p-TOLUALDIMINE

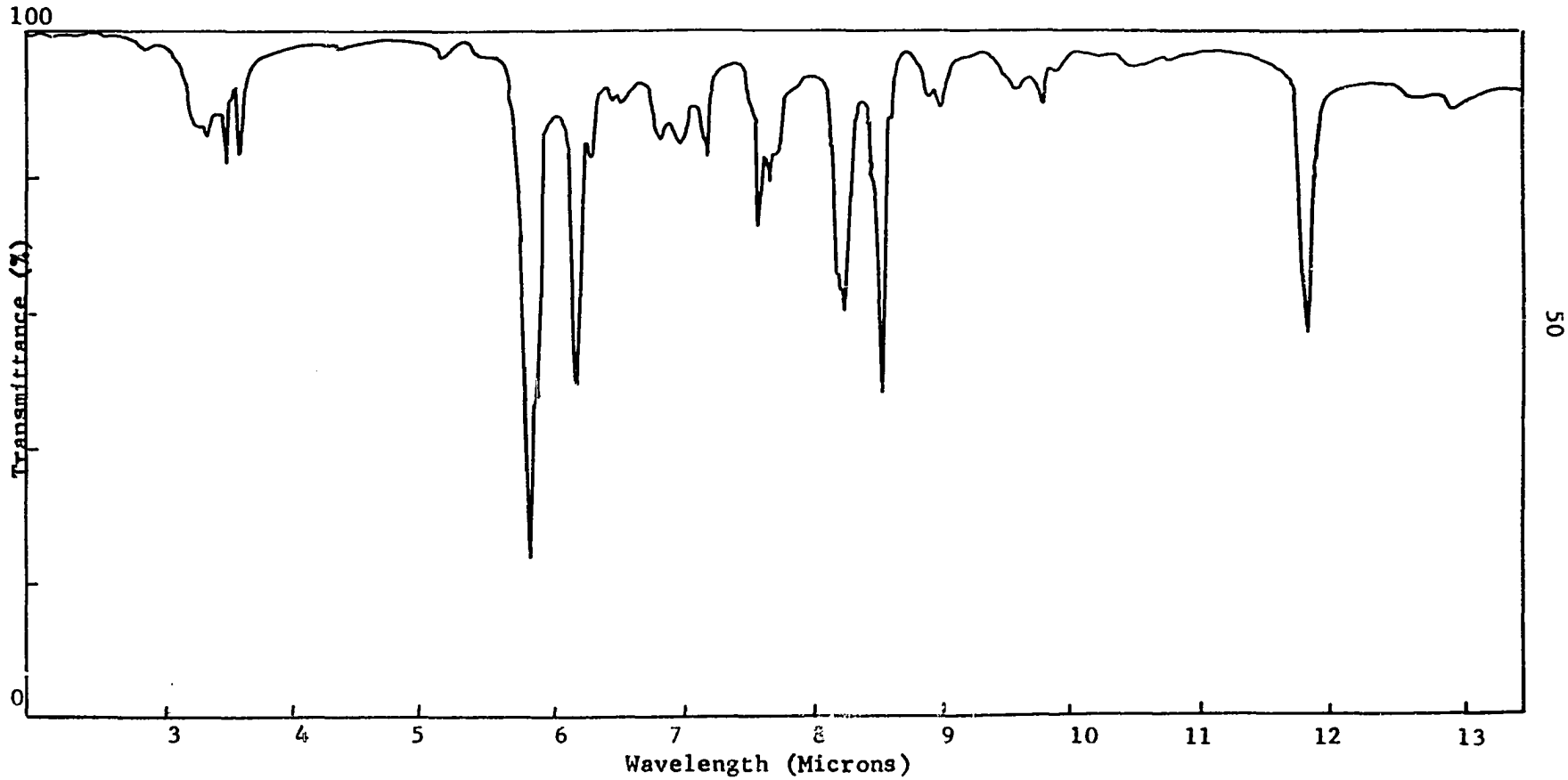


FIGURE V

SPECTRUM IV - INFRA-RED ABSORPTION SPECTRUM OF o-CHLOROBENZALDIMINE

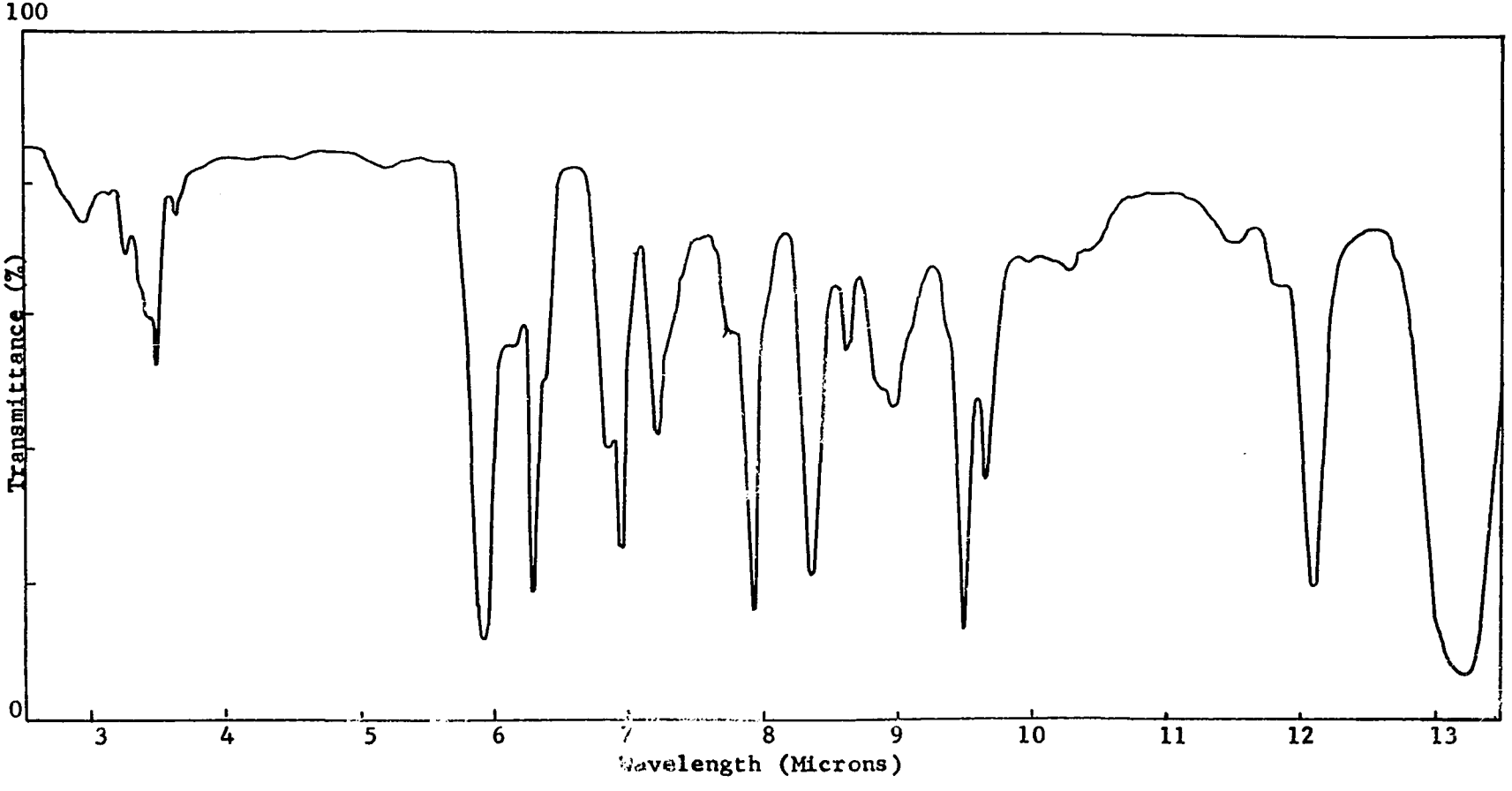


FIGURE VI

SPECTRUM V - INFRA-RED ABSORPTION SPECTRUM OF p-CHLOROBENZALDIMINE

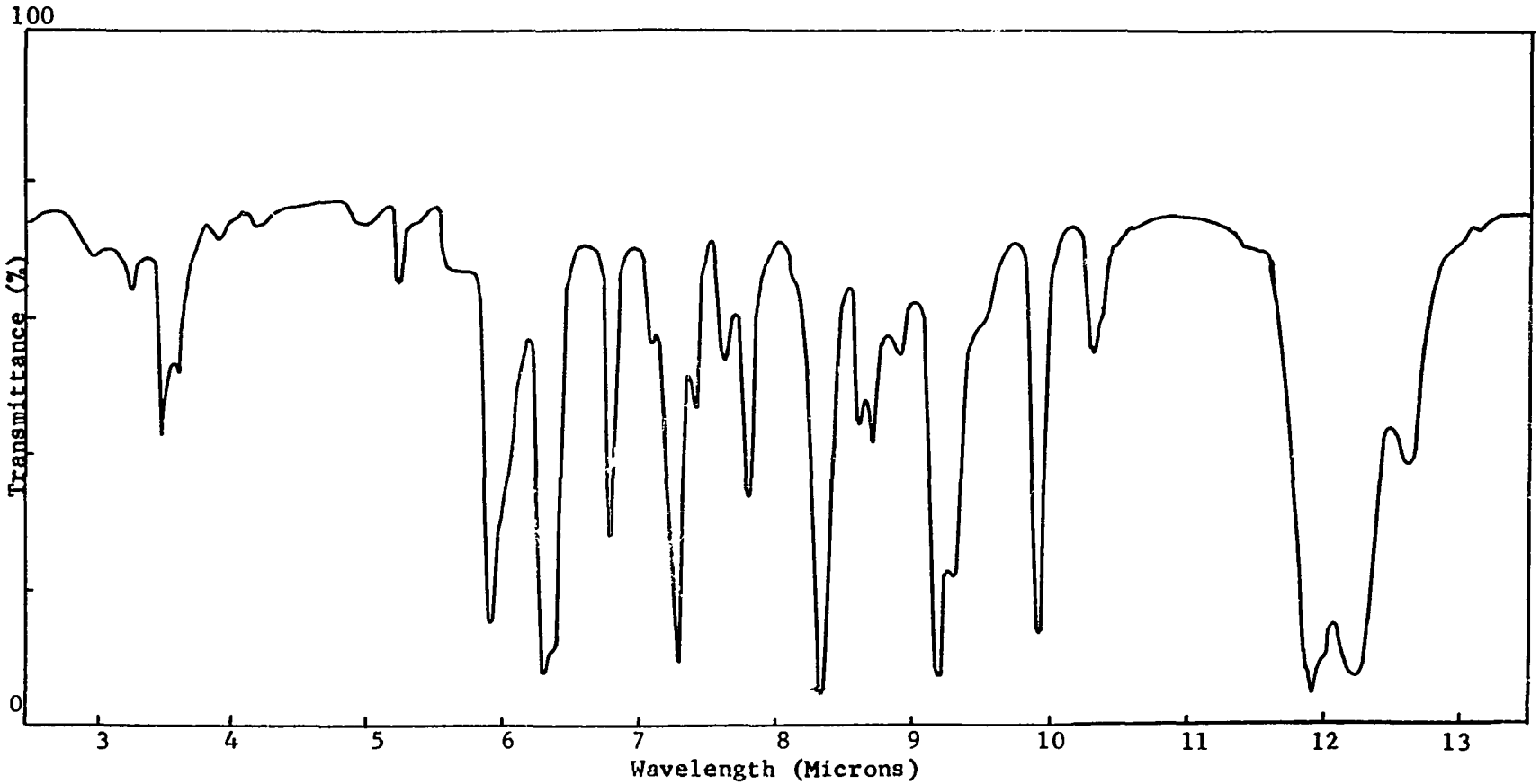


FIGURE VII

SPECTRUM VI - INFRA-RED ABSORPTION SPECTRUM OF p-ALDIMINOBENZOIC ACID

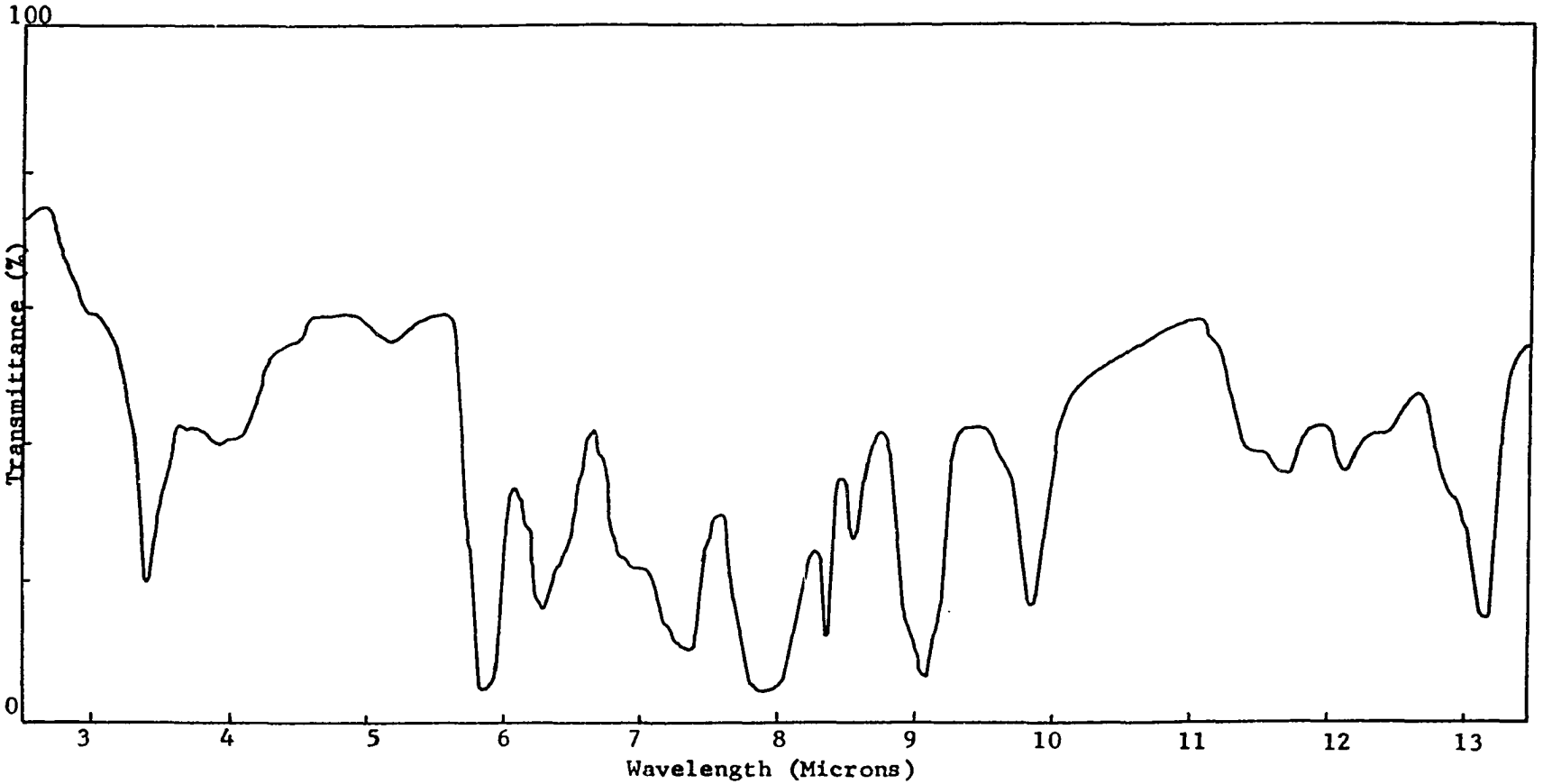


FIGURE VII

SPECTRUM VII - INFRA-RED ABSORPTION SPECTRUM OF ∝ -NAPHTHYLACETALDIMINE

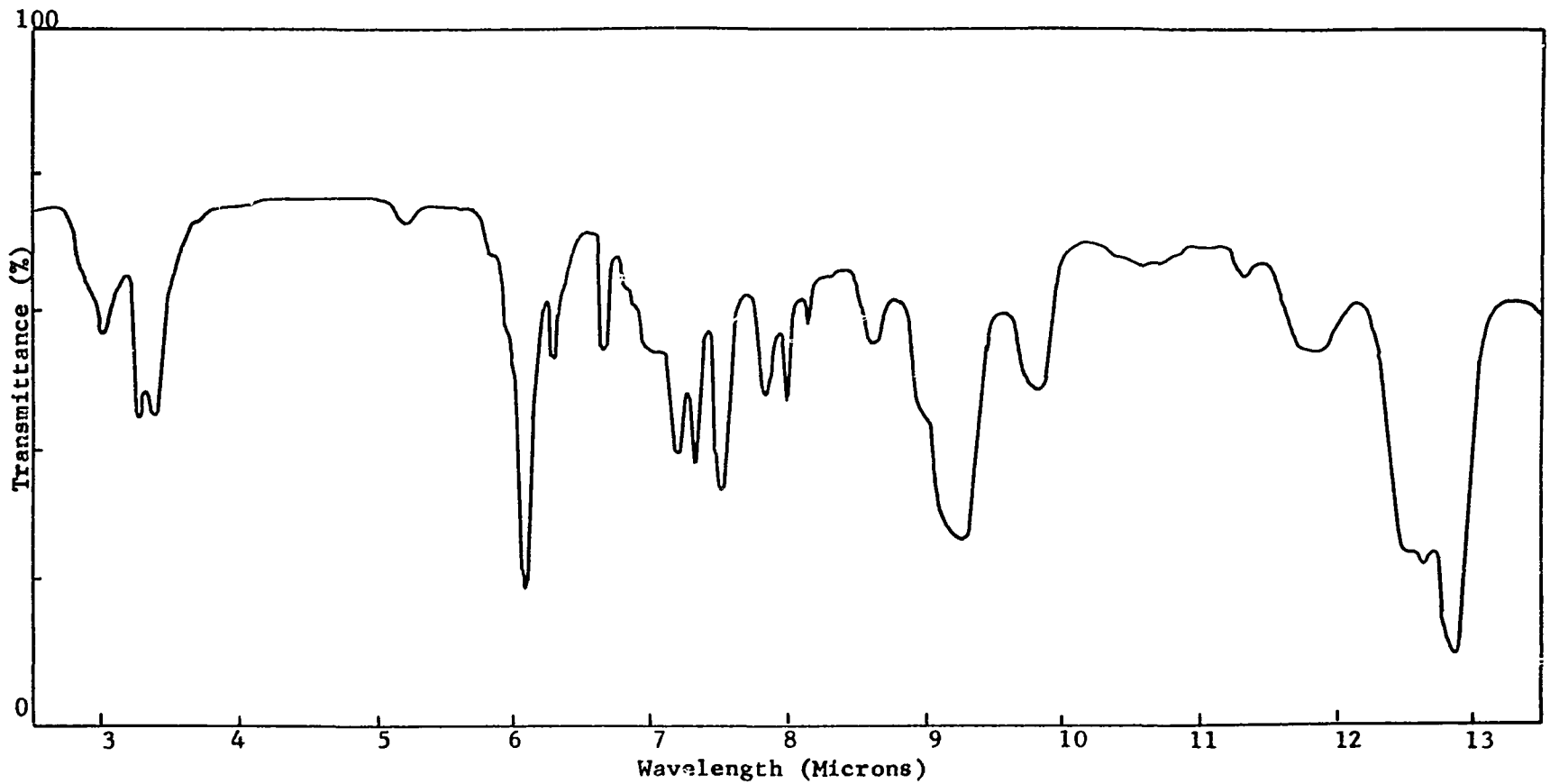
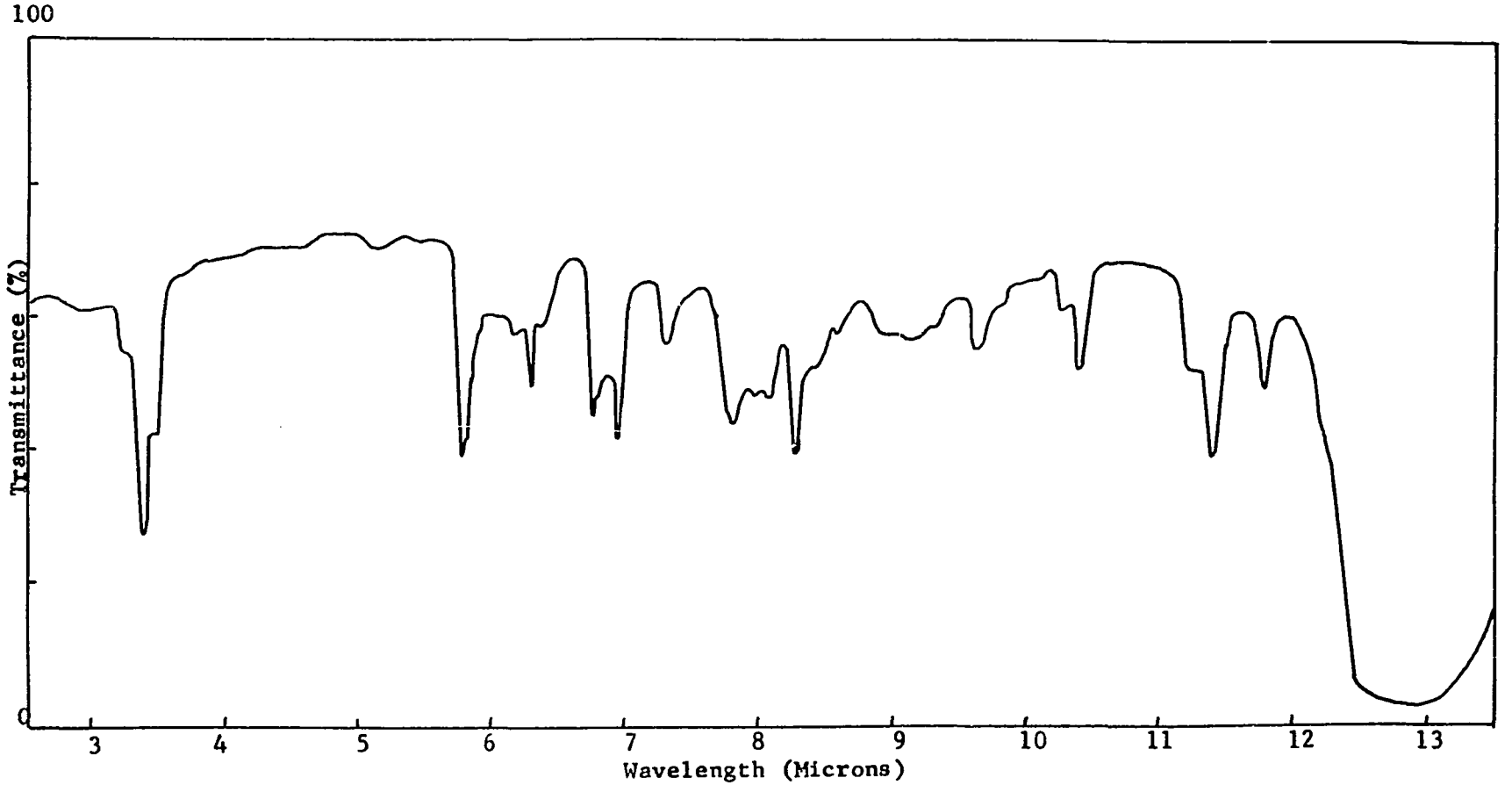


FIGURE IX

SPECTRUM VIII - INFRA-RED ABSORPTION SPECTRUM OF o-TRICHLOROMETHYLBENZALDIMINE



CHAPTER III

RELATED EXPERIMENTAL

This chapter is devoted to the discussion of preparations and procedures which were performed but which are not directly connected with imine preparation and isolation.

Preparation of Cerous Chloride. Although chromous, vanadous, and titanous salts had been reported (16) as ineffective replacements for stannous halides in the Stephen reaction, it was felt that cerous salts might be effectively used. Unfortunately the only cerous halide available was cerous chloride heptahydrate and all attempts to dehydrate the salt proved unsuccessful. The cerous ion was consequently not tried as a reducing agent for nitriles.

The attempts at dehydration of the heptahydrate included the use of heat and vacuum, dehydrating agents such as magnesium perchlorate in an evacuated, heated system, and partial solution of the salts in solvents which form azeotropes with water. The last method was the most successful. Using ethanol as the solvent and long periods of reflux followed by careful distillation, some of the cerous salt was prepared which contained only 0.20 moles of water per mole of salt. This was the most nearly anhydrous form of the salt obtained, and this contained far too much water for use in imine preparation. Although

further dehydration of the salt was probably possible, production of sufficient quantities of the reducing agent by this method did not seem practical and the attempt was abandoned.

Analysis of the various cerous chloride hydrates which were produced was by the volumetric sodium bismuthate method of Metzger. The procedure as presented in volume one of "Scott's Standard Methods of Chemical Analysis" (62) was followed exactly.

Analysis of Stannous Bromide. Analysis of the stannous bromide which was used was by electrolytic deposition of the tin from an oxalic acid solution. The analysis was done on a Sargent-Slomin Electrolytic Analyser; the electrodes used were copper. The general method of analysis is presented in H. J. S. Sand's "Electrochemistry and Electrochemical Analysis" (63). Analysis showed the stannous bromide used to be 98.5% pure.

Preparation of Standard Solutions for Alkalinity Titrations. Several of the aldimines which were prepared were titrated for total alkalinity, the results being used as a measure of purity and as a method of determining equivalent weight. The method was developed for use with imines by Iddings (58); it involves the nonaqueous potentiometric titration of the imine in a leveling solvent.

Glacial acetic acid was used as the solvent for the titrations. The titrating agent was perchloric acid. A standard 0.1 N solution of this acid was prepared by mixing 9 mls. of 72% perchloric acid in small portions with 50 mls. of glacial acetic acid at 0°C. This mixture was diluted to volume with glacial acetic acid in a 1000 ml. volumetric flask. This solution was standardized against a solution of standard

base. The basic standard was prepared using potassium acid phthalate as a primary standard in glacial acetic acid.

Preparation of p-Cyanobenzylbromide. This compound was prepared by the photobromination of p-tolunitrile using liquid bromine and light from a 200 watt, unfrosted, incandescent light bulb. The method was developed by R. C. Fuson (64). The compound was obtained in 47% yield.

Preparation of Salicylaldoxime. Salicylaldoxime was prepared in 90% yield by the method of Raiford and Clark (65). The general method was the reaction of salicylaldehyde and hydroxylamine hydrochloride in an alkaline solution.

Preparation of Benzaldimine by the Method of H. H. Strain. In 1927 H. H. Strain (8) reported the preparation of a compound he believed to be benzaldimine. The compound was prepared by allowing hydrobenzamide to slowly dissolve over a period of 30-40 hours in liquid ammonia containing a trace of ammonium chloride. Concentration and cooling of the mixture resulted in the separation of the imine as a crystallizable oil. Decomposition of the large, transparent crystals of imine occurred if it was dissolved in any solvent other than liquid ammonia. The melting point was that of hydrobenzamide. Many of the reactions reported are also those of hydrobenzamide.

Since the properties and reactions of Strain's compound are so different from those of the compound isolated and reported in this work as benzaldimine, an effort was made to prepare the compound which Strain reported. Four attempts were made to repeat the reported work; all were unsuccessful. The directions given in the report were

followed exactly in the first preparation. When this was unsuccessful, the amount of hydrobenzamide was varied and additional time for reaction allowed. Although both more and less amide per volume of ammonia was used, neither oil nor crystals were obtained. In the last preparation, the amount of ammonium chloride used was increased; Strain's report mentioned that an acid should be used in the reaction. Again nothing was found on concentration of the mixture but ammonia, ammonium chloride and hydrobenzamide. The preparation was not pursued further.

CHAPTER IV

DISSCUSSION OF RESULTS

Previous workers have reported the preparation and isolation of five aldimines; these are benzaldimine, phenylacetaldimine, diphenylacetaldimine, acetaldimine, and ∝ -methoxyacetaldimine. In this work attempts were made to prepare and characterize the first three of these, but only the preparations of benzaldimine and diphenylacetaldimine were successful. This chapter is devoted to a discussion of possible reasons for the variations in description of benzaldimine as previously reported and as reported here, and to possible reasons for the lack of success in preparing phenylacetaldimine. In the course of preparing the compounds described in Chapter II patterns of imine reactivity and of yields obtained have evolved which seem to suggest ways in which imines may react. These are also discussed.

Benzaldimine and its derivatives have been investigated by more workers than any other aldimine. Unfortunately there has been very little agreement as to its properties. It was pointed out in Chapter II that because of this disagreement special care was taken in purification and characterization of the compound described there as benzaldimine. Derivatives were prepared which show the presence of a basic and incompletely substituted nitrogen, while others were

prepared which collectively characterize the hydrolysis product of the compound. After comparison of the physical constants of the derivatives of the hydrolysis product with the values reported for the derivatives of various aldehydes, there can be little doubt that this product is benzaldehyde. The nitrogen compound prepared was subjected to two entirely different types of analysis. The total alkalinity, and from this an equivalent weight, was determined; in the second analysis the nitrogen content was found by the well known, semimicro Dumas method. In each case the value obtained agreed with that of benzaldimine. The presence and type of nitrogen in the compound and the structure of the non-nitrogen containing portion of the molecule had been shown by derivative preparation, and analyses of two types concurred with the proposed structure. It remained only to show the structural relationships of the intact molecule. An indication of this structure is given by the infra-red spectrum of the prepared compound. Study of this spectrum, presented in Chapter II, shows absorption bands falling in the ranges of absorption of the =N-H, and -C=N- groups. The remaining portions of the spectrum show absorption in the regions usually associated with mono-substituted benzenoid compounds. On the basis of all the evidence, it seems highly probable that the prepared compound is benzaldimine.

The physical constants of benzaldimine and its derivatives reported by other workers and in this study are shown in Table V. The values presented in Chapter II and those of Grignard and Escourrou (6) for density and refractive index differ too greatly to be explained on the basis of the temperatures at which the determinations were made.

The French authors prepared their compound by the catalytic hydrogenation of benzonitrile using nickel as a catalyst. Their report mentions difficulty in obtaining pure, stable imine by distillation and that some benzylamine was formed in the hydrogenation reaction. For this reason it seems possible that the sample of benzaldimine which they obtained was not entirely pure and that the reported physical constants are those of a mixture. That the sample of Grignard and Escourrou did contain some of the imine is substantiated by the agreement in melting point of the hydrochloride derivative reported by them and in this report.

It was mentioned in Chapter I that this same imine hydrochloride was reported in an earlier article by M. Busch (5). The melting point reported was 22°C lower than that found by the French workers and in this study. This wide variation would lead one to suspect either another compound or an impure sample.

In Chapter III the unsuccessful attempts to repeat H. H. Strain's preparation of "benzaldimine" are described. This compound is described by Strain as translucent crystals unstable in any medium, including dry air, other than liquid ammonia. No derivatives, of the nitrogen portion of the molecule, such as the hydrochloride, are reported; aldehyde derivatives are reported. This substance which Strain describes is very unlike the one described in Chapter II and by Grignard and Escourrou. In consideration of the evidence supporting the structure of the compound prepared and reported here, it seems likely that the translucent crystals were not benzaldimine.

Catalytic hydrogenation of phenylacetonitrile was used by

Grignard and Escourrou to obtain phenylacetaldimine. They purified the compound by distillation at atmospheric pressure and describe it as being stable and easily handled. The stability under these conditions is not surprising for a compound of this type and molecular weight. However, when one considers that the imine is a tautomer of styrylamine and that the amine is the more conjugated form, some tendency to tautomerization and polymerization might well be expected. The occurrence of a low melting polymer is mentioned in the French article, but no indication of a rapid or spontaneous polymerization is given.

Many attempts to prepare phenylacetaldimine were made, but a stable monomer such as was described by Grignard and Escourrou was never obtained. The preparation of the monomer in solution and its rapid polymerization on concentration or distillation has been described. Even when a fraction of monomer was obtained by vacuum distillation, formation of a polymer from the fraction was almost immediate. Free radical scavangers in the system only slowed polymerization and changed the form of polymer obtained. The refractive index of the monomer, even when determined immediately after distillation, was markedly different from that of the earlier report.

One explanation of the discrepancy between the French report and this work which seems plausible is that the compounds were formed in different ways and so contained different impurities. In each case the nitrile was reduced to the imine, but in the earlier case the reaction was catalytic while in this work a chemical reduction was used. Tin compounds are often used as polymerization agents; some of these same compounds are quite volatile. Undoubtedly, any unrefined, imine

monomer solution which was prepared contained a variety of tin containing impurities. These might easily have been the cause of polymerization on concentration of the solution. Because of their volatility, these same impurities might possibly have been distilled or entrained along with monomer in a distillation. If such were the case, the distilled imine might also polymerize. These explanations are supposition. It is certain, however, that for some reason the phenylacetaldimine prepared in this work polymerized, while that of Grignard and Escourrou did not. No explanation is offered for the very great difference between the refractive index reported and the one found. Although the imine hydrochloride obtained was thoroughly washed and was reprecipitated after isolation of the salt and regeneration of the imine with liquid ammonia, it melted 7°C lower than that reported in the French article.

The physical constants of the solid diphenylacetaldimine and its derivatives which were prepared agreed with those obtained by Kohler and Drake (9) in 1923. Although the yield of the imine was small due to incomplete decomposition of the intermediate complex, sufficient amounts of the compound were obtained to identify it as the imine reported in 1923. This compound darkens and forms a polymer-like material when held above its melting point for a few minutes, but no polymeric material was isolated in its preparation. Since the impurities present in the imine solution resulting from decomposition of the intermediate complex were undoubtedly much the same as those present in an unrefined solution of phenylacetaldimine, the lack of polymerization must be ascribed to factors other than impurity. The primary factors

here were probably that the compound crystallized on concentration of its solution and that it was purified by recrystallization rather than distillation. The milder conditions of purification and the removal of monomer from solution by precipitation could have made a great deal of difference in the rate and amount of polymerization which occurred. Some contribution to stability, however, may have come from steric hindrance to reaction by the phenyl groups on the carbon atom adjacent to the imine group. The isolation of a substantial amount of α-naphthylacetaldimine, a substituted acetaldimine with a large group adjacent to the imine group, seems to support the possibility of a steric effect.

Table VI shows the relative amounts of intermediate precipitate, isolated monomer, and isolated polymer plus monomer obtained from the preparation of each aldimine. Generally speaking the yields of isolated complex and of polymer plus monomer were good, but the amount of monomer isolated was low. Exceptions to this in which a fairly high yield of monomeric imine was obtained were in those cases where the imine group was alone on a benzene ring or where other substituents on the ring were of an electron withdrawing nature. Polymerization was greatest and the most rapid with the aliphatic, substituted, acetaldimine, and the benzaldimines substituted with electron donating groups.

This study was not extensive enough to give a definite and positive picture of the ease with which imines could be prepared and isolated. However, the data obtained did seem to indicate certain patterns of stability and reactivity. Any conclusions drawn from this

information were still supposition, but had enough basis to be of value in pointing out areas of attack and study in the later work.

Possible reasons for the reactivity of the aldimines containing an alpha hydrogen atom have been discussed earlier in this chapter, and the apparent stability of the completely conjugated imines, benzaldimine and α -naphthaldimine, might have been expected. An area of particular interest which one might not have predicted, however, is the large apparent difference in reactivity of the monosubstituted benzaldimines. Although complete information is lacking, the benzaldimines substituted with electron withdrawing groups seem considerably less reactive, and hence more easily isolable, than those substituted with electron donars. Such reactivity might be taken as support for an imine reaction mechanism in which an additional electron supply is required by the imine double bond for spontaneous reaction at room temperature. All of these compounds seem to react with themselves if enough heat energy is supplied, but apparently only those richly supplied with electrons have sufficient energy at room temperature for immediate reaction. Thorough testing of this idea remains to be done.

The way is open for some very interesting future studies, now that a definite method of aldimine preparation and isolation has been developed. In addition to the studies of inductive effects on imine reactivity previously mentioned, there are several areas of study which should be especially interesting and productive. Among these are comparisons of steric effects in influencing yield and compound stability, determinations of the ease with which incompletely conjugated aldimines tautomerize, and comparisons of reactivity of unsubstituted aliphatic and aromatic aldimines.

TABLE V

COMPARISON OF PHYSICAL CONSTANTS

Benzaldimine and its derivatives

Data Source	M.P.	B.P.	Refractive Index	Density	M.P. (A*)	M.P. (B*)	M.P. (C*)
Busch (5)					181°C		
Grignard and Escourrou (6)		140°C/50mm.	n_D^{12} 1.5725	d^{13} 1.009	203-240°C		
Strain (4)	101°C						35°C
Chapter II		58°C/4mm.	n_D^{20} 1.5259	d^{20} 0.9799	203°C	222°C	35°C
		Phenylacetaldimine and its Derivatives					
Grignard and Escourrou (6)		212-213°C/750mm.	n_D^{20} 1.5402		180°C		
Chapter II		212°C/731mm.	n_D^{20} 1.5251		173°C	153-4°C	

TABLE V (Continued)

Diphenylacetaldimine and its Derivatives

Kohler and Drake (9)	129d	120°C
Chapter II	129d	120°C

*A - Aldimine Hydrochloride
B - Semicarbazone of Aldimine Hydrolysis Product
C - Oxime of Aldimine Hydrolysis Product

TABLE VI

COMPARISON OF ALDIMINE YIELDS OBTAINED

Substituted Aliphatic Imines

Imines	Yield of Complex[1]	Monomer Yield[2]	Combined Yield[3]
Phenylacetaldimine	79.8%		70%
Diphenylacetaldimine		6%	
∝-Naphthylacetaldimine	1.3%	23%	
Unsubstituted Benzaldimine			
Imine			
Benzaldimine	90%	93.9%	
Disubstituted Benzenoid Imines			
Imines with Electron Donating Substituent			
o-Tolualdimine	30%	11.2%	21.3%
m-Tolualdimine	98%		50%
p-Tolualdimine	70%	25%	70%
Imines with Electron Withdrawing Substituent			
o-Chlorobenzaldimine	72.5%	21.8%	
p-Chlorobenzaldimine	99%	72%	
p-Aldehydobenzaldimine			
p-Aldiminobenzoic Acid	95%	26.2%	

TABLE VI (Continued)

o-Trichloromethylbenzaldimine	44%
p-Trichloromethylbenzaldimine	1%

Unsubstituted Naphthaldimine

Imine		
∝-Naphthaldimine	15.4%	49.5%

1 - The weight of the precipitated intermediate was taken as pure complex for the yield calculation. The yield shown was not necessarily the percent of nitrile complex formed.
2 - This yield was calculated from the amount of nitrile used in the reaction
3 - The combined yield was calculated by taking the weight of polymer isolated as that of imine, and adding this to the amount of monomer isolated.

CHAPTER V

SUMMARY

Although secondary imines and substituted primary imines have been studied and characterized, very little attention has ever been paid to the unsubstituted terminal imines. These aldimines are considered to be intermediates in many organic reactions such as the Gattermann aldehyde synthesis and the reduction of nitriles, but, due to the difficulty of isolating them and, perhaps, lack of interest, only a very few of the compounds have been described. This important and relatively untouched field of aldimine preparation and characterization was chosen as the subject of this study.

The general approach to imine preparation was a modification of the Stephen aldehyde synthesis. This synthesis involves the formation of a stable, isolable intermediate complex from reaction of a nitrile with a diethyl ether solution of stannous halide which has been saturated with the corresponding hydrogen halide. This complex has the general form, $(R\text{-}CH{=}NH\cdot HX)_2SnX_4$. Decomposition of this intermediate under anhydrous conditions produces the corresponding aldimine.

Attempts were made to prepare nineteen aldimines. In five of these cases attempts to prepare the Stephen complex were unsuccessful, although a complex of some kind was obtained each time. In all but two

of the remaining fourteen preparations imine monomer was isolated, and even in these cases a polymeric substance formed from the imine was obtained. The aldimines were characterized by determination of physical constants, analysis for nitrogen content and for total alkalinity, preparation of derivatives, and study of their infra-red spectra.

A number of compounds needed for the imine synthesis were also prepared. The methods of preparation are reported.

In addition to the preparative and identification work mentioned, a short study of the polymeric material formed by imines was made. It was found that hydrolysis of the polymers resulted in high yields of aldehydes corresponding to the monomeric imines. Unfortunately, all attempts to obtain the imine monomers from the polymeric substances were unsuccessful. Infra-red studies of polymer formation suggested that the polymers formed in the presence of heat were the same as those initiated by addition of free radicals and heat. The only difference seemed to be a faster polymerization rate in the latter case.

Due to the almost complete lack of information on the chemical reactivity of aldimines, particularly their ability to form a variety of tin containing complexes and their tendency to polymerize, progress on this problem has not been rapid. Now that many of the difficulties in preparation and isolation have been solved, the way is open for some very interesting studies in the future. Among those which should be particularly important and fruitful are comparisons of steric effects in influencing yield and compound stability, and studies of inductive effects on imine reactivity. The author hopes that interest and work on these compounds does not end with this dissertation.

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