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A STUDY OF SOME MIXED AZO NITRILES

by
Chester E. Smith, Jr.

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A STUDY OF SOME MIXED AZO NITRILES

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ABSTRACT

A study of mixed azo nitriles, which have an aromatic group attached directly to the azo linkage on one side and an α-aliphatic nitrile group on the other, has been undertaken with the purpose of providing azo compounds that would produce free radicals at higher temperatures than formerly known azo nitriles do.

Previous studies of aliphatic azo compounds, particularly aliphatic azo nitriles, have shown that the thermal decomposition of these compounds follows first order kinetics. It has been demonstrated that the decomposition involves a free radical mechanism and that these radicals are useful as polymerization initiators.

Seven new mixed azo nitriles and five new and one known mixed hydrazo nitriles have been prepared. Most of the azo compounds were obtained by oxidation of the corresponding hydrazo compounds. Most of the hydrazo compounds were produced by reaction between phenylhydrazine and an aliphatic ketone cyanohydrin.

The mixed azo nitriles were found to decompose thermally at temperatures above 140° . The products of the decomposition of α-phenylazoisobutyronitrile at 165° were shown to include nitrogen, diphenyl, tetramethylsuccinonitrile, α-phenylisobutyronitrile, and hydrogen cyanide. These products substantiate the free radical mechanism proposed for the decomposition.

The kinetics of the thermal decomposition of six of the mixed azo nitriles were studied at 165° by measurement of the nitrogen evolved at definite time intervals. The rate for one compound was also measured at 175° . First order kinetics were observed. In general, less than stoichiometric amounts of nitrogen were obtained. The most reasonable explanation for the nitrogen retention seems to be the occurrence of a simultaneous first order rearrangement to an hydrazone by migration of a group from the α -carbon atom to the nitrogen adjacent to the aromatic nucleus. In this event, the rate constant which was determined would be the sum of the rate constants for the cleavage reaction and the isomerization. Relatively small differences in the rate of decomposition were observed among the azo compounds.

Infra-red absorption spectra were determined for the mixed azo and hydrazo nitriles with the hope of obtaining evidence concerning the wave length of the N=N stretching vibration. This could not be definitely established. In addition to characteristic bands for the N-H and C≡N groups, it was observed that the band for the cyano group was much weaker in the case of the azo compounds and a possible explanation is suggested for this phenomenon.

Ultraviolet absorption spectra for a mixed azo nitrile show an absorption band at 3820-3850 Å, comparable to the band for the aliphatic azo nitriles at 3450-3500 Å, but the band is stronger and has been shifted toward longer wave lengths by conjugation of the azo linkage with the aromatic group.

To my wife,

Ruth

Acknowledgments

The author wishes to express his deep gratitude to Professor Leigh C. Anderson for his help, direction, and encouragement during the course of this investigation. He also wishes to thank the other members of the doctoral committee and Dr. Robert C. Taylor for helpful suggestions.

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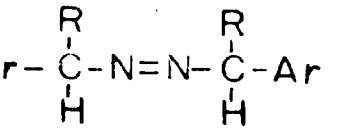
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A Study of Some Mixed Azo Nitriles

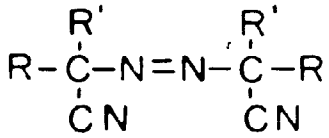
I Introduction

Historical. The simple aliphatic azo compounds[1,2] are well known. The primary interest in the azo compounds containing only alkyl groups attached to the nitrogen atoms lies in their ability to produce free alkyl radicals and nitrogen at elevated temperatures (about 250-300°).[3,4] The kinetics of this thermal decomposition have been studied in the gas phase. It has been found that the decomposition is a first order, unimolecular reaction and that the energies of activation are 40-50 kilocalories. Comparison of azomethane with azoisopropane shows that substitution of the hydrogens of azomethane by methyl groups causes an appreciable decrease in the energy of activation, for example, the decomposition of azomethane has an energy of activation of 51 kilocalories while that of azoisopropane is 41 kilocalories.[5]

A number of azo-alkanes have been prepared which have aromatic groups as substituents, such as  .[6-11] These azo compounds are said to rearrange to their hydrazone tautomers with greater ease than the simple azo-alkanes.[6,7] This is probably due to the enhanced activity of the hydrogen atom caused by its position in relation to both the azo group and the aryl group. The thermal decomposition of this type of compound has been studied. Kinetic work[11] has shown that the decompositions in solution are first order reactions and that the energies of activation are 32-35 kilocalories. They decompose at a convenient rate at temperatures of 100-110° giving the theoretical amount of nitrogen. (One case was noted in which only 68%

of the theoretical nitrogen was evolved and this was attributed to rearrangement to its hydrazone tautomer.) The major products of the decompositions, besides nitrogen, are the substituted ethanes,[6-9] which would have been produced by the union of a pair of the free radicals, presumed to be formed as the nitrogen is lost. The presumption that free radicals were formed was initially based on analogy with other aliphatic azo compounds, but was then substantiated by the fact that these substances promoted polymerization of styrene under conditions which would not otherwize cause its polymerization.[11]

Considerable interest has been shown recently in azo-bis-nitriles, i.e. compounds of the type:



The first of this type of compound was α, α'-azo-bis-isobutyronitrile, prepared by Thiele and Heuser[12] in 1896 who prepared tetramethyl-succinonitrile by thermal decomposition of this azo compound. Following this work a few other derivatives have been described prior to the very recent papers on the subject.[13,14]

Overberger et al. have published a series of papers dealing with these symmetrical aliphatic azo nitriles.[15-23] Their method of preparation, adapted from that of Thiele and Heuser, consisted of shaking for a few days an aqueous or aqueous dioxane solution of a ketone, hydrazine sulfate, and sodium cyanide, from which the hydrazo compound was obtained.[15] In the cases of p-chloro and p-nitro-phenylacetones, the probuct obtained by this procedure required the addition of one molecule of hydrogen cyanide, which addition was accomplished by allowing this product to stand several days with liquid hydrogen cyanide in the presence of traces of hydrochloric acid.[18]

The hydrazo compounds were oxidized to the azo nitriles with bromine in the presence of hydrochloric acid in either aqueous alcohol or absolute alcohol.[15]

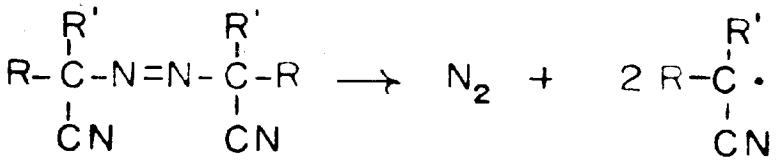
Kinetic data on the thermal decomposition in solution of several azo nitriles have been presented by Overberger et al.[15,17,18,22] and also by Lewis and Matheson.[24] The rates were determined by measurement of the volume of nitrogen evolution. The experimental V_∞ values agreed well with stoichiometric values. These compounds decompose at convenient rates at 70-80° and have activation energies of 29-34 kilocalories. Using α, α'-azo-bis-isobutyronitrile as a standard for comparison, it is seen that addition of methyl groups on a β carbon atom (replacement of a methyl group by ethyl, isopropyl, or t-butyl) decreases the rate of the decomposition to little more than half. Addition of methyl groups on a γ-carbon atom (replacement of a methyl group by n-propyl or isobutyl) increases the rate of decomposition. The azo compound obtained from cyclohexanone decomposes much slower than any of the other compounds tested.[15]

Consideration of Fisher-Hirschfelder molecular models indicated that only the trans configuration of the azo group is possible. Although the reason for increased stability, when methyl groups are added at the β position, is obscure, Overberger suggests a steric explanation for the other differences in rate of decomposition. A study of these models shows that there is increased steric interaction of groups across the azo linkage from each other when methyl groups have been added at the γ position. There is considerably less interference in the case of the cyclohexyl compound.[15]

In the course of work which showed that meso- and dl- forms of the trans-azo compounds decomposed at nearly the same rate, Overberger and Berenbaum found that the azo nitrile prepared from methyl cyclopropyl ketone decomposed much faster than any compound previously measured. Since the steric explanation above is quite unsatisfactory for this case, they suggest that the effect may be due to increased possibilities for hyperconjugation in the cyclopropyl group contributing to the stability of the free radical.[17]

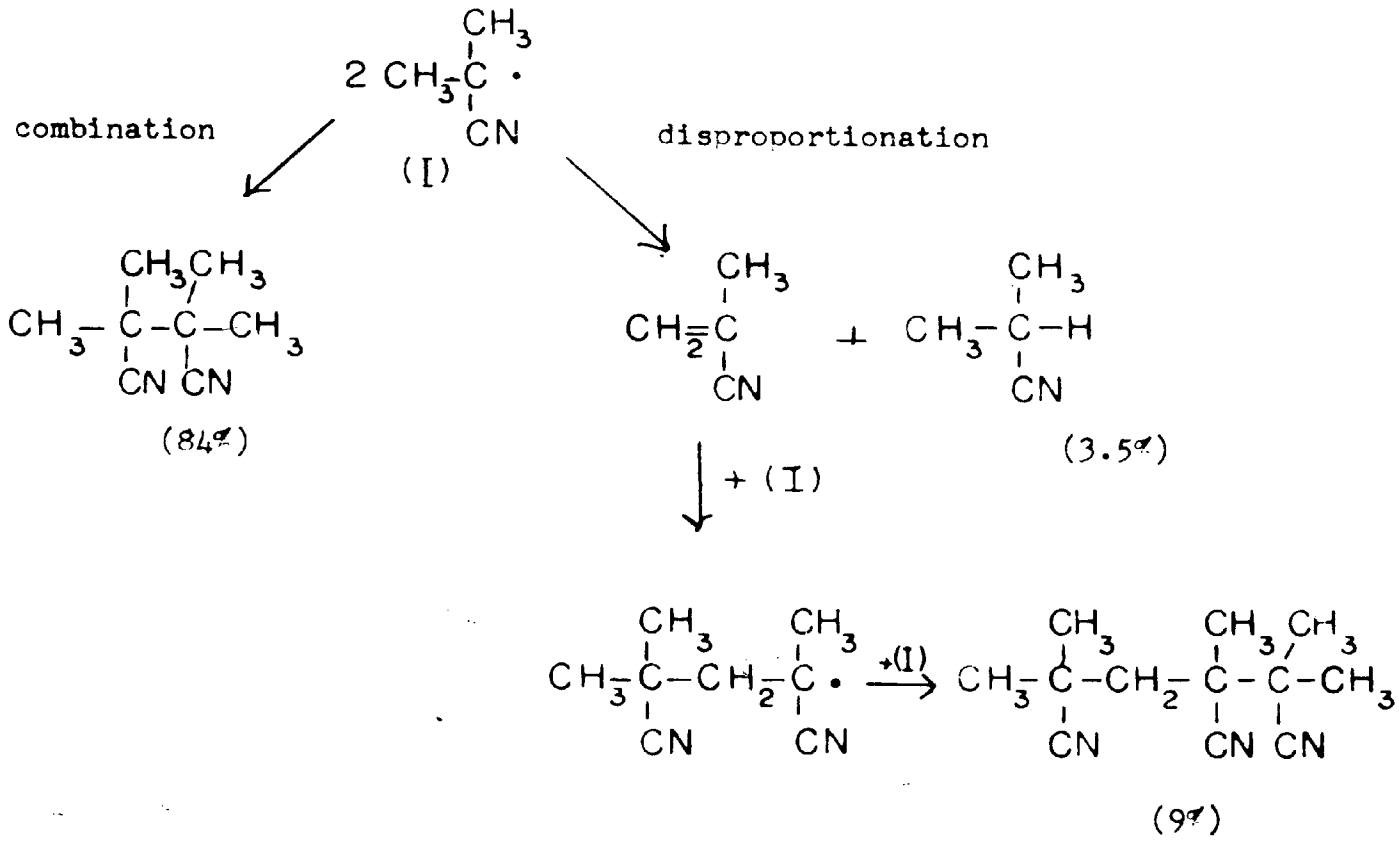
In further work with azo nitriles which were derived from cycloalkanones, Overberger et al. have investigated the effect of ring size on the rates of decomposition, energies of activation, and entropies of activation. Some very striking differences were observed. Since molecular models indicate that there should be little or no steric interference across the azo group, they relate the variations to "ring strain", or more properly to the amount of strain relieved in going to the free radical.[22]

Using several different solvents, it has been shown by rate measurements that the effect of the solvent on the decomposition of the aliphatic azo nitriles is small.[15,24] Ultraviolet absorption spectra which have been determined indicate that these compounds have an absorption band at about 3450-3500 $\overset{\circ}{A}$.[15] Thermal decomposition of these azo nitriles in the presence of styrene, butadiene, or vinyl acetate has been shown to cause polymerization.[15,16,24] This fact is good evidence for the free radical mechanism proposed[15] for the decomposition:



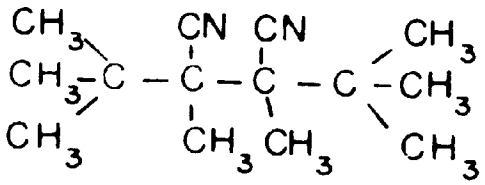
These compounds also decompose at room temperature when irradiated with ultraviolet light. Lewis and Matheson have shown that they are highly efficient photosensitizers for vinyl type polymerizations. Vinyl acetate and styrene were polymerized at 30° by irradiation with a mercury arc lamp. The quantum yields were very high.[24]

Bickel and Waters have investigated the products of the decomposition of α, α'-azo-bis-isobutyronitrile in toluene.[25] They propose the following scheme for the fate of the free radicals on the basis of the products isolated, the yields of which are shown in parentheses.

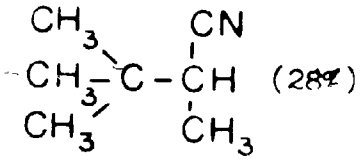


A similar study by Overberger and Berenbaum of the decomposition products from the azo nitrile obtained from pinacolone shows that the free radical disproportionates to a high degree rather than simply combining.[21] However they could find no evidence of any rearrangement.

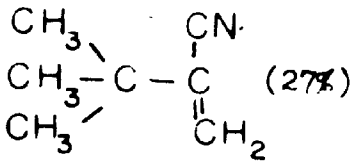
The compounds which they isolated were:



(both meso- and dl- forms total yield 7%)

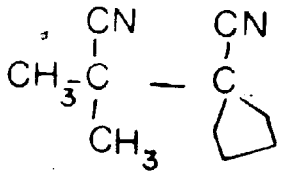


(28%)



(27%)

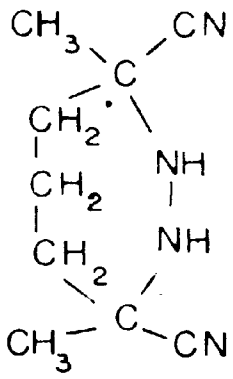
They also carried out two other sets of experiments which gave some evidence about the life of the free radicals.[19] In one set of experiments it was indicated that decomposition of either the meso- or the dl- form of 2,2'-azo-bis-2,4-dimethylvaleronitrile gave essentially the same mixture of the meso- and dl- forms of α, α'-dimethyl- α, α'-diisobutylsuccinonitrile. This indicates that the free radical assumes a planer configuration regardless of the configuration of the initial azo compound before decomposition. In the other set 2,2'-azo-bis-isobutyronitrile and 1,1'-azo-bis-1-cyclopentanecarbonitrile were decomposed simultaneously in the same solution. The three expected coupled products, tetramethylsuccinonitrile, 1,1'-dicyano-1, 1'-dicyclopentyl, and the mixed coupled product α, α-dimethyl- α', α'-tetramethylenesuccinonitrile,



were all isolated in considerable amounts. In addition evidence was

given for the formation of isobutyronitrile and 1-cyclopentene-carbonitrile. The isolation of the mixed coupled product indicates that the free radical has sufficient life to combine with free radicals other than the one from the same azo molecule.

Overberger et al. have also taken an interest in azo nitriles which might be prepared from diketones, particularly where the azo nitrogen atoms are part of a ring.[20,23] Although they have not been able to prepare any such azo compounds, apparently due to their great instability, they have prepared a few corresponding hydrazo compounds (two 7-membered rings and one 6-membered ring). On oxidation, the azo intermediate is apparently too unstable to allow isolation and there is an immediate and quantitative evolution of nitrogen. Three products were isolated all of which substantiate the presumption that biradicals were formed by decomposition of the expected azo compound. From the oxidation of 3,7-cyano-3,7-dimethylhomopiperidazine,



both the cis- and trans- forms of 1,2-dicyano-1, 2-dimethylcyclopentane were isolated and characterized and also 2,6-dicyanoheptene-2 which apparently resulted from an internal radical displacement or disproportionation reaction. A cyclic transition state is depicted for the mechanism of this displacement reaction.

In a recent patent Hill describes preparation of polymeric azo nitriles from diketones having the carbonyl groups separated by more carbon atoms than in the cases mentioned above.[26] He also has shown that these polymeric azo compounds can be used as polymerization initiators.

A number of other patents relating to azo nitriles have been issued.[27-31] They describe the preparation of many of the compounds and their use in polymerization reactions.

Of particular note is the patent of Pease and Robertson[32] who prepared α, α'-azo-bis- α -phenylpropionitrile and showed it to be an effective polymerization initiator at 5°. Anderson and Nersasian, in unpublished work from this laboratory, have found that aliphatic azo nitriles with aromatic substituents at the α-carbon atom decompose rapidly in solution at 0-10° and have activation energies of about 20 kilocalories.

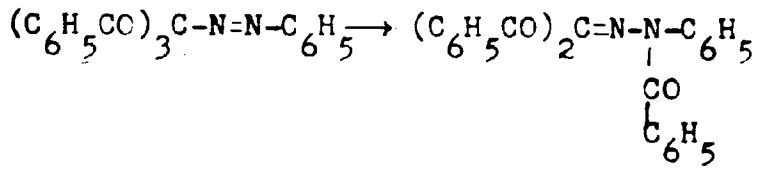
The thermal stability of the aromatic azo compounds is very much greater than that of the aliphatic azo compounds. Whereas all aliphatic azo compounds decompose more or less readily giving nitrogen and free radicals, the aromatic azo-compounds show a high degree of stability to heat. Azobenzene, for example, boils without decomposition at 295°. However, azobenzene has been thermally decomposed by passage of its vapor through a red hot tube. In this treatment nitrogen is eliminated and an abundant quantity of coke is obtained together with a complex mixture of diphenyl, chrysene, and anthracene.[33] In addition, the formation of aniline, benzene, hydrogen cyanide, and ammonia have been observed.[33,34] Apparently, the typical aliphatic decomposition giving nitrogen and the corresponding free radicals does not take place

smoothly with azobenzene even at sufficiently high temperatures to cause decomposition.

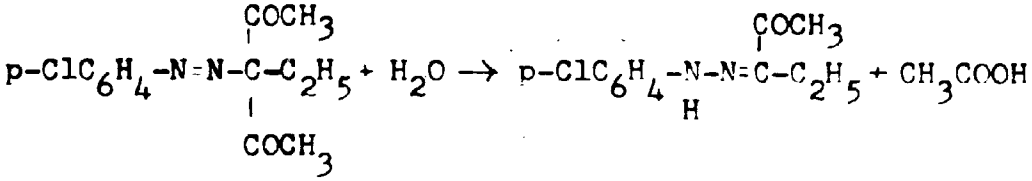
Mixed azo compounds, i.e. having an aromatic group attached directly to the azo linkage on one side and on the other an aliphatic group, were first prepared by Fischer and Ehrhard.[35] Under the influence of even dilute acids or bases the mixed azo compounds isomerize irreversibly into hydrazones.[36,39]



This isomerization takes place very readily when there is an hydrogen atom attached to the carbon atom α to the azo group. In cases where there is no hydrogen attached to this α-carbon, isomerization still takes place but with the migration or loss of one of the groups attached to this carbon. In some cases heat alone is sufficient to bring about the isomerization. Thus when phenylazotribenzoylmethane is heated at 120° a benzoyl group migrates readily.[40,41]



Loss of a group is demonstrated by the reaction of p-chlorophenylazoethyldiacetylmethane when treated with aqueous acids.[42]



Apparently even an alkyl group can migrate under suitable conditions. When p-bromobenzene diazonium chloride is added to a weakly alkaline

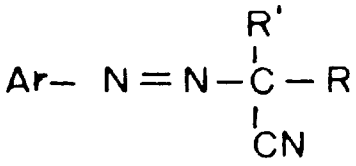
solution of ethylcyanoacetic ethyl ester, a bromophenylethylhydrazone can be obtained.[43]

$$p\text{-}BrC_6H_4N_2^+\ Cl^- + C_2H_5\text{-}CH(CN)COOC_2H_5 \rightarrow p\text{-}BrC_6H_4\text{-}\underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{N}}\text{-}N{=}C\begin{matrix}\diagup\ COOC_2H_5\\ \diagdown\ CN\end{matrix}$$

Although the reasons and mechanism for these transformations are still unknown, nearly all of the investigations of mixed azo compounds have been concerned with this type of transformation. In spite of the fact that mixed azo compounds are said to lose one mole of nitrogen by thermal decomposition much less readily than aliphatic azo compounds,[44,45] no investigation of this phenomenon was found in the literature.

Purpose of this investigation and approach. Interest was drawn to the azo nitriles because their clean-cut, easily controlled thermal decompositions in solution at convenient temperatures indicated them to be good sources of free radicals and hence polymerization initiators. Examination of the azo nitriles which have been investigated reveals that the temperatures at which they are useful as free radical sources range from about -20° to about 120°. The purpose of this work was to provide azo nitriles which could serve as useful sources of free radicals at higher temperatures and to study their thermal decompositions.

Since it appeared that further study of the symmetrical aliphatic azo nitriles would not be likely to reveal any compounds of greater stability at higher temperatures and since it seemed that the presence of an aromatic group attached to the azo linkage imparted this property, it was decided that the mixed azo nitriles would be worthy of investigation. This type of compound may be represented by the general formula:



Because of the great tendency for mixed azo compounds to rearrange to hydrazones, especially when an hydrogen atom is adjacent to the azo group, and since it was desirable to prevent this from occurring, it was decided to investigate only those cases in which R and R' are alkyl groups and to arrange experimental conditions to eliminate this possibility insofar as possible.

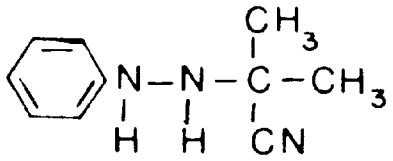
In studying the thermal decomposition of these substances, it was intended to isolate products, which it was hoped would substantiate a free radical mechanism and indicate something about the relative degree of freedom of the radicals formed. In addition the rates of decomposition were to be determined at a convenient temperature and one or more energies of activation measured. It was also hoped that some correlation between structure and rate could be found.

A further object of this work was to be the determination of infra-red absorption curves for both the hydrazo and azo compounds to obtain evidence to more definitely locate the N=N stretching frequency.

Certain preparative work described in the literature should be mentioned here since it served as a guide for the approach to the preparative problem. Although none of the mixed azo nitriles studied in this work had been previously prepared, it was thought that methods used for making some of the other mixed azo compounds might be applicable. Of particular interest was the method used by Fischer[35-37]

and by Tafel[38] to produce phenylazomethane, phenylazoethane, etc. They oxidized the corresponding hydrazo compound by shaking it in ether solution with mercuric oxide. It seemed that such a mild, neutral oxidant used in a non-polar media would certainly preclude any isomerization. Aside from the possibility of rearrangement, any halogen oxidation, such as that used by Overberger, was to be avoided because of the probability of getting simultaneous substitution in the aromatic group.

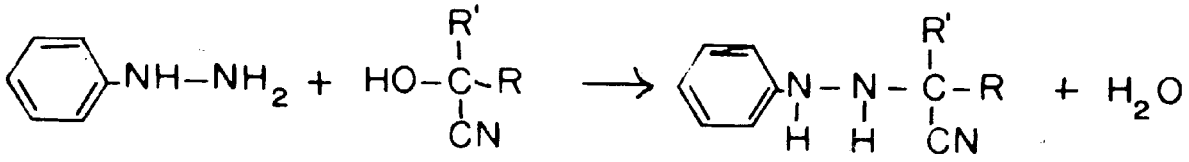
With regard to the corresponding hydrazo nitriles, one such compound had been previously prepared. This was α-(β-phenyl-hydrazino)-isobutyronitrile:



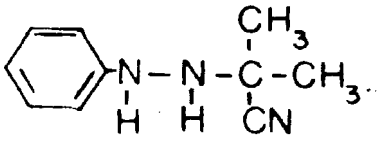
It was first prepared by Reissert[46] by allowing phenylhydrazine to react with acetone cyanohydrin. The procedure was later improved by Bucherer and Grolée.[47]

II Discussion of Results

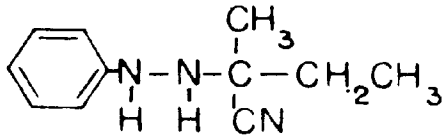
Preparation of compounds. The procedure of Bucherer and Grolée[47] was found to be quite general for the preparation of mixed hydrazo nitriles in those cases where the aromatic group is an unsubstituted phenyl group and the nitrile group does not contain an α-aromatic substituent. This method consists of allowing equivalent amounts of phenylhydrazine and the appropiate aliphatic cyanohydrin in ether solution to stand for periods of about two weeks. The reaction may be indicated:



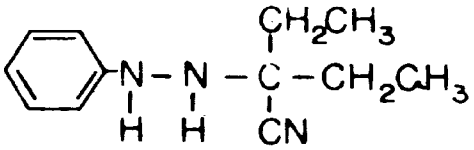
The following mixed hydrazo nitriles, only the first of which was previously known, were prepared in this way.



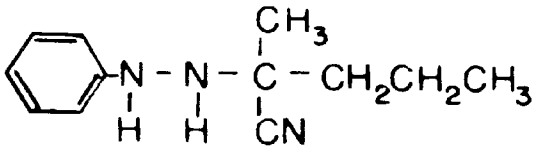
(I)



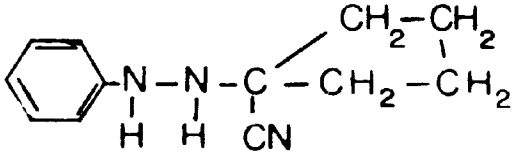
(II)



(III)



(IV)

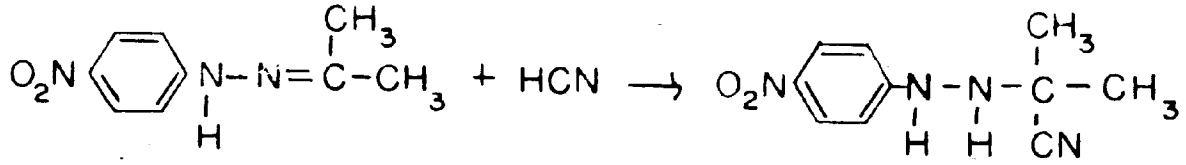


(V)

This method failed completely in efforts to make an hydrazo nitrile from p-nitrophenylhydrazine. In one trial, using dioxane as a solvent, the mixture was allowed to stand one year with apparently no reaction.

In an attempt to form an hydrazo nitrile from p-methoxyphenylhydrazine by this procedure, a reaction occurred and a white, crystalline product was obtained. However, it could not be oxidized to an azo compound, its infra-red absorption curve differed appreciably from those of the other hydrazo compounds studied, and its analysis did not correspond to the expected product. The method also failed to give the desired reaction between phenylhydrazine and acetophenone cyanohydrin. The only product which was isolated was the phenylhydrazone of acetophenone.

It was found that hydrogen cyanide could be added to the p-nitrophenylhydrazone of acetone very readily, producing the desired hydrazo nitrile (VI). This was accomplished by stirring a mixture of the hydrazone and excess hydrogen cyanide in acetonitrile-acetic acid solution at room temperature.



(VI)

All of these hydrazo nitriles are relatively unstable. On heating they easily eliminate hydrogen cyanide and go over to the corresponding hydrazone. They are somewhat sensitive to oxidation by air and thus form tarry materials. However, they could be stored in closed containers in a refrigerator for several months without

serious deterioration. They are all white crystalline substances when pure, except (VI).

It was early found that a commercial preparation of yellow mercuric oxide readily oxidized (I) in ether solution to the corresponding azo compound by the procedure of Fischer.[37] This was done with yellow mercuric oxide which had been on the shelves of this laboratory for many years. When this bottle was exhausted, no other commercial preparation could be found which would give comparable results. The difference may lie in the alkali content or in the drying temperature. Very possibly freshly precipitated mercuric oxide would have solved the problem. However, it was found that silver oxide was superior as the oxidizing agent in that it was more reactive and hence required less time. Commercially prepared silver oxide was used and no trouble was experienced in changing to other bottles. The procedure consisted of adding excess silver oxide in small portions to a stirred ether solution of the hydrazo nitrile. By this method (I), (II), (III), (IV), and (V) were all oxidized to their corresponding azo nitriles.

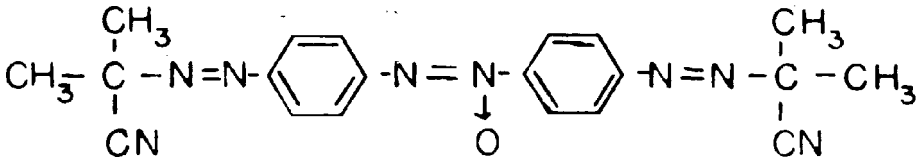
There was no evidence of oxidation beyond the azo stage and the azo nitriles were obtained in high yield. To show that no isomerization took place during the oxidation, the azo compound from (I) was hydrogenated in ether solution over palladium on barium sulfate as catalyst. The product obtained was shown to be identical to the original hydrazo nitrile (I).

Nothing seems to be known about the mechanism of this type of oxidation. An interesting observation was made which may give some indication about it. If the ether solution is filtered off after the silver oxide has been added and the initial reaction is apparently

over, a clear yellow solution is obtained and the silver and excess silver oxide remain on the filter. This solution, even after drying in some cases, continued to deposit a small amount of silver. Thus it would seem that some ether soluble silver complex is present as an intermediate in the oxidation.

In the case of the nitro compound (VI), bromine oxidation in acetonitrile-water solution was used at first to oxidize the hydrazo compound. It was found more satisfactory, however, to perform the oxidation in the original reaction mixture from the preparation of this hydrazo nitrile without its prior isolation. This was more convenient and higher yields of the azo compound could be obtained. After removal of the excess hydrogen cyanide and some acetonitrile from the acetonitrile-acetic acid solution of the hydrazo compound, an acetonitrile solution of bromine was added. It was deemed feasible to try bromine oxidation in this case since a nitro group on a benzene nucleus decreases the reactivity of the ring toward substitution by halogen.

Another compound which was prepared incidentally to this work but not studied further is probably the azo nitrile:



This substance resulted when p-nitrophenylhydrazone of acetone in methanol solution was heated at 100° with excess hydrogen cyanide in the presence of a trace of hydrochloric acid in a sealed tube. Apparently, under these conditions the nitro group oxidizes the hydrazo

group to azo and is then further reduced either by more hydrazo molecules or by the methanol to an azoxy group.

All of these azo compounds, except the last mentioned material, are yellow crystalline substances below their melting points, melt to yellow or orange liquids without decomposition, and give yellow or orange solutions. They decompose thermally at temperatures above 140°, but appear to decompose slowly even at room temperature in the presence of sunlight.

In azo compounds of this type there is no possibility of having both dl- and meso-isomers as there is in the aliphatic azo nitriles. Consideration of molecular models indicates that, unlike the aliphatic azo nitriles, the cis configuration of the azo group is possible. Hence both cis- and trans-isomers may exist. No study of this matter was made and it is not known which of these isomers were prepared. The pecular behavior of the azo compound prepared from (II) may possibly be explained by this isomerization. The first time this compound was made it could be crystallized from petroleum ether, but when filtered in a cold room at -10° it melted and ran through the filter. When it was later prepared again, it was recrystallized from petroleum ether by another technique designed to keep it cold enough to remain solid. After two recrystallizations, it melted quite sharply at 4-5°. One more recrystallization brought the melting point to 16-19.5° which could not be raised by further recrystallization. This behavior may be due to slow conversion of one stereoisomer to an equilibrium mixture of the two forms.

For the preparations discussed above it was necessary to produce certain previously known cyanohydrins to be used as starting materials.

The cyanohydrins of acetone, methyl ethyl ketone, diethyl ketone, methyl n-propyl ketone, and cyclopentanone were prepared. Essentially two different techniques were used.

Acetone cyanohydrin was produced by the procedure in Organic Syntheses.[48] This method consists of adding sulfuric acid slowly to an aqueous solution of sodium cyanide and acetone while keeping the mixture cold. The cyanohydrins of methyl ethyl ketone and n-propyl ketone were prepared by similar procedures. This method has two disadvantages: (1) the rate of addition of the acid must be slow and carefully controlled to keep the temperature down due to the considerable amount of heat liberated; (2) the separation of large amounts of sodium sulfate and bisulfate during the course of the acid addition makes it difficult to get adequate stirring. The latter factor necessitates filtering off the salts and washing them thoroughly to remove adhering product.

The cyanohydrins of diethyl ketone and cyclopentanone were prepared by the procedure described by Colonge and Joly.[49] To a flask containing a mixture of monopotassium phosphate, water and the ketone, an aqueous solution of sodium cyanide is added all at once. The flask is stoppered and shaken for two hours. Yields are reportedly at least as good as from other methods and the difficulties mentioned above are completely avoided. The writer highly recommends this technique because of its convenience. If it had come to his attention earlier, he would have applied it to all of these aliphatic ketones.

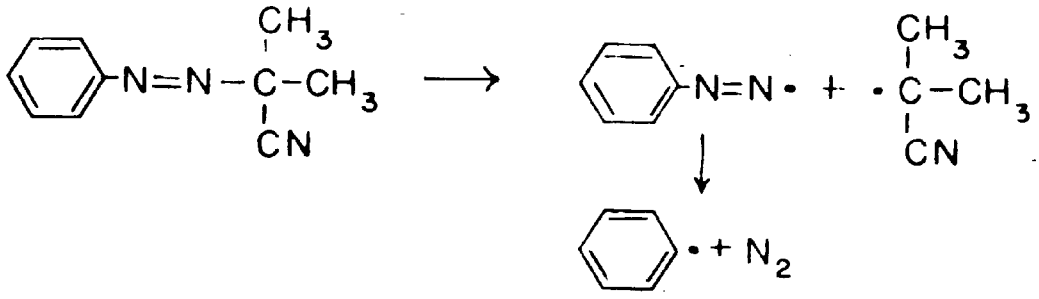
Products of Decomposition. The products of the thermal decomposition of one of these mixed azo nitriles, α-phenylazoisobutyronitrile, were investigated, since they might shed some light on

the type of reaction involved. Preliminary observations showed that it was necessary to heat this compound to 140° or higher before any appreciable evolution of gas occurred. 165° appeared to be a convenient temperature for the decomposition. The material was decomposed without solvent because if a solvent boiling above this temperature were used, the separation of the solvent from the decomposition products would be difficult and besides it was believed that the expected free radicals would react with any solvent at this temperature.

α-phenylazoisobutyronitrile was heated at 165° in a thermostatic bath until decomposition was complete. A portion of the gas produced was passed through a Dry Ice trap. From the material collected in the trap it was shown that a small amount of hydrogen cyanide was formed in addition to the nitrogen. The residue in the decomposition vessel was steam distilled. The major part of the residue seemed to be a dark red polymeric mass which would not distill with steam. The material which did distill was then subjected to a Craig counter-current extraction process using separatory funnels. The solvents employed were acetonitrile and petroleum ether (b.p. 60-75°). By this process the material was separated into thirteen fractions. From the fractions containing the material soluble in petroleum ether, there was obtained a substance which after purification was shown to be diphenyl by a mixed melting point determination with a sample of authentic material. A less clear cut separation was obtained for the fractions of the material more soluble in acetonitrile. This separation was complicated by the fact that they contained appreciable amounts of polymeric material apparently formed by air oxidation. Further separations were made by sublimation, crystallization, and distillation.

A white crystalline substance which was obtained was shown to be tetramethylsuccinonitrile by comparison of its infra-red absorption curve with that of an authentic sample of the substance which had been prepared by the decomposition of α - α'-azo-bis-isobutyronitrile. There was also obtained a light yellow oil which was shown to be α-phenylisobutyronitrile. This was established by conversion to its amide and to its acid, which are white, crystalline, previously characterized substances.

Although all of the decomposition products, which were identified, could only be isolated in very small yields, the very fact that they were formed is strong evidence of a free radical mechanism for the decomposition. This does not, of course, eliminate the possibility of another decomposition mechanism operating in addition. Upon noting the relative instability of aliphatic azo compounds and particularly aliphatic azo nitriles compared to aromatic azo compounds, it seems logical for the bond between the azo group and the aliphatic carbon atom to be the first to cleave. Hence, the mechanism proposed for this reaction is:



All three of the possible products which could be formed by straight-foward recombinations of the phenyl and isobutyronitrile radicals, were isolated. Another reasonable product, azobenzene, could not be found among the products. For this reason it is assumed that the life

of the phenylazo radical is short compared to the life of the phenyl radical. One probable side reaction is rearrangement, of the type discussed in the introduction, to an hydrazone by migration of a group attached to the α-carbon atom. The hydrogen cyanide may have been eliminated by either the starting azo nitrile or one of its decomposition products.

Kinetic measurements. The rates of thermal decomposition of these mixed azo nitriles were determined by measurement of the volume of nitrogen evolved at definite time intervals. The compounds were dissolved in molten ceresine, a purified naturally occurring hydrocarbon wax. The solutions were heated in a nitrogen atmosphere in a thermostatic bath.

In the standard mathematical treatment of the first order reactions,[50] the expression,

$$-\frac{dc}{dt} = kc \quad ,$$

where c is the concentration of the reacting substance at time t, is converted to its equivalent,

$$-\frac{d(a-x)}{dt} = k(a-x) \text{ or } \frac{dx}{dt} = k(a-x) \quad ,$$

where a is the initial concentration and x is the decrease in concentration after time t. Integration and evaluation of limits gives

$$kt = \ln\frac{a}{(a-x)} \quad *$$

In a reaction of this type where one mole of gas is formed for each

* The symbol ln signifies natural logarithm while log indicates logarithm to the base 10.

mole of substance which has reacted, the total volume, V_∞ , of gas evolved after a very long time is proportional to the initial concentration, a, of the reactant and volumes, V_t, at times t are proportional to the decreases of concentration of the reactant by the same proportionality factor, providing the temperature and pressure of the gas are constant. Therefore, by substitution for a and x the equation becomes:

$$kt = \ln \frac{V_\infty}{V_\infty - V_t} .$$

For a first order reaction a plot of $\ln \frac{V_\infty}{V_\infty - V_t}$ vs. t should, then, give a straight line passing through the orgin with slope k, the specific rate constant, or a plot of $\log \frac{V_\infty}{V_\infty - V_t}$ vs. t should have a slope of k·log e.

This treatment suffers badly in that the value of V_∞ is weighted approximately equal to the sums of the weights of all the other readings, and an error in the value of V_∞ has the same effect on k as a systematic error of the same magnitude in all of the other readings. This treatment can be justified only if V_∞ is known with much greater accuracy than the other readings. In the present work the V_∞ readings were probably the least accurate and therefore the above treatment cannot be justified except on the basis of conventionality.

The treatment of first order reactions by Guggenheim[51] has several advantages. It is not necessary to know the initial concentration, the initial gas volume, the final gas volume, the starting time, nor the final volume, and each reading is used once and only once, and all readings are weighted equally. The method follows in brief.

The equation obtained by the conventional method may be written in an equivalent exponential form:

$$V_\infty - V_t = V_\infty \; e^{-kt} \quad .$$

Now suspose that n gas volume readings, v_1, v_2, ...v_i,....v_n, are taken at times t_1, t_2, ...t_i, ...t_n (without any restriction as to the intervals), and that n more readings v_1', v_2', ...v_i',.....v_n', are taken at times $t_1+\tau$, $t_2+\tau$, ...$t_i+\tau$,....$t_n+\tau$, each a constant time, τ, after one of the previous set. Substitution in the above equation then gives

$$V_\infty - v_i = V_\infty \; e^{-kt_i}$$

and

$$V_\infty - v_i' = V_\infty \; e^{-kt_i \; -k\tau} \quad .$$

By subtraction,

$$v_i' - v_i = V_\infty \, (1-e^{-k\tau})e^{-kt_i} \quad ,$$

or taking logarithms,

$$\ln(v_i' - v_i) = -kt_i + \ln\left[V_\infty(1-e^{-k\tau})\right]$$

or

$$\ln(v_i' - v_i) = -kt_i + \text{constant}$$

Hence, if $\ln(v_i' - v_i)$ is plotted against t_i, the slope of the straight line obtained will be $-k$; or if $\log(v_i' - v_i)$ is plotted against t_i, the slope will be $-k \cdot \log e$. The fact, that the intercept at $t_i = 0$ is $\ln V_\infty\left[(1-e^{-k\tau})\right]$, gives a means of calculating V_∞, using the value of k obtained from the slope.

The Arrhenius equation, $k = A^{-E/RT}$, relates the rate constant to the frequency factor, A, the energy of activation, E, and the absolute temperature, T. On taking logarithms,

$$\ln k = \ln A - \frac{E}{RT} \quad .$$

If k_1 and k_2 are the specific rate constants at temperatures T_1 and T_2, and these are inserted in this equation, and the two resulting expressions subtracted from one another, it is found that[52]

$$\ln \frac{k_2}{k_1} = \frac{E}{R} \frac{T_2 - T_1}{T_1 T_2}$$

or

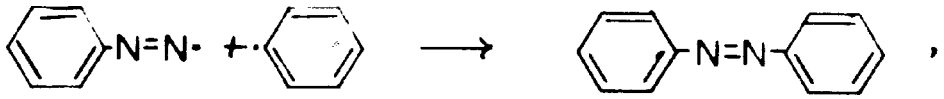
$$E = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1} \quad .$$

The rates of decomposition of the mixed azo nitriles were determined at 165°. The data obtained were plotted by both the standard method and the Guggenheim method. Representative graphs of these data are shown in Figures I, III, IV, V, VI, and VII. The points for the standard plots are indicated by ○ and the scales on the left and bottom apply. The Guggenheim points are indicated by □ and the right and upper scales are applicable. In addition the reaction rate for α-phenylazoisobutyronitrile was determined at 175° and the energy of activation for its decomposition was calculated from the Arrhenius equation. Figure II shows a plot used for the determination of this higher temperature rate.

A summary of the results of the kinetic measurements is shown in Table A. Figure VIII is a graphical summary of the rates of decomposition at 165°. This graph shows the same curves as are found in Figures I, III, IV, V, VI, and VII, except that the V_∞ values used were those calculated from the Guggenheim plots. In this way the advantages of the Guggenheim method are obtained, while retaining the conventionality of the standard plots. The data near

the orgin, except for α-phenylazoisobutyronitrile, was omitted on this graph to avoid crowding. Since curve 2 lies so close to curve 3 many of its points have been omitted to avoid confusion. The data at longer times for curve 6 would lie beyond the limits of the figure and hence are not shown.

Inspection of Table A reveals that the stoichiometric amounts of nitrogen were never obtained, but only 70-95%, except in the case of the nitro compound which gave more than 100%. Obviously nitrogen is retained in the reaction mixture by some reaction other than those shown in the proposed mechanism. The other reaction or reactions may involve formation of products, which do not eliminate a gas under the conditions, by either the phenylazo radical or the original azo nitrile. The absence of any azobenzene among the decomposition products indicates that the reaction,



is not responsible. The possibility of retained nitrogen by reaction of the phenylazo radical with the hydrocarbon solvent is also ruled out because in the case of α-phenylazoisobutyronitrile the yield of nitrogen was approximately the same when decomposed without solvent. Thus a side reaction involving the original mixed azo nitrile is probably the cause. Since first order kinetics were observed, any simultaneous reaction would very probably be first order also. In view of this and the apparent ease of rearrangement of the other mixed azo compounds, it seems probable that rearrangement to an hydrazone occurs by migration of a group from the α-carbon atom. In this event, the rate constant for the decomposition which

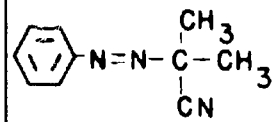
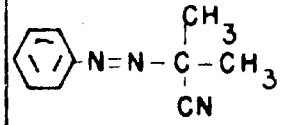
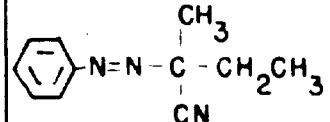
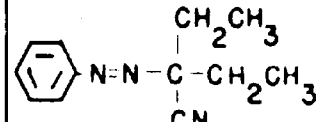
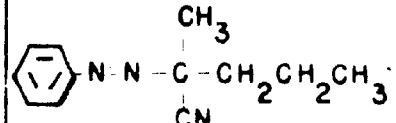
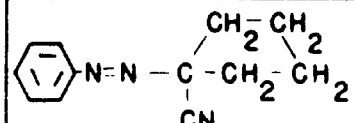
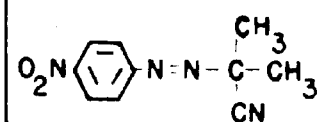
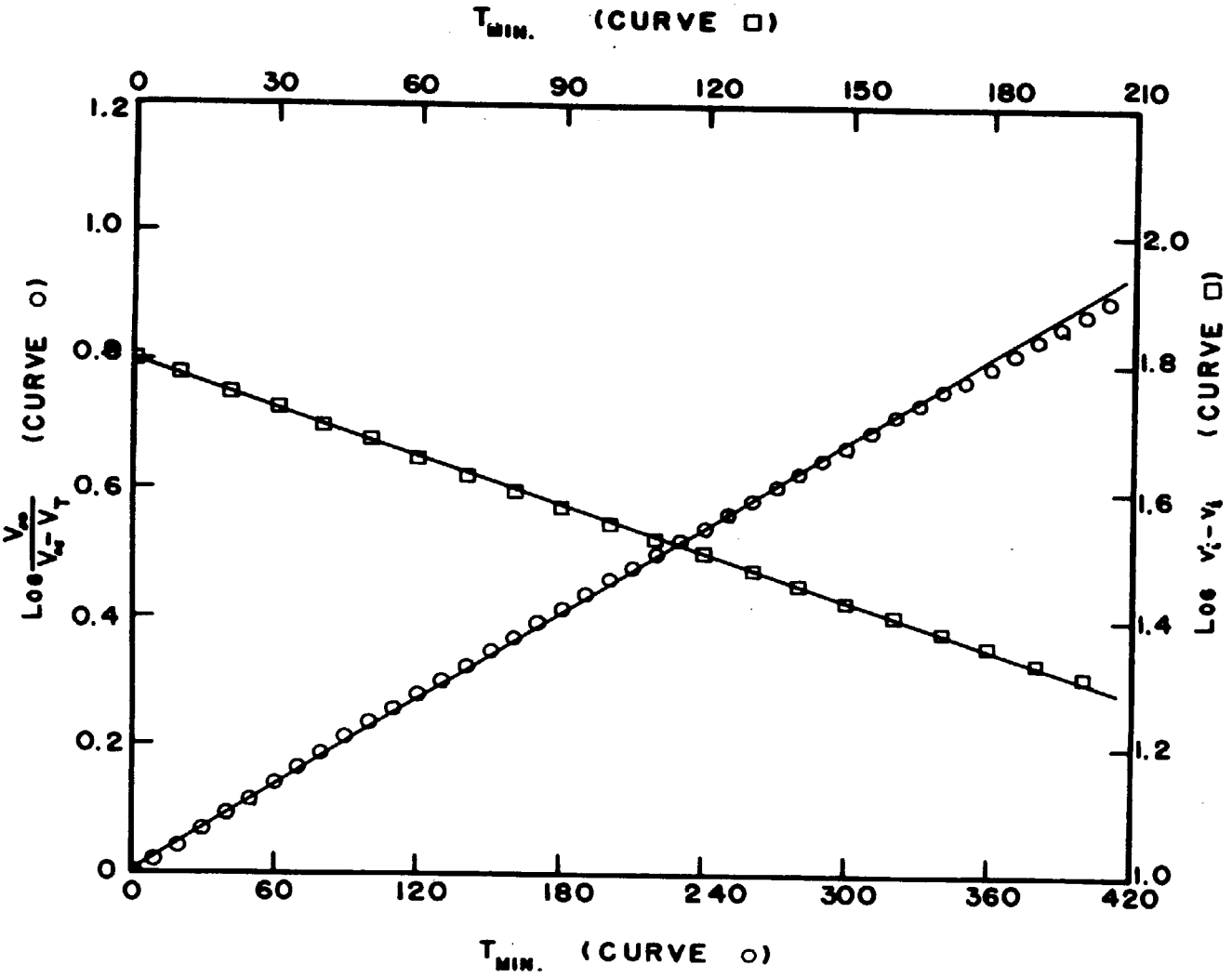
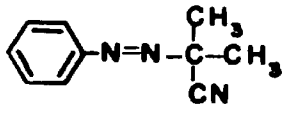
Compound	Temp. °C	Fig. #	% of theor. N_2 exp't'l	% of theor. N_2 calc. from Gugg. plot	k (Std.) $min.^{-1}$	k (Gugg.) $min.^{-1}$	E kcal.
	165	I	78.7 79.5	76.2 76.9	0.00511 0.00511	0.00570 0.00568	41.6 ±0.6
	175	II	83.8 82.6	81.0 80.0	0.0147 0.0150	0.0163 0.0168	
	165	III	83.9 84.8	79.5 82.6 82.6	0.00449 0.00454	0.00491 0.00485 0.00487	
	165	IV	93.7 94.5	90.8 92.8	0.00442 0.00444	0.00475 0.00469	
	165	V	87.3 87.2	86.1 85.3	0.00709 0.00721	0.00733 0.00743	
	165	VI	72.1 74.4	72.3 70.9	0.00393 0.00365	0.00392 0.00388	
	165	VII	107.1 109.8	106.9 112.6	0.00276 0.00264	0.00262 0.00258	

Table A



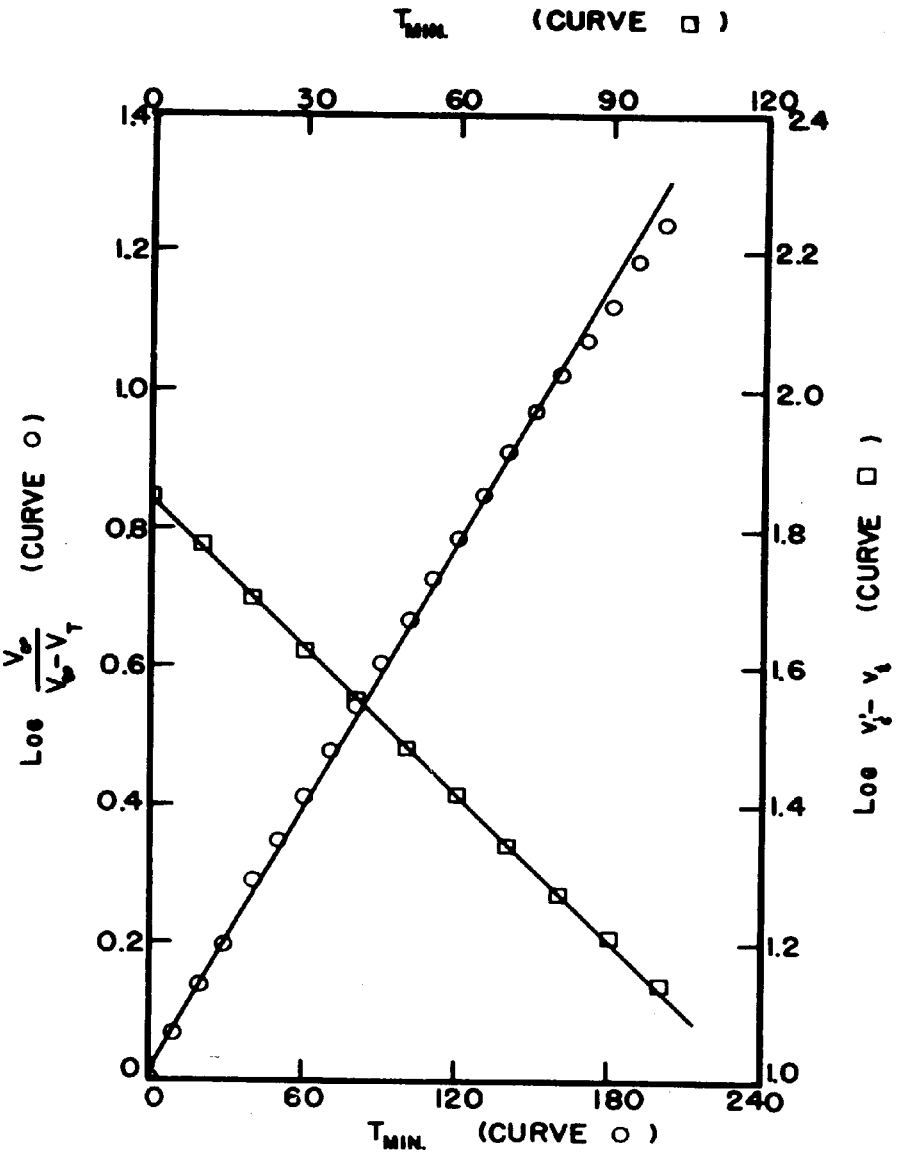
RATE OF DECOMPOSITION OF 

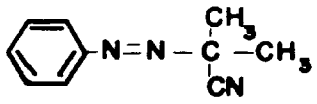
AT 165°C. IN CERESINE.

STANDARD METHOD ○

GUGGENHEIM METHOD □

FIGURE 1

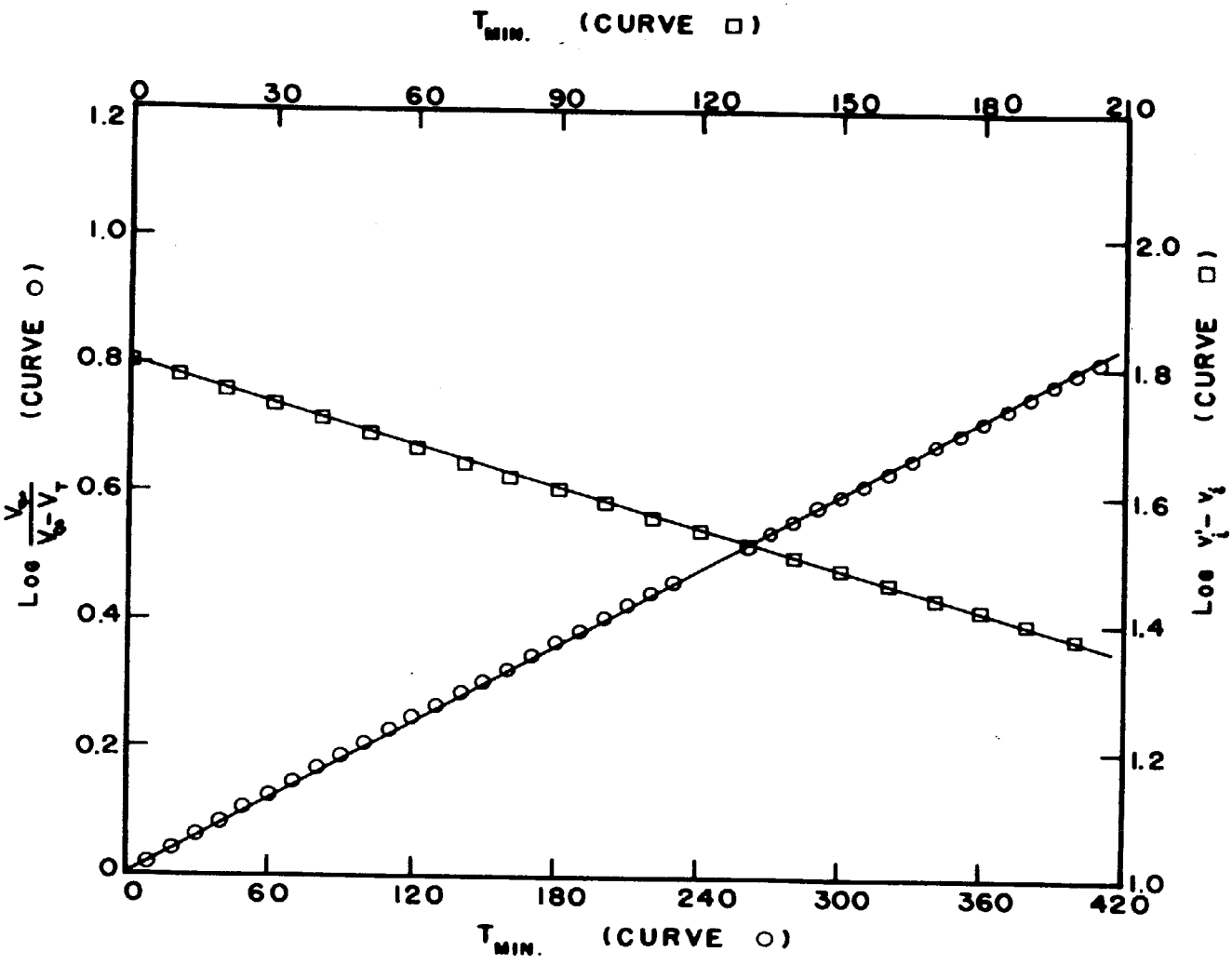


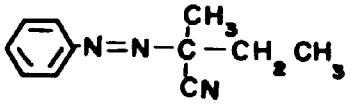
RATE OF DECOMPOSITION OF  AT 175°C. IN CERESINE.

STANDARD METHOD □

GUGGENHEIM METHOD ○

FIGURE II



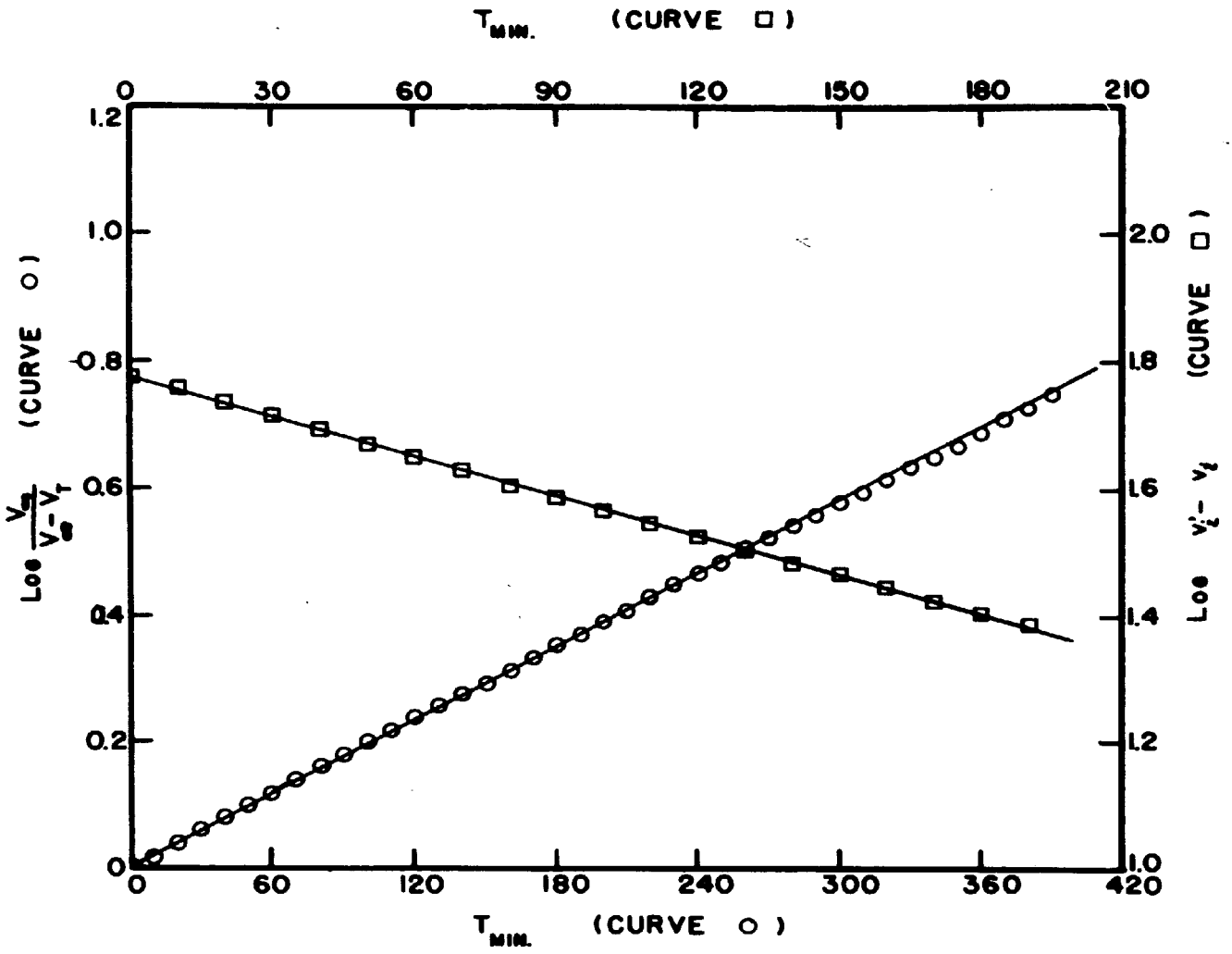
RATE OF DECOMPOSITION OF 

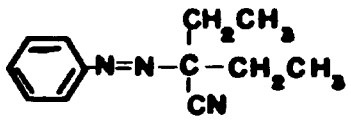
AT 165°C. IN CERESINE.

STANDARD METHOD ○

GUGGENHEIM METHOD □

FIGURE III



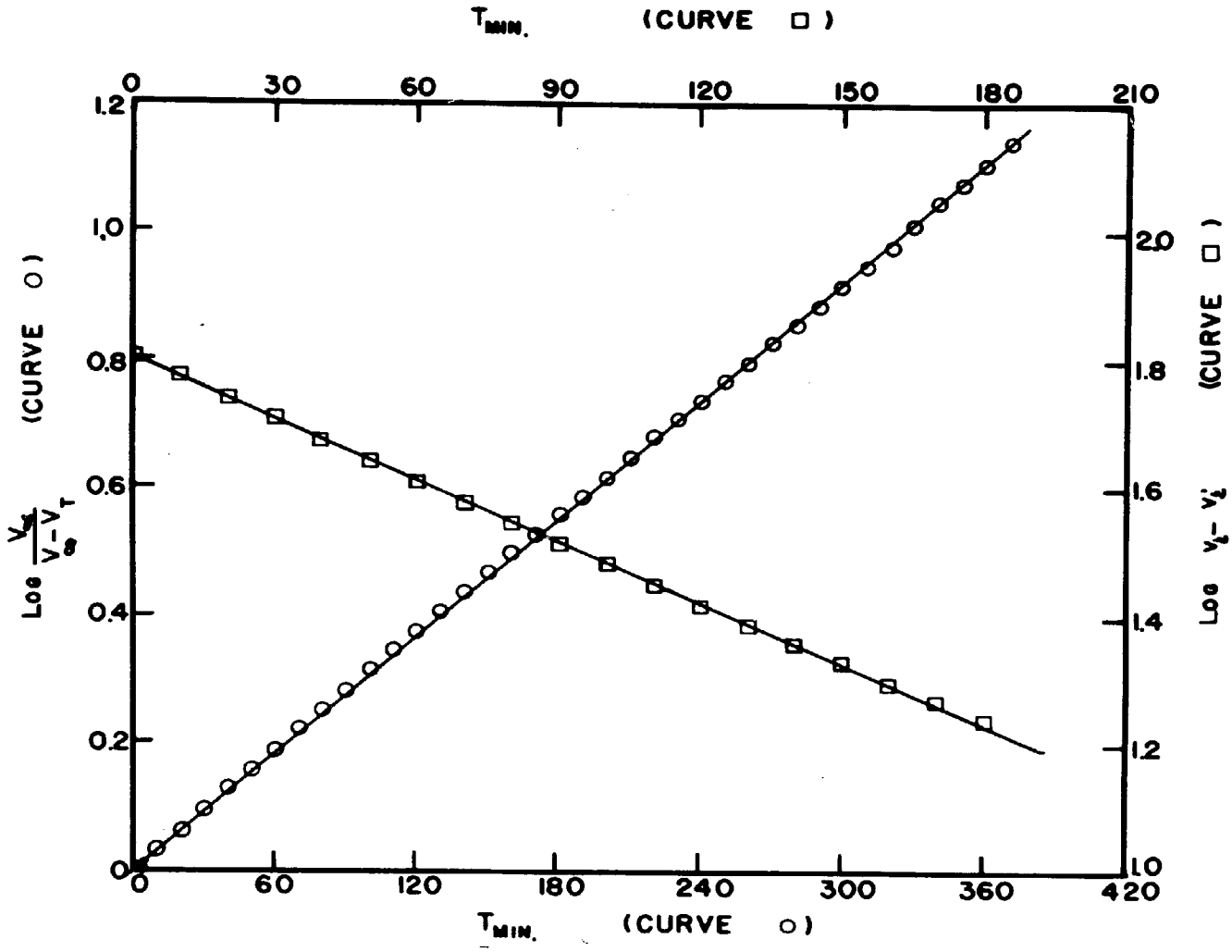
RATE OF DECOMPOSITION OF 

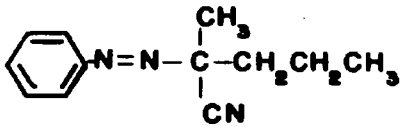
AT 165 °C. IN CERESINE.

STANDARD METHOD ○

GUGGENHEIM METHOD □

FIGURE IV.



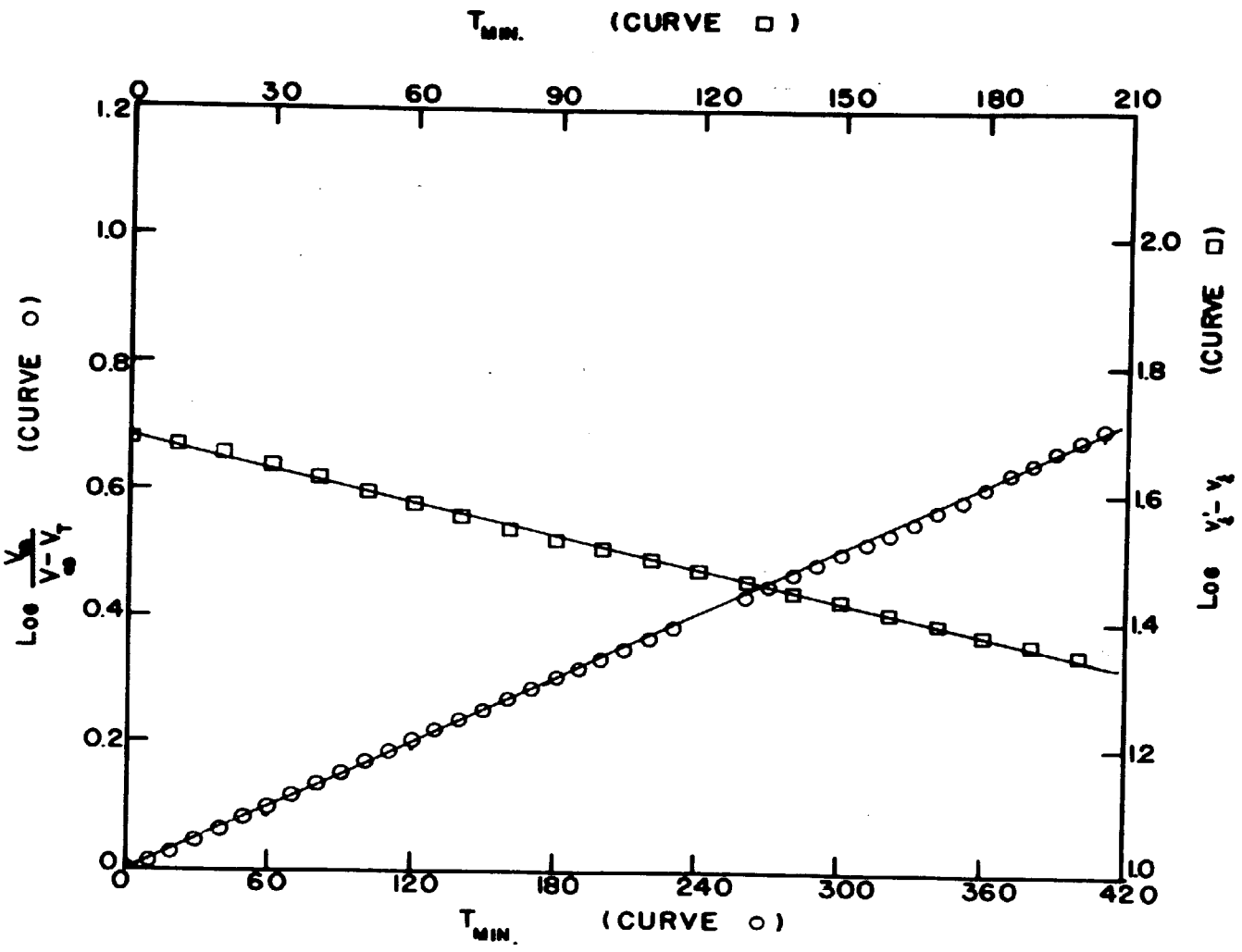
RATE OF DECOMPOSITION OF 

AT 165 °C. IN CERESINE.

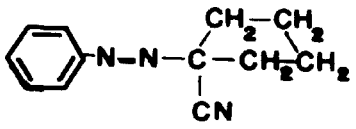
STANDARD METHOD ○

GUGGENHEIM METHOD □

FIGURE V



RATE OF DECOMPOSITION OF

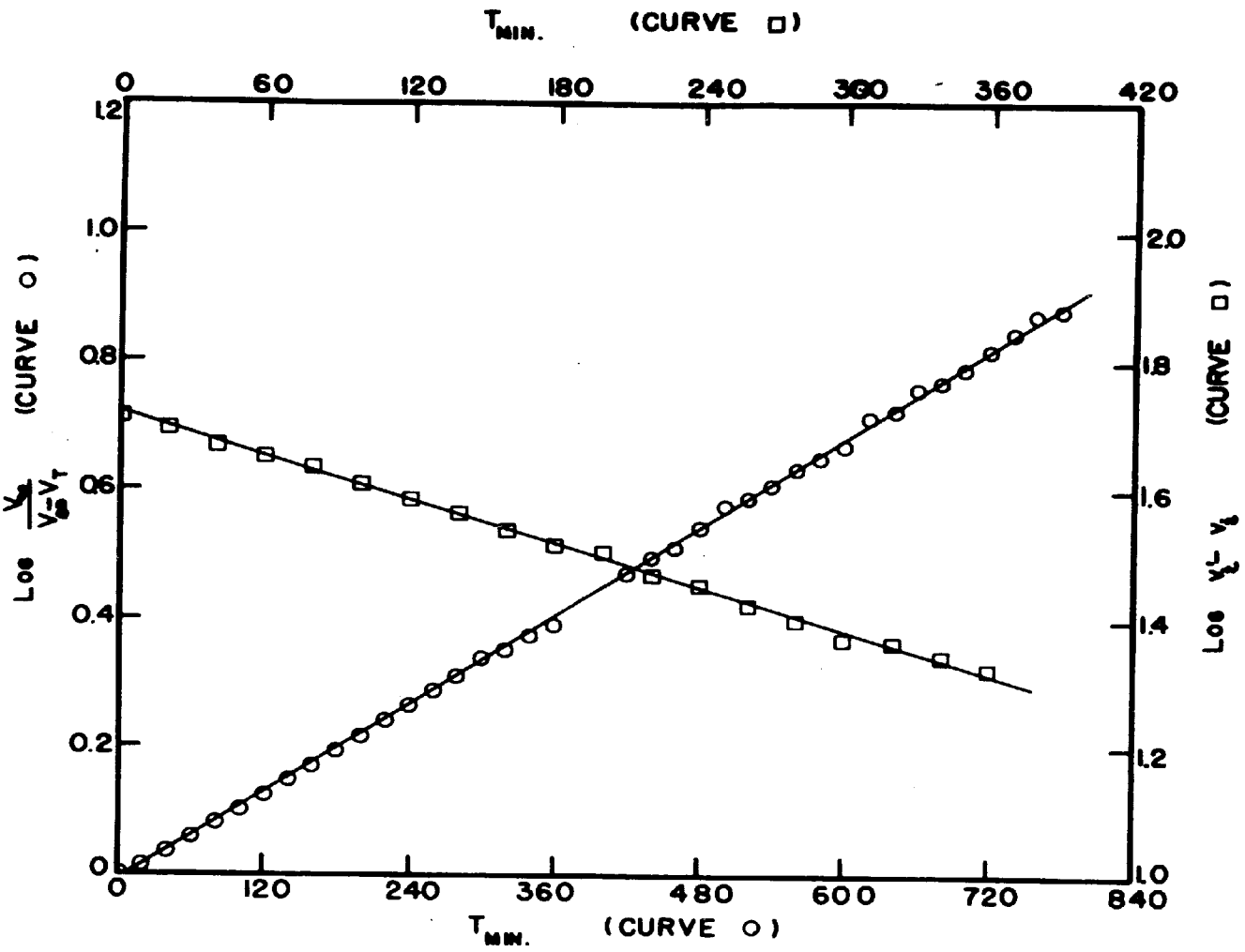


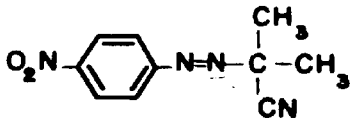
AT 165°C. IN CERESINE.

STANDARD METHOD ○

GUGGENHEIM METHOD □

FIGURE VI



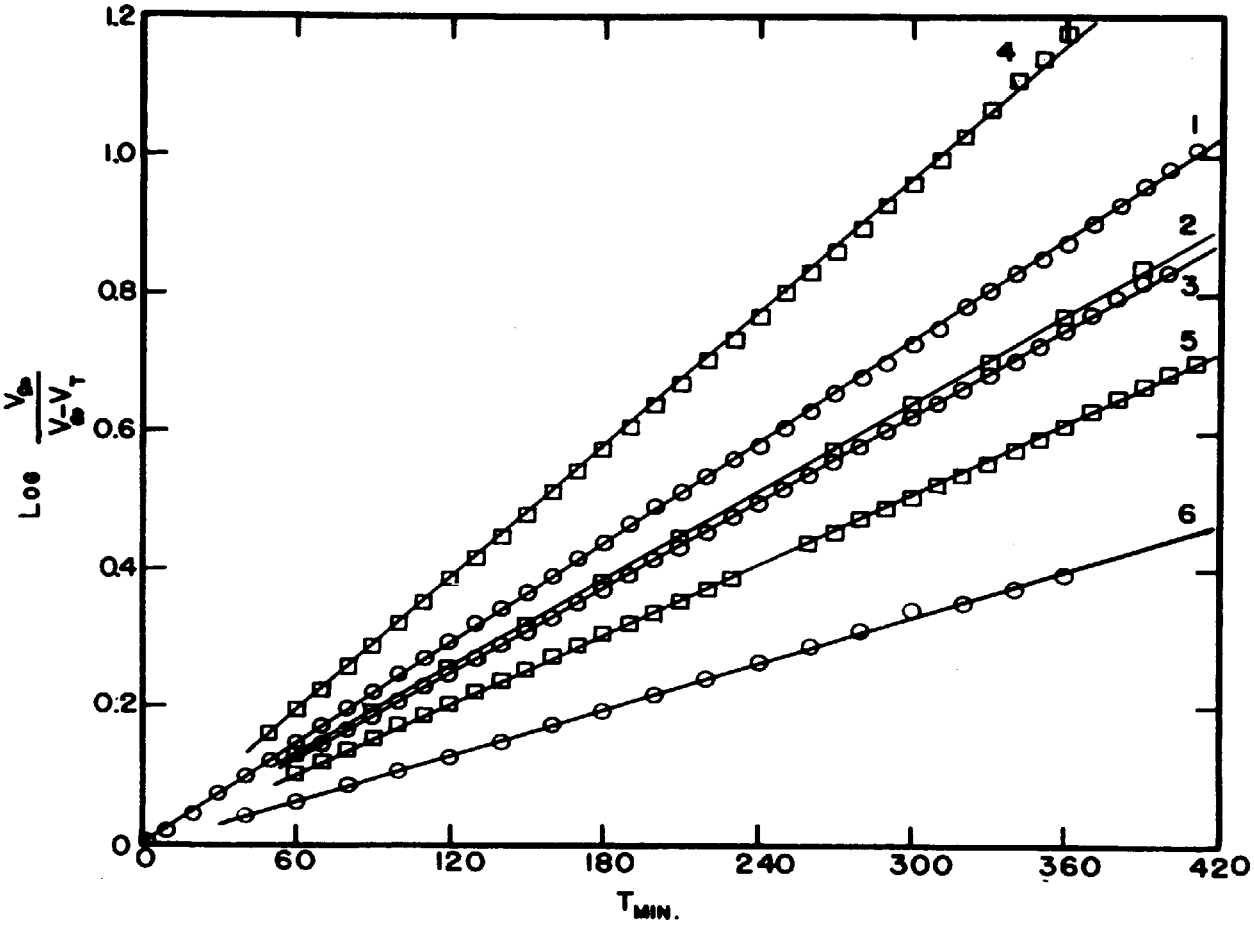
RATE OF DECOMPOSITION OF 

AT 165° C. IN CERESINE .

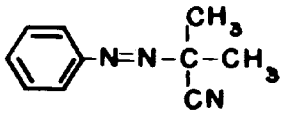
STANDARD METHOD ○

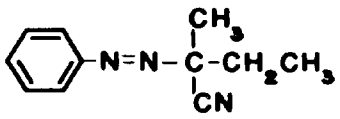
GUGGENHEIM METHOD □

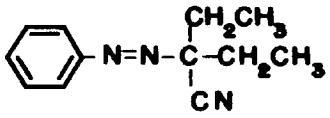
FIGURE VII

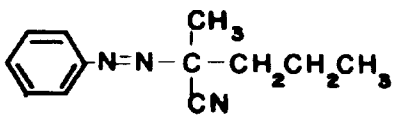


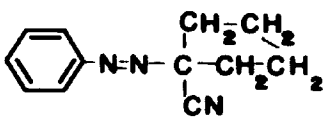
RATES OF DECOMPOSITION IN CERESINE AT 165°C. OF

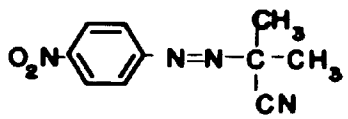
(1) 

(2) 

(3) 

(4) 

(5) 

(6) 

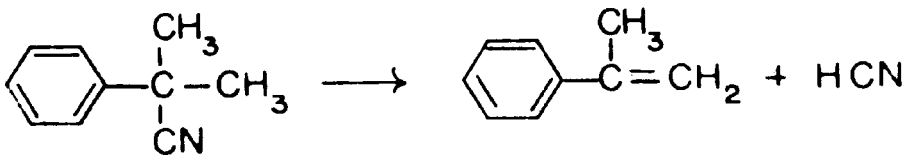
(V_∞ CALCULATED BY THE GUGGENHEIM METHOD.)

FIGURE VIII

was found would be the sum of the rate constants for the cleavage reaction and the isomerization.

The excess gas in the case of the nitro compound may be due to oxidation of the solvent by the nitro group. Such an oxidation may be accompanied by the formation of hydrogen and water. (When nitrobenzene oxidizes methyl alcohol in the presence of alkali, hydrogen is formed in considerable amounts.)

Another significant point, to be noted from Table A, is that the experimental V_∞ values were, in all cases except that of the nitro compound, greater than those calculated from the Guggenheim plots. This caused a slight curvature in the standard plots which was not apparent in the Guggenheim plots. Lower values for the rate constants were obtained from the standard curves, also apparently due to V_∞ values being too great. There are at least two reasonable ways to explain high V_∞ values. It is probable that benzene and a dialkylacetonitrile were formed in small amounts during the decompositions by disproportionation reactions of the free radicals and/or by hydrogen abstraction from the solvent. While such relatively volatile materials would be expected to be retained in the reaction vessel by the condenser, it is possible that over the long period of time necessary to get the V_∞ reading they would slowly volatilize into the gas beyond the condenser. When decomposed without solvent, hydrogen cyanide is produced. If this also occurs in solution by a very slow decomposition of one of the direct products, it might well have very little effect on the earlier readings but have an appreciable effect on a reading taken after a long period of time. An example of such a reaction might be:



The energy of activation given for α-phenylazoisobutyronitrile was calculated from the Guggenheim values for the rate constants. Just how much significance can be attached to this value is doubtful since the k's used are very possibly sums of two other rate constants as noted earlier. However, it is probably of the right order of magnitude for the cleavage reaction. The error shown for this value is the deviation from the mean of the maximum and minimum values obtainable from these rate constants.

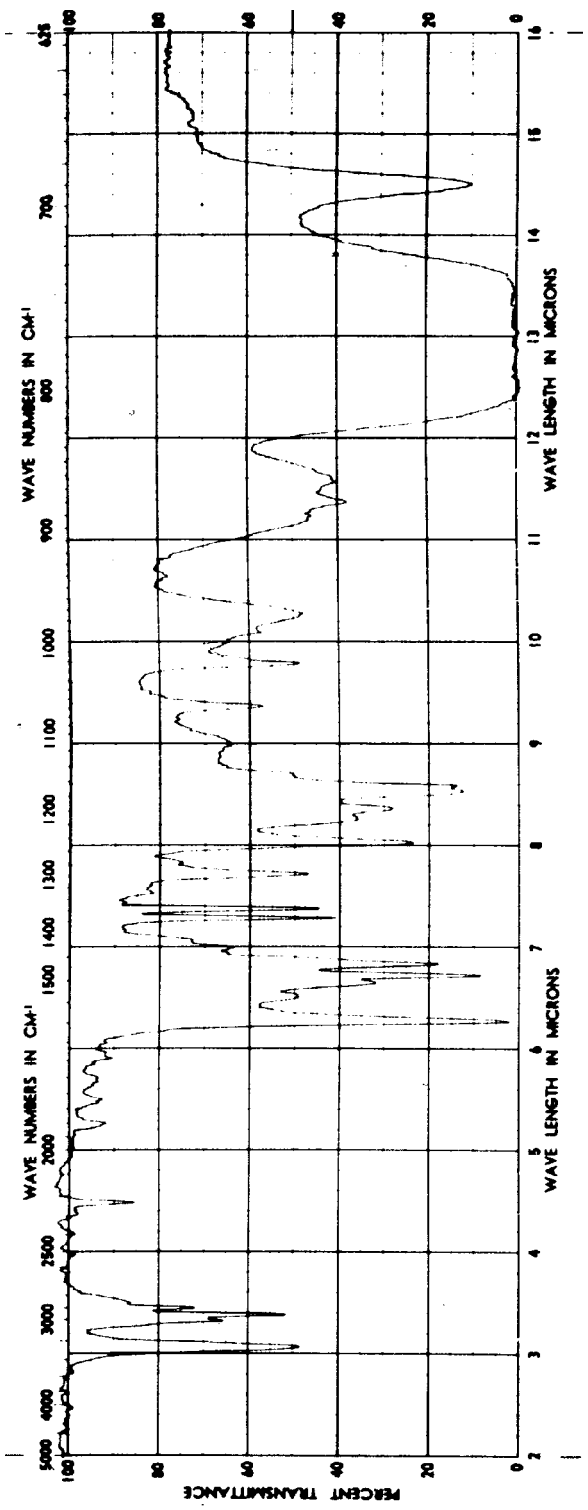
The rates of decomposition of these mixed azo nitriles show no really striking differences among the compounds tested. The variations are qualitatively, although not quantitatively, in the same direction as the analogous results of Overberger. Consideration of molecular models indicates that there can be no steric interference of groups across the azo linkage from each other, except in the case of α-phenylazo- α-methylvaleronitrile. Even in this compound the model can be easily made and there is only slight limitation in the degree of freedom of rotation about the various single bonds. Nevertheless, this may explain the fact that this compound had the highest decomposition rate of the substances tested. There is no apparent reason for the other small differences observed. It was found here that replacement of methyl groups by ethyl groups on the α-carbon atom caused a small decrease in rate, which parallels Overberger's findings.

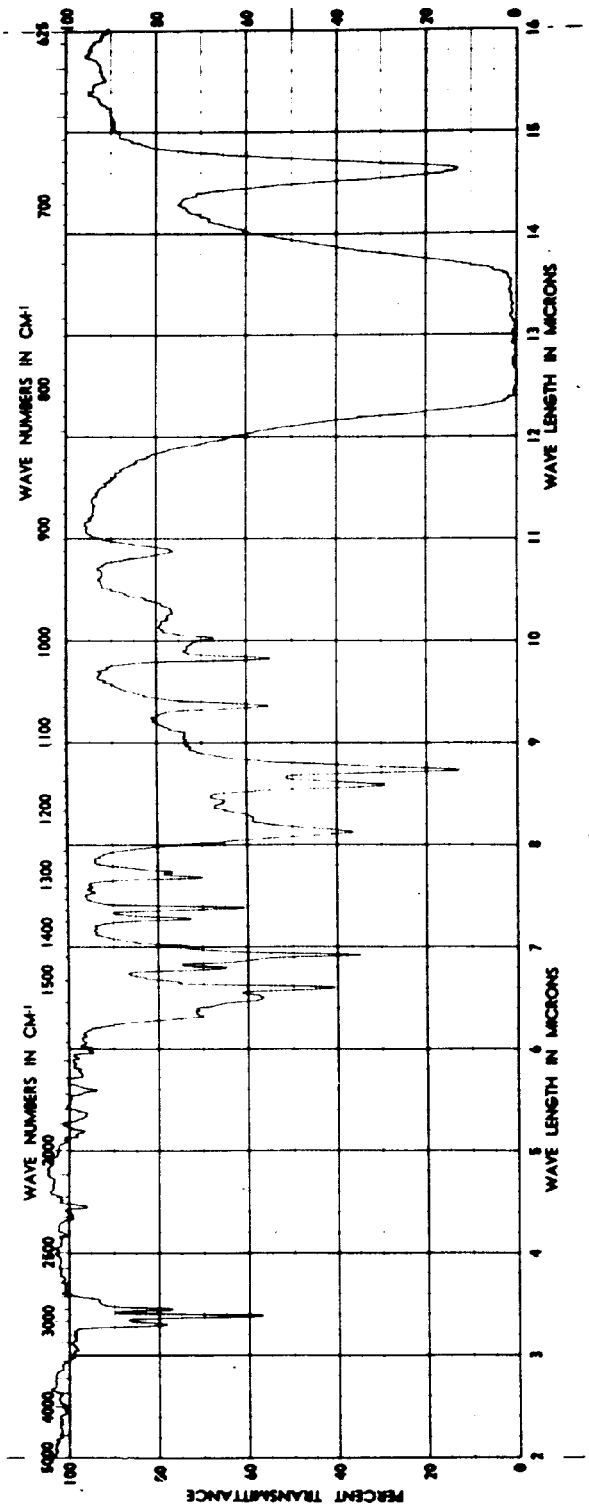
Absorption Spectra. The infra-red absorption spectra were determined for all of the mixed azo nitriles and their corresponding hydrazo nitriles. These curves are shown on the following pages. Absorption bands due to the N=N bond can not be definitely established as was hoped.

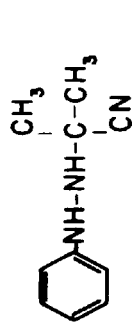
A characteristic band for N - H stretching vibrations appears at about 3.05 microns for all of the hydrazo compounds and is absent for all of the azo nitriles. Another identifying feature is the characteristic band for C≡N stretching vibrations occurring at about 4.45 microns for all of the hydrazo and azo nitriles. The band at about 6.25 microns which occurs in the spectra of all of the hydrazo compounds and is virtually non-existent in the spectra of the azo nitriles is apparently due to an N - H deformation vibration.

There are certain other points of interest in connection with these infra-red spectra. In going from hydrazo to azo the 6.25 N - H deformation disappears, but a smaller band remains at 6.3 microns. This latter band could be due to the N=N stretching vibration, but may simply be a phenyl band which was obscured by the strong N - H band in the case of the hydrazo compounds. A series of very small absorptions, probably due to the phenyl group, occur between 5 and 6 microns, but in every case the azo compound shows one more such band than the hydrazo compound. The one that looks most likely to be the new band is that at 5.6 microns. In any event, the extra band seems likely to be associated with the azo group.

In every case, except for the compounds containing the cyclopentyl group, the strength of the cyano band was markedly less for the azo compound than the hydrazo compound even though the solutions were of

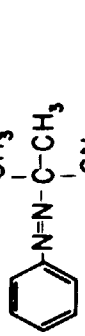






0.8 MOLAR IN CCl_4

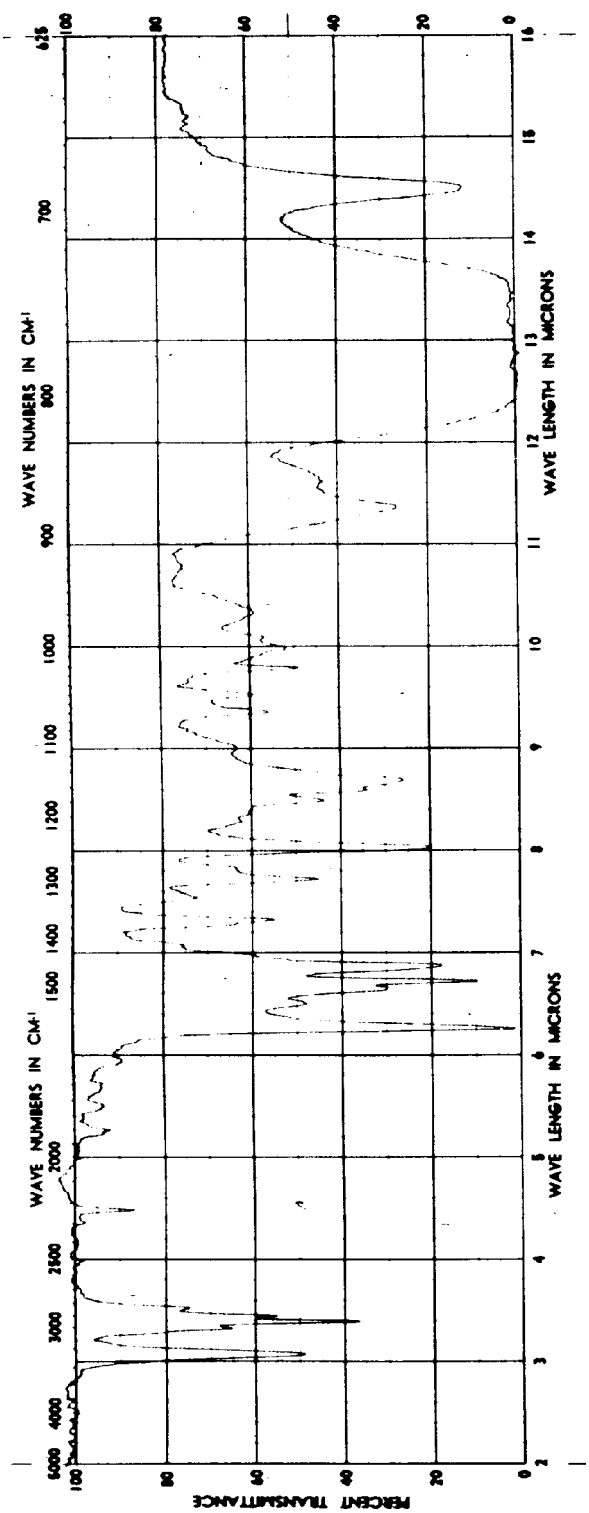
0.1 MM. NaCl CELL

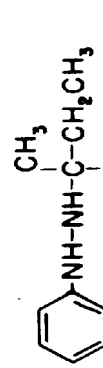


0.8 MOLAR IN CCl_4

0.1 MM. NaCl CELL

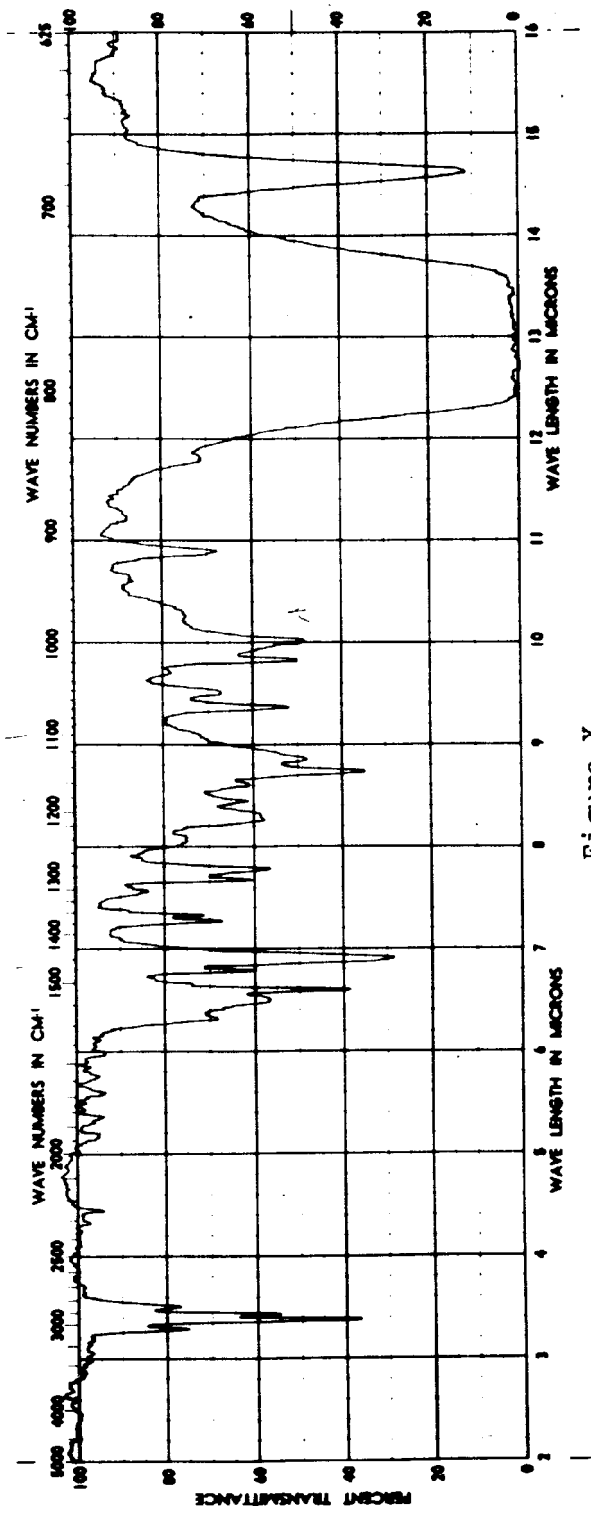
Figure IX

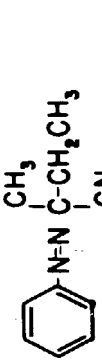




0.8 MOLAR IN CCl_4

0.1 MM. NaCl CELL

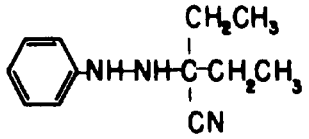




0.8 MOLAR IN CCl_4

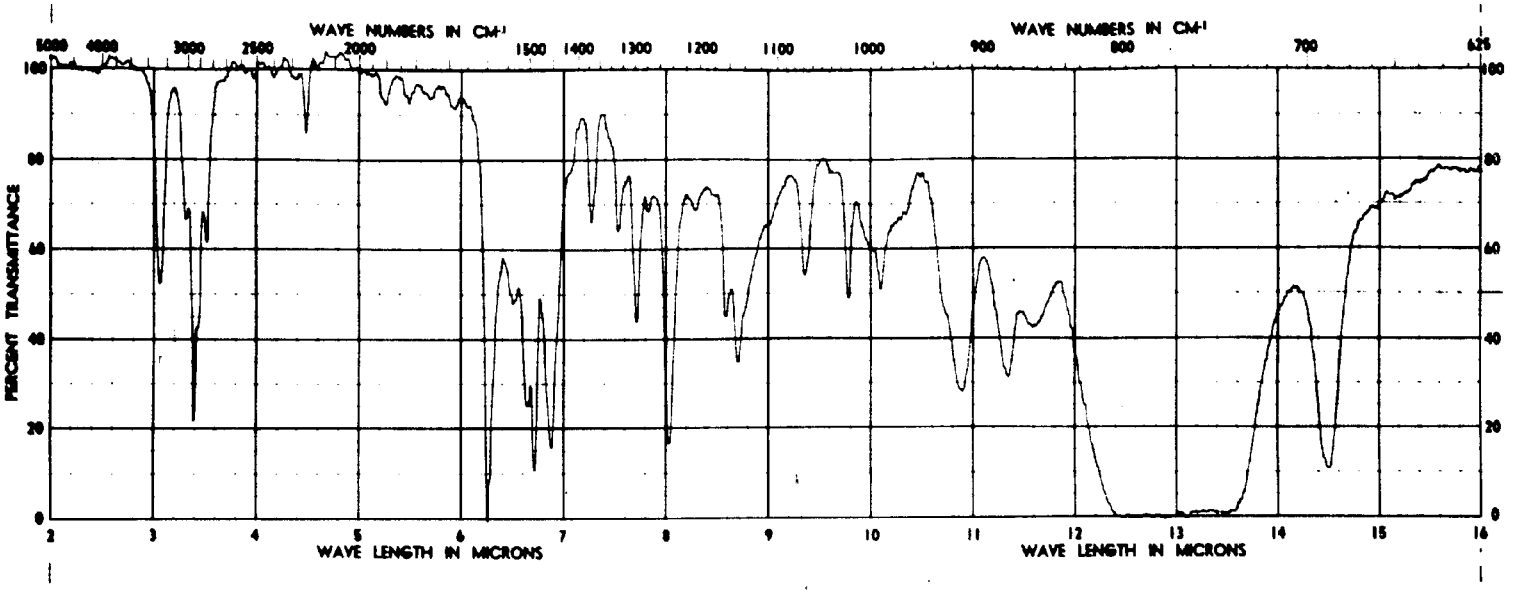
0.1 MM. NaCl CELL

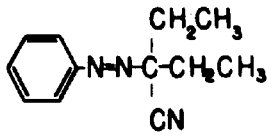
Figure X



0.8 MOLAR IN CCl_4

0.1 MM. NaCl CELL





0.8 MOLAR IN CCl_4

0.1 MM. NaCl CELL

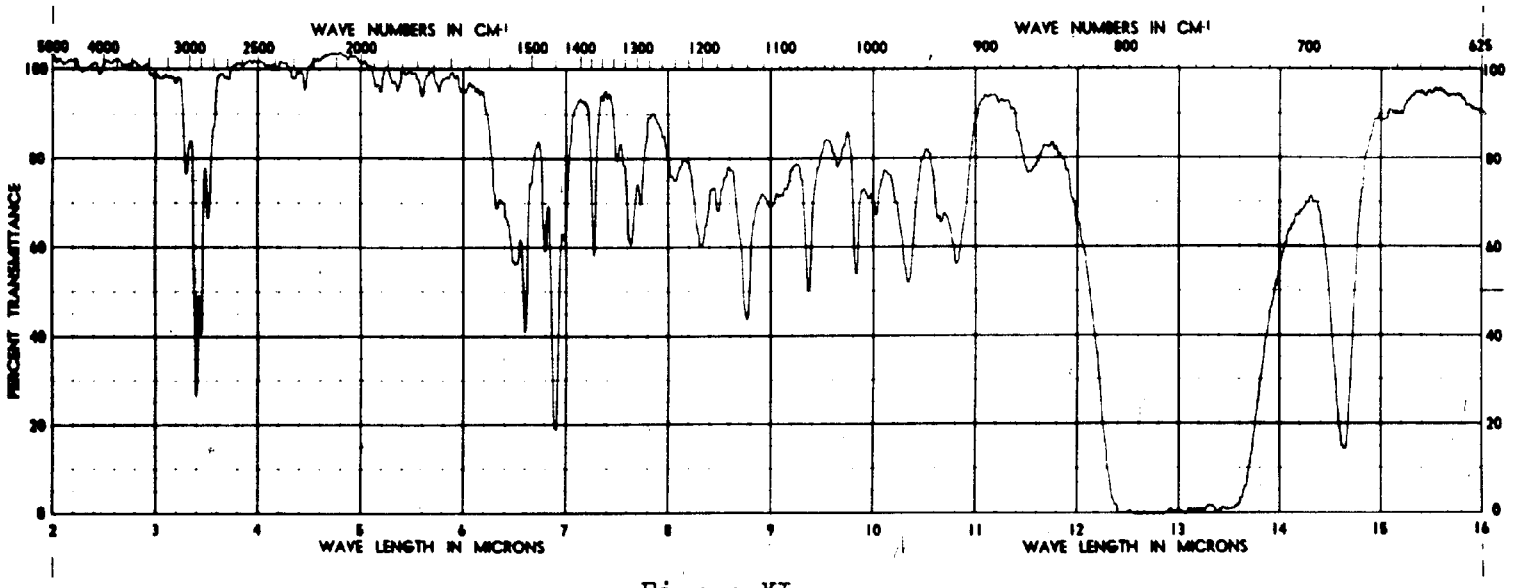
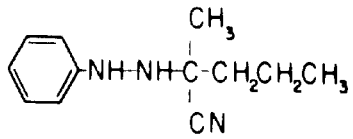
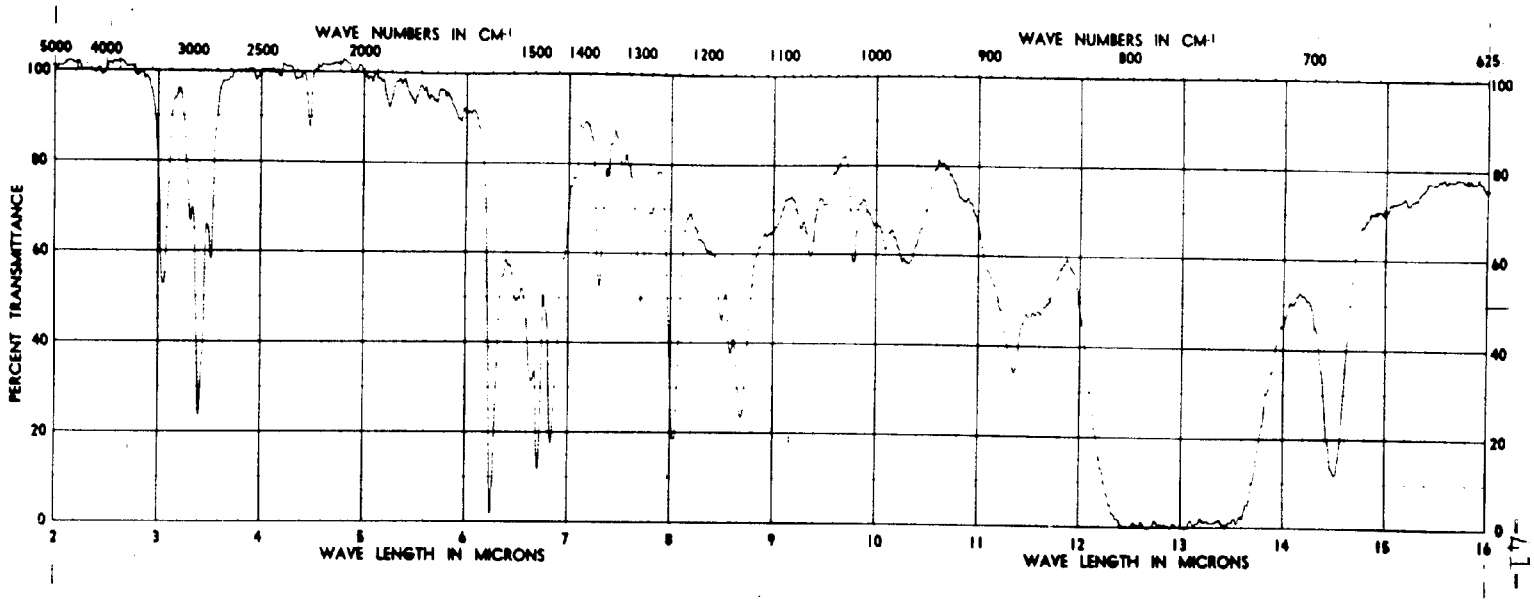


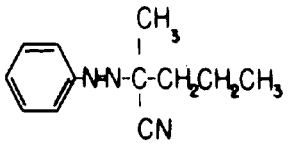
Figure XI



0.8 MOLAR IN CCl_4

0.1 MM. NaCl CELL





0.8 MOLAR IN CCl_4

0.1 MM. NaCl CELL

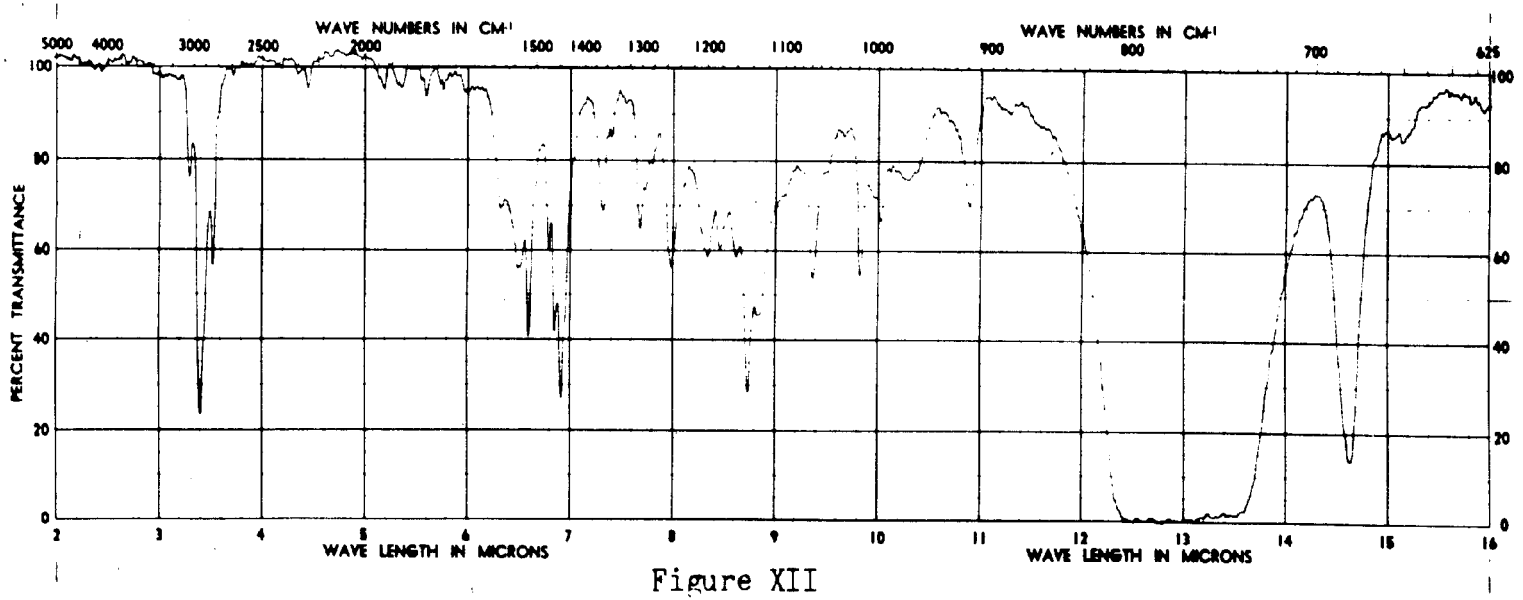
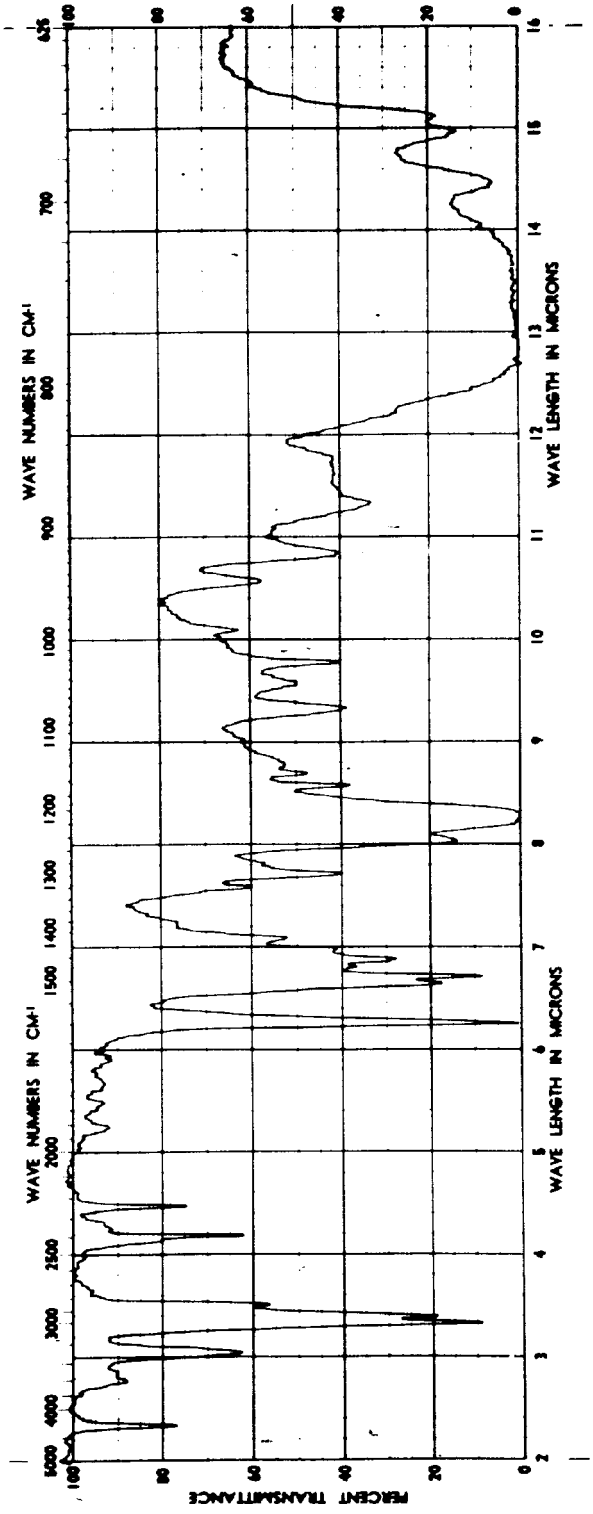
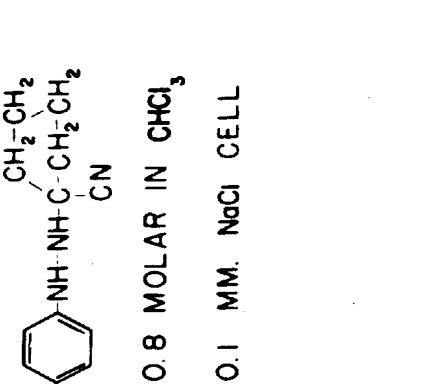


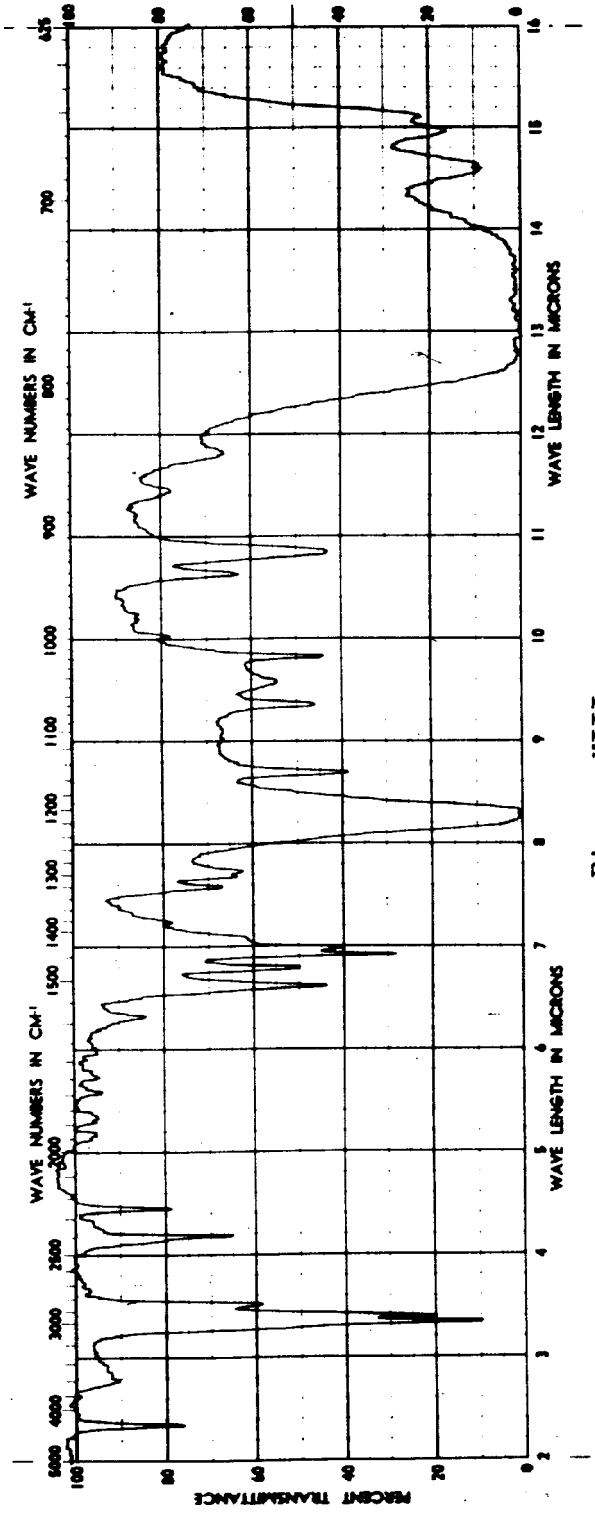
Figure XII

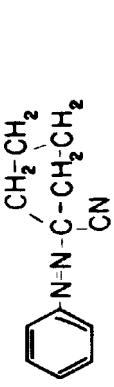




0.8 MOLAR IN $CHCl_3$

0.1 MM. NaCl CELL

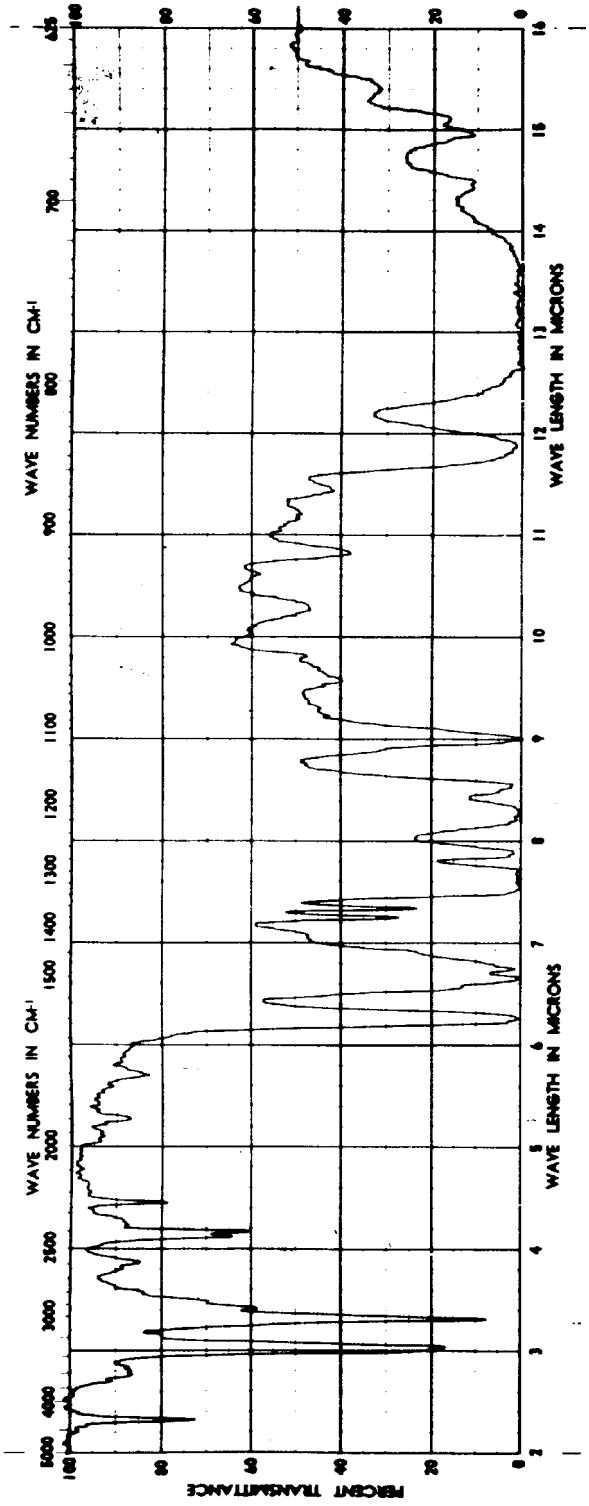


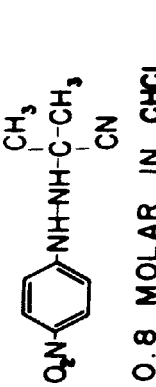


0.8 MOLAR IN $CHCl_3$

0.1 MM. NaCl CELL

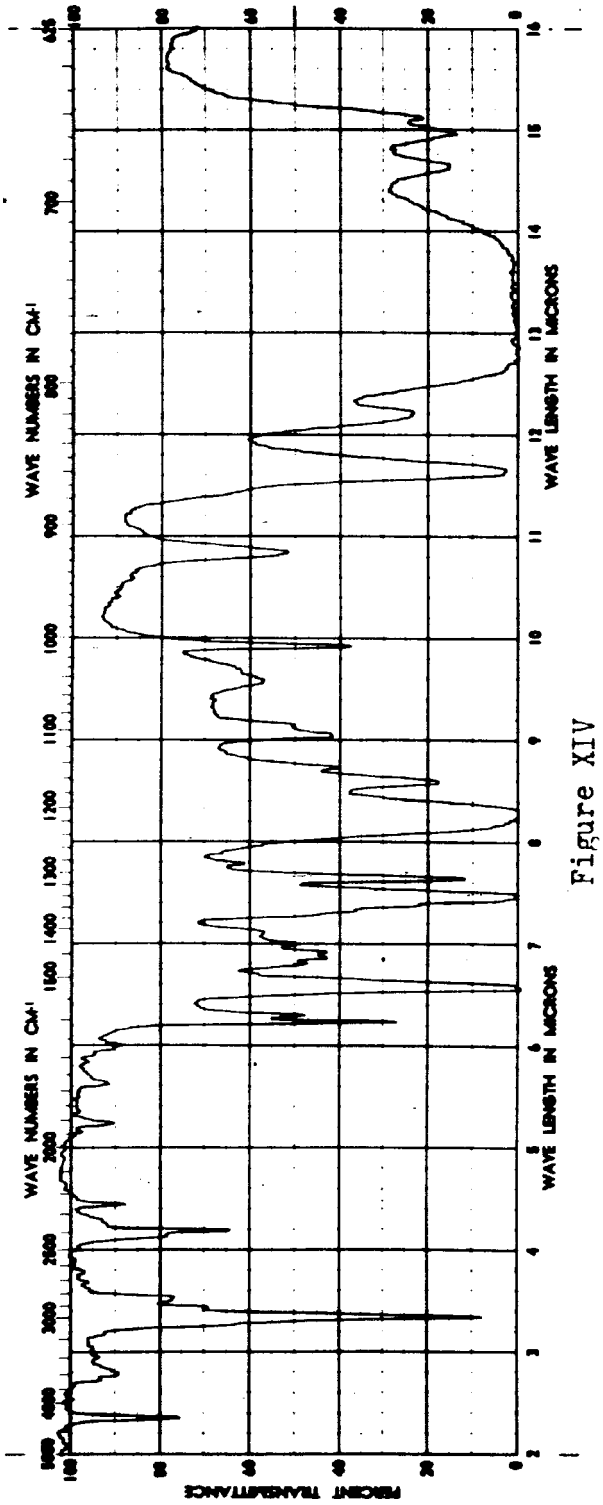
Figure XIII

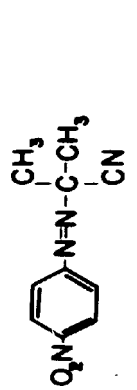




0.8 MOLAR IN $CHCl_3$

0.1 MM. NaCl CELL

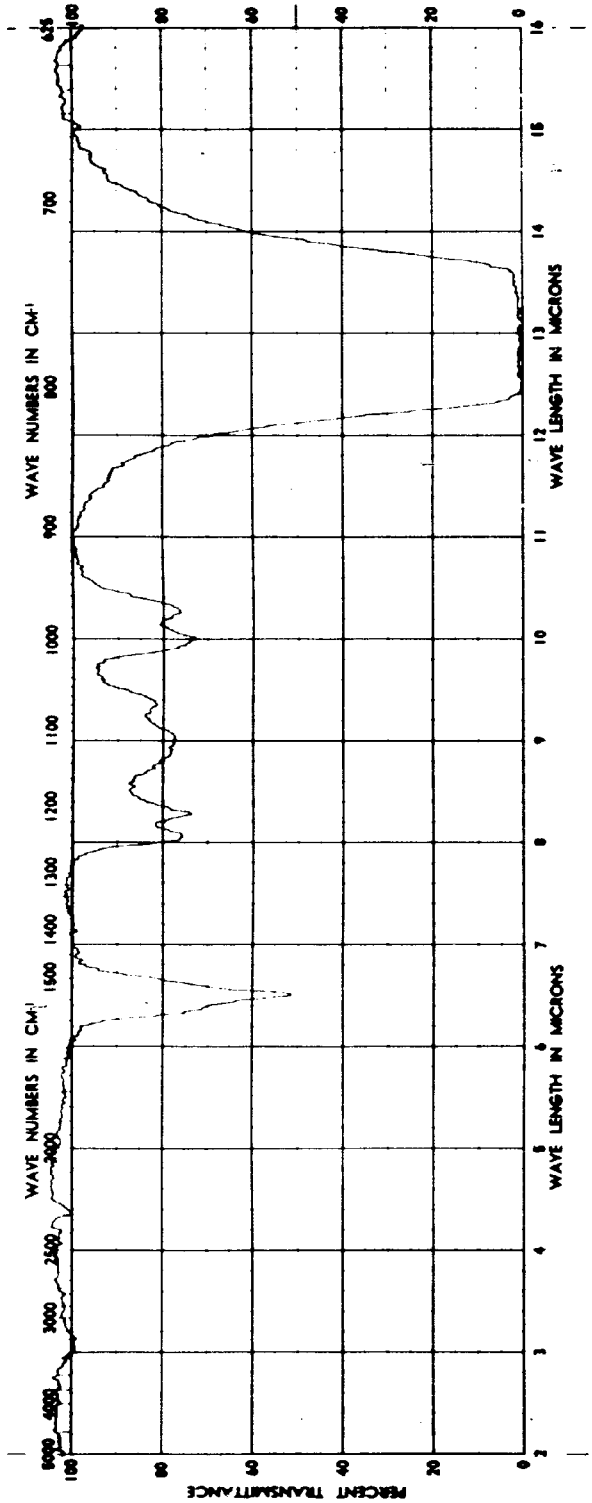




0.8 MOLAR IN $CHCl_3$

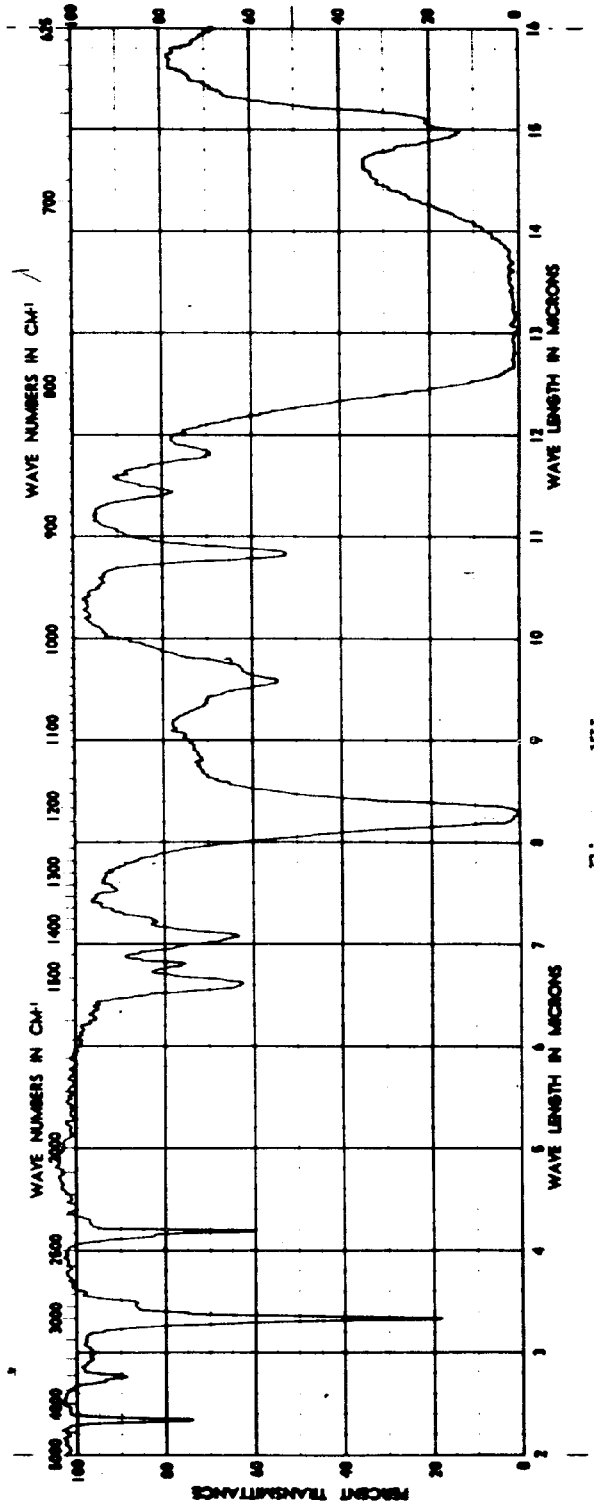
0.1 MM. NaCl CELL

Figure XIV



CCl_4

0.1 MM. NaCl CELL

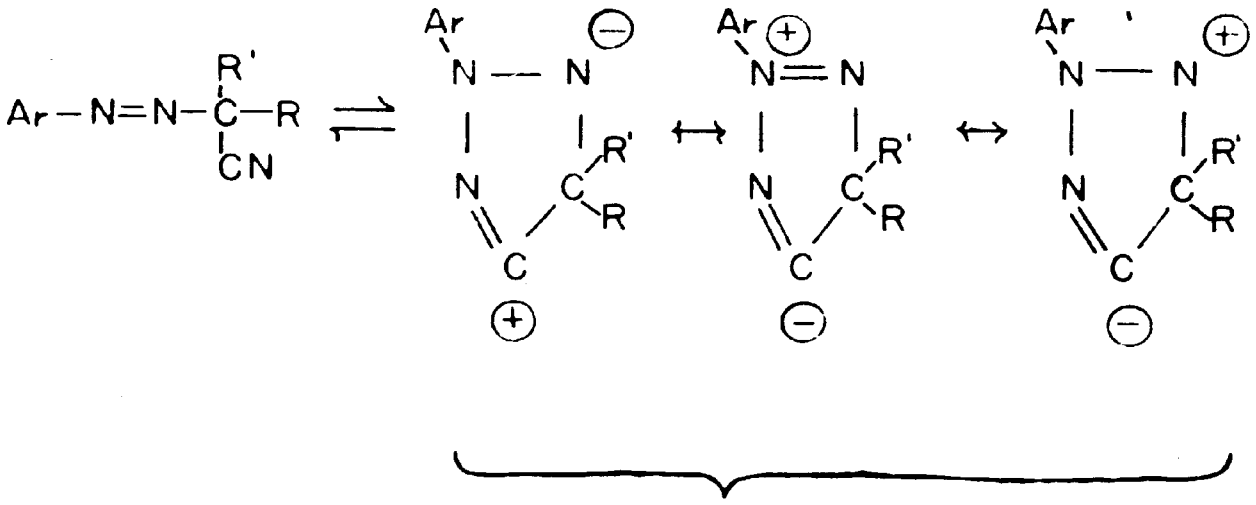


$CHCl_3$

0.1 MM. NaCl CELL

Figure XV

the same concentration. When the nitrile is unconjugated in both cases, it is difficult to explain this intensity difference when the structures are so closely related as in hydrazo and azo compounds. For this reason, it was postulated that in solution the open chain structure as depicted on the graphs might exist in equilibrium with a cyclic form wherein the C≡N character is lost. Thus,

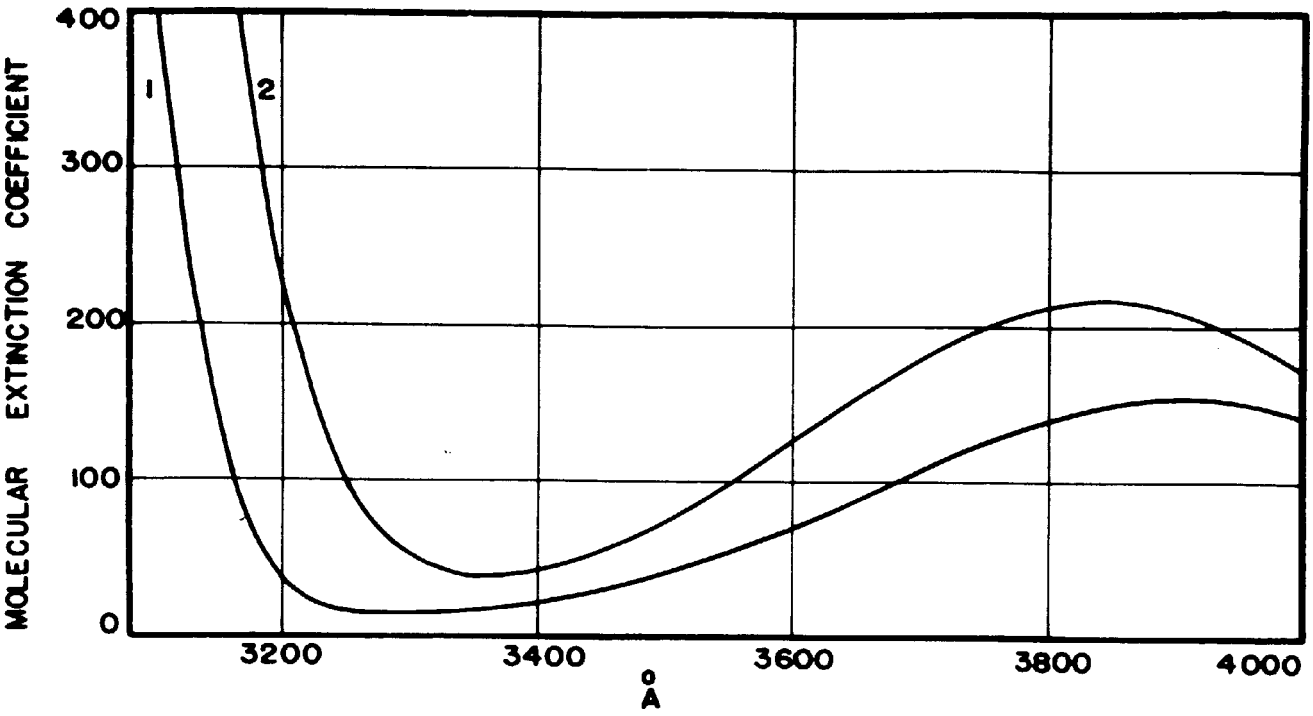


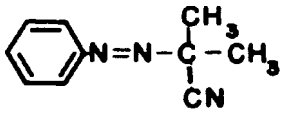
resonance forms

Since it seemed that the ring structure, as written here, would be more polar than the open chain form, the point of equilibrium between the two was expected to vary appreciably with the polarity of the solvent. Therefore, ultraviolet absorption curves were determined for the one substance, α-phenylazoisobutyronitrile, in petroleum ether and in alcohol-water solution. These results are shown in Figure XVI. There is too little difference between the curves to warrant drawing any conclusions about this possibility.

The absorption band at 3820-3850 Å is comparable to the band for the aliphatic azo nitriles at 3450-3500 Å, but is stronger and has

been shifted toward longer wave lengths by conjugation of the azo linkage with the phenyl group. Apparently radiation of this wave length can cause decomposition of these mixed azo compounds at room temperature. A silica boiling stone was placed in each of the solutions used for the ultraviolet measurements and the solutions were left in the sunlight where the light passed through three thicknesses of glass before reaching the solutions. Both solutions gave a steady stream of bubbles for several days. The petroleum ether solution became cloudy, deposited a brown sludge, and became colorless, while the alcohol-water solution remained yellow even after the gas evolution had stopped.





IN: (1) PETROLEUM ETHER (B.P. 60 – 75°)

(2) 50% (VOL.) ETHANOL – WATER

FIGURE XVI

III Summary

1. Seven new mixed azo nitriles have been synthesized. These are:

   α-phenylazoisobutyronitrile

   α-phenylazo- α-methylbutyronitrile

   α-phenylazo- α-ethylbutyronitrile

   α-phenylazo- α-methylvaleronitrile

   1-phenylazo-1-cyanocyclopentane

   α-(p-nitrophenylazo)-isobutyronitrile

   p,p'-azoxy-bis- α-phenylazoisobutyronitrile

2. The mixed azo nitriles have been shown to decompose at higher temperatures than aliphatic azo nitriles and their decomposition produces nitrogen and free radicals.

3. The products of thermal decomposition of α-phenylazoisobutyronitrile have been shown to include diphenyl, tetramethylsuccinonitrile, and phenylisobutyronitrile. No azobenzene was found.

4. The kinetics of thermal decomposition of all but the last named of the above azo nitriles have been studied.

5. Five new mixed hydrazo nitriles and one which was previously known have been prepared. These correspond to each of the above azo compounds except the last named.

6. Infra-red absorption spectra have been determined for both the hydrazo and azo compounds. The ultraviolet absorption spectrum of α-phenylazoisobutyronitrile was determined in two solvents of widely differing polarities.

IV Experimental

A. Preparation of the mixed hydrazo nitriles.

α-(β-Phenylhydrazino)-isobutyronitrile. This compound was prepared by the method of Bucherer and Grolee.[47] In a 500 ml. glass stoppered flask 135 gms. of phenylhydrazine (1.25 moles), 106.5 gms. of acetone cyanohydrin (1.25 moles), and 170 ml. of ether (sodium dried) were mixed and allowed to stand at room temperature. After about a week drops of water began to appear and after two weeks the water was separated off. Most of the ether was evaporated and replaced by petroleum ether (b.p. 30-40°). The mixture was cooled in ice with stirring and scratching. After storing in a refrigerator overnight, the crystals were filtered off and washed well with cold petroleum ether and dried. Yield: 163 gms. (74.5%) of slightly yellow crystals, m.p. 63-69°. Further purification was not necessary for the oxidation. A small sample recrystallized from ether-petroleum ether mixture gave pure white crystals, m.p. 67-70°.

Procedures similar to the above were used for the following four compounds.

α-(β-Phenylhydrazino)-α-methylbutyronitrile. This material was prepared from 108 gms. of phenylhydrazine and 99 gms. of methyl ethyl ketone cyanohydrin in 145 ml. of ether. The product was recrystallized from petroleum ether (b.p. 30-40°). Yield: 110 gms. of white crystals, m.p. 39-41° and 16.5 gms. of slightly yellow crystals, m.p. 36-39° (overall, 67%).

α-(β-Phenylhydrazino)-α-ethylbutyronitrile. The reaction product from 77 gms. of phenylhydrazine and 80.5 gms. of diethyl ketone cyanohydrin in 110 ml. of ether gave, after recrystallization from petroleum ether (b.p. 30-40°), 100.2 gms. (69.5%) of white crystals, m.p. 37-40°.

α-(β-Phenylhydrazino)-α-methylvaleronitrile. This compound was obtained from 54 gms. of phenylhydrazine and 56.6 gms. of methyl n-propyl ketone cyanohydrin in 77 ml. of ether. 65 gms. (64%) of slightly yellow crystals was obtained, m.p. 56-59°.

1-(β-Phenylhydrazino)-1-cyanocyclopentane. This substance was prepared by using 54 gms. of phenylhydrazine and 55.6 gms. of cyclopentanone cyanohydrin in 77 ml. of ether. During the separation of water, the product suddenly crystallized. It was filtered off, the filtrate concentrated and a second crop obtained. Yield: 66.0 gms. (66%) of nearly white crystals, m.p. 90-94°. Recrystallization of a small sample gave pure white crystals, m.p. 93-95°.

α-[p-Nitro-(β-phenylhydrazino)]-isobutyronitrile. This compound was prepared by the addition of hydrogen cyanide to the C=N bond of the hydrazone. In a sealed flask 3.6 gms. of p-nitrophenylhydrazone of acetone, 22 ml. of acetonitrile, 8 ml. of glacial acetic acid, and 12 ml. of liquid hydrogen cyanide were stirred until an homogenous solution resulted. After this solution had stood over-night, the solvents were boiled off under vacuum at room temperature until the product crystallized.

After cooling in ice, the crystals were filtered off and washed thoroughly with ether. The product melted at 115-118° with decomposition. When heated to 155° and then cooled, the melting point was that of acetone p-nitrophenylhydrazone, 146-148°.

Anal.: Calcd. for $C_{10}H_{12}N_4O_2$: N, 25.44

Found : N, 25.38

B. Preparation of the mixed azo nitriles.

α-Phenylazoisobutyronitrile. This substance was obtained by oxidation of the corresponding hydrazo compound. A solution of 30 gms. of α-(β-phenylhydrazino)-isobutyronitrile in 200 ml. of ether was placed in a 500 ml. three necked flask fitted with a stirrer, reflux condenser, and a large rubber tube, which connected one neck to an Erlenmeyer flask containing 54 gms. of silver oxide. The silver oxide was added slowly (over about 45 min.) to the stirred solution. There was frequently an induction period and since considerable heat is evolved, cooling was sometimes necessary to keep the mixture in the flask. After four hours additional stirring and standing over-night, the mixture was filtered by gravity and the residue washed well with ether. After drying the solution over anhydrous sodium sulfate and filtering, the ether was removed under reduced pressure and replaced by 70 ml. of petroleum ether (b.p. 30-40°). Crystallization by cooling in a Dry Ice freezing mixture, scratching as the product began to oil out, and filtration in a cold room at -10° gave 26.4 gms. (89%) of bright yellow crystals, m.p. 6-9°. Recrystallization from petroleum ether gave a material, m.p. 9.5-10°.

Anal.: Calcd. for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26

Found : C, 69.73; H, 6.44; N, 23.77

Procedures similar to the above were used for the following four compounds.

α-Phenylazo-α-methylbutyronitrile. This substance was made from 32.4 gms. of α-(β-phenylhydrazino)-α-methylbutyronitrile in 200 ml. of ether by oxidation with 54 gms. of silver oxide. After two recrystallizations from petroleum ether, there was obtained 28.6 gms. (89%) of yellow crystals, m.p. 4-5°. One more recrystallization from petroleum ether gave a material, m.p. 16-19.5° which did not change further on repeated recrystallizations from petroleum ether, ether, and methanol.

Anal.: Calcd. for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; N, 22.44

Found : C, 70.60; H, 7.17; N, 22.62

α-Phenylazo-α-ethylbutyronitrile. This material was prepared from 25.4 gms. of α-(β-phenylhydrazino)-α-ethylbutyronitrile in 150 ml. of ether by treating with 39 gms. of silver oxide. The yield of bright yellow crystals, m.p. -2 to -1°, was 22.3 gms. (89%). Recrystallization from petroleum ether gave a material, m.p. -1 to 0°.

Anal.: Calcd. for $C_{12}H_{15}N_3$: C, 71.61; H, 7.51; N, 20.88

Found : C, 71.56; H, 7.52; N, 20.93

α-Phenylazo-α-methylvaleronitrile. This substance was obtained in an analogous manner. In this case, however, the

silver oxide could be added all at once. To oxidize 19 gms. of α-(β-phenylhydrazino)-α-methylvaleronitrile in 90 ml. of ether, 30 gms. of silver oxide was used. 16 gms. (85%) of bright yellow crystals was obtained melting at 2-4°. Recrystallization gave a product, m.p. 4-5°.

Anal.: Calcd. for $C_{12}H_{15}N_3$: C, 71.61; H, 7.51; N, 20.88
Found : C, 71.28; H, 7.89; N, 21.23

1-Phenylazo-1-cyanocyclopentane. The oxidation of 16 gms. of 1-(β-phenylhydrazino)-1-cyanocyclopentane dissolved in 240 ml. of ether was accomplished by treatment with 24 gms. of silver oxide. After drying the ether solution, the solvent was not replaced by petroleum ether. The product was crystallized directly from the ether solution after concentrating. Yield: 14.5 gms. of large yellow crystals, m.p. 85-87°.

Anal.: Calcd. for $C_{12}H_{13}N_3$: C, 72.33; H, 6.57; N, 21.09
Found : C, 72.58; H, 6.67; N, 21.14

α-(p-Nitrophenylazo)-isobutyronitrile. Although this substance could be made by oxidation of the pure hydrazo compound, it was found to be more convenient and higher yields were obtained when the hydrazo nitrile was not isolated prior to oxidation. Into a 200 ml. two necked flask, fitted with a sealed stirrer and stopper, were charged 25 gms. of p-nitrophenylhydrazone of acetone, 80 ml. of acetonitrile, 20 ml. of glacial acetic acid, and 51 ml. of liquid hydrogen cyanide. The mixture was stirred in the closed vessel at room temperature until a homogenous solution was obtained and then allowed to

stand over-night. The hydrogen cyanide and some of the solvent were removed below room temperature under reduced pressure. Some of the hydrazo compound crystallized in the process and enough acetonitrile was added to dissolve it. Over a 10 minute period 7 ml. of liquid bromine was added to the cooled solution with vigorous stirring. After another 10 minutes the solution was poured into about 700 ml. of water and the product removed by filtration and dried. After recrystallization from methanol, the yield was 20.4 gms. (72% based on acetone p-nitrophenylhydrazone) of yellow needles, m.p. 122-127°. Further recrystallization gave the product, m.p. 127-129°.

Anal.: Calcd. for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68

Found : C, 54.78; H, 4.58; N, 25.82

p,p'-Azoxy-bis- α -phenylazoisobutyronitrile. This compound was formed when 5 gms. of p-nitrophenylhydrazone of acetone, 15 ml. of methanol, about 1/4 ml. of concentrated hydrochloric acid, and 15 ml. of liquid hydrogen cyanide were sealed in a tube and heated in a steam bath for four hours. On cooling a solid suddenly crystallized out before the tube reached room temperature. After opening the tube, the mixture was filtered. The crystals were digested with 400 ml. of boiling methanol in which they did not dissolve and after cooling to room temperature, they were filtered off. Yield: 1.5 gms. (30%) of orange-red crystals, m.p. 173-175°. After recrystallization from acetonitrile, it melted at 174-176° with slight decomposition. An infra-red absorption spectrum showed a cyano band but no N-H band.

Anal.: Calcd. for $C_{20}H_{20}N_8O$: C, 61.84; H, 5.19; N, 28.85

Found : C, 61.87; H, 5.64; N, 28.60

C. Preparation of intermediates.

Acetone cyanohydrin. This material was prepared according to the procedure of Organic Syntheses,[48] except that half of the quantities specified therein were used. This method consists of slowly adding 40% sulfuric acid to a cold, vigorously stirred solution of sodium cyanide and acetone in water. The limiting reactant is sodium cyanide. The yield was 295 gms. (72%) of colorless liquid, b.p. 78-82°/15mm.

Methyl ethyl ketone cyanohydrin. This compound was prepared by the same procedure, using half of the quantities mentioned in Organic Syntheses. Instead of acetone, 440 gms. of methyl ethyl ketone were employed and the acetone washings of the sodium bisulfate replaced by washings with methyl ethyl ketone. Yield: 402 gms. of colorless liquid (84%), b.p. 90-95°/18-22mm., mostly 93.5°/20mm.

Methyl n-propyl ketone cyanohydrin. This substance was made in a similar manner, by adding 390 ml. of 40% sulfuric acid to a vigorously stirred mixture of 163 gms. of methyl n-propyl ketone and 93 gms. of sodium cyanide in 223 ml. of water at 3-5°. The sodium bisulfate was washed with ether instead of the ketone. Yield: 128.5 gms. (63%) of colorless liquid, b.p. 104-106°/21mm., mostly at 106°.

Diethyl ketone cyanohydrin. This compound was prepared by the method of Colonge and Joly,[49] which seems to be a very convenient means for making cyanohydrins (see discussion). In each of two 500 ml. flasks were placed 70 gms. of mono-potassium phosphate, 125 ml. of water, and 43 gms. of diethyl ketone. No attempt was made to dissolve the potassium phosphate. In each of two other flasks 27 gms. of sodium cyanide was dissolved in 125 ml. of water and the solutions cooled in an ice bath. The two sodium cyanide solutions were added to the two ketone-phosphate mixtures all at once. The flasks were stoppered and shaken for two hours on a mild shaking machine. The two mixtures were combined in a separatory funnel, 50 ml. of ether added, the funnel shaken, and the organic layer separated. After extracting the mother liquor with 50 ml. of ether, the combined extracts were washed with 100 ml. of 5% hydrochloric acid, then with 100 ml. of water, and dried over anhydrous sodium sulfate. Distillation gave 81 gms. (72%) of colorless liquid, b.p. 87.5-98.5°/10mm.

Cyclopentanone cyanohydrin. This substance was produced in the same way as diethyl ketone cyanohydrin. From 42 gms. of cyclopentanone 80.3 gms. (72.5%) of colorless liquid, b.p. 123-125°/23-24mm., was obtained.

Acetone p-nitrophenylhydrazone. This compound was made by refluxing 20 gms. of p-nitrophenylhydrazine in 50 ml. of acetone and 1 ml. of glacial acetic acid for one half hour. After cooling in a refrigerator, the orange-yellow crystals formed were filtered off and washed with alcohol; m.p. 147-149°.

Hydrogen Cyanide (anhydrous liquid). This material was obtained by the procedure in Organic Syntheses.[53] This method consists of generating the gas by reaction of sodium cyanide solution and sulfuric acid, drying it with anhydrous calcium chloride, and condensing it with an ice cooled condenser.

D. Products of decomposition of α-phenylazoisobutyronitrile.

In a 50 ml. flask 18 gms. of α-phenylazoisobutyronitrile was placed and nitrogen passed through the liquid and flask to remove oxygen. The flask was then connected to a trap cooled by Dry Ice and placed in a thermostatic oil bath at 165°. When enough material had been condensed out of the escaping gas and frozen by the trap to clog it, it was removed. On warming to room temperature, the material in the trap melted and had a strong, characteristic odor of hydrogen cyanide. The material boiled when warmed with the hand and the gas formed gave a white precipitate when passed into a silver nitrate solution: silver cyanide.

The residue in the flask was kept at 165° for about 20 hours. It was then subjected to a continuous steam distillation with continuous chloroform extraction of the distillate for 30 hours. Most of the material did not distill but remained behind as a dark red polymeric mass. The chloroform solution was dried over anhydrous sodium sulfate before boiling off the chloroform. The residue was then subjected to a Craig counter-current extraction using twelve 60 ml. separatory funnels. The solvents employed were petroleum ether (b.p. 60-75°) (30 ml.) and acetonitrile (15 ml.). Each of these solvents had been previously saturated with the other.

This material was thus distributed into thirteen fractions: #1, petroleum ether soluble; #13, acetonitrile soluble. Both solvents were removed by evaporation.

Fractions #1 and 2 contained very little material and were discarded. Fractions #3,4,5,6, and 7 were combined using methanol as the solvent. After concentrating the solution and cooling with Dry Ice, a solid crystallized out. The two crops of crystals which were obtained were combined and sublimed at 65-70°/17.5mm. The sublimate (0.15 gm.) was recrystallized from methanol and gave 0.1 gm. of crystals, m.p. 69-70.5°. The melting point of a mixture of this material with authentic diphenyl was the same.

Fraction #13, which had now become very tarry, apparently due to air oxidation or polymerization, was placed in a sublimation apparatus at about 150° and atmospheric pressure. A nearly white, but very oily solid was collected. Fractions #11 and 12, which contained a dark mixture of oil and crystals, were combined and given the same treatment. The solid sublimate was even more oily, and the residue was an oil. This oil was treated again in the same way but a small beaker was placed under the condenser to collect the oil which condensed. This oil was retained until fractions #8,9, and 10 were worked up. The oil on these oily sublimates was absorbed with filter paper and the remaining solids were combined and recrystallized from ether-petroleum ether (b.p. 30-40°) mixture, by cooling with Dry Ice. There was obtained 0.1 gm. of slightly green-gray crystals, which started to soften at about 155° and melted at 165-168°. Recrystallization from alcohol-water mixture gave a material, m.p. 168-169°, corresponding

to that of tetramethylsuccinonitrile. Its infra-red curve was identical with that of an authentic sample prepared by thermal decomposition of α, α'-azo-bis-isobutyronitrile.[12]

Fractions #8,9, and 10 were combined and distilled. A fraction was collected at 105-155°/26mm. This material was combined with the oil condensate from fractions #11 and 12. When this was distilled, a fraction boiling at 117-119°/22mm. was collected. This substance was heated on a steam bath with 4.5 gms. of 85% sulfuric acid for three hours. On pouring this solution into water, a crystalline substance separated, which was filtered off, washed with water, and dried. 0.15 gm. of fairly white, slightly tan crystals was obtained. A small portion was sublimed and then recrystallized from ether-petroleum ether (b.p. 30-40°) mixture. Pure white crystals, m.p. 158.5-160°, were obtained. The balance of this substance was boiled with 5 gms. of 20% sulfuric acid for two hours. This mixture was diluted with 20 ml. of water and extracted with ether. The ether solution was filtered and extracted with aqueous potassium hydroxide solution. When the alkaline solution was acidified with hydrochloric acid, an oil separated which crystallized to a light colored solid with a yellow-green appearance, m.p. 77-79°. Recrystallization from alcohol-water mixture gave white crystals, m.p. 78-80°. These data indicate that the oil was α-phenylisobutyronitrile. According to the literature,[54] α-phenylisobutyronitrile, b.p. 116°/20mm., can be hydrolyzed by these procedures to its amide, m.p. 160°, and to its acid, m.p. 80-81°.

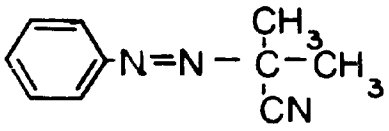
E. Rates of Decomposition.

The rates of decomposition of the mixed azo nitriles in ceresine solution were determined by measurement of the rate of increase of gas volume of the system at constant temperature and pressure. The reaction vessel was a 50 ml. flask with a gas inlet tube, a tube or neck for inserting the compound, and a neck fitted with a water jacketed tube to serve as a reflux condenser. A "Tygon" tube led from the condenser to a water jacketed, mercury filled burette. About 25 gms. of molten ceresine wax (white, natural) was poured into the flask. The condenser and "Tygon" tube were attached. The flask was then placed in a thermostatic mineral oil bath at 165° (175° for one pair of runs) with a control of ± 0.1° and a stream of nitrogen (freed of oxygen) was passed through the solvent and apparatus for an half hour or more. The burette was then connected and the nitrogen stream stopped. After allowing another 20 minutes or more to attain thermal equilibrium, a weighed amount of the compound (0.6-0.9 gm.) was added. In the case of liquid azo nitriles, this addition was made through a microstopcock by means of an hypodermic syringe. The solids were poured in through a powder funnel. Timing began with the addition of the azo nitrile and the initial volume reading was taken immediately after adding the compound. It was found necessary to shake the flask vigorously for at least 30 seconds before each reading to prevent supersaturation of the nitrogen in the solvent.

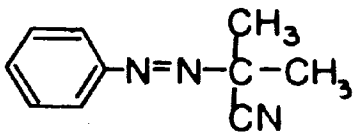
Table B shows the complete set of data obtained, which was used for plotting Figure I. This table illustrates the data obtained in these experiments.

Table B

Data for Fig. I

Rate of decomposition of  at 165° in ceresine.

wt. of tube, syringe, comp'd. before: 44.0730
wt. of tube, syringe, comp'd. after : 43.2686
0.8044 gm.



added from syringe to 25 gms. of ceresine (white, natural) at 165° ± 0.1° through which N_2 had been passed to remove O_2 . Average barometric press.: 740 mm. (range 739.0-741.5 mm.); burette temp.: 27.5°. The solution was shaken before readings to prevent gas supersaturation in the solvent.

time	vol. ml.	t min.	v	$V_{ml.}$	$\frac{V_\infty}{V_\infty - V_t}$	$v_i' - v_i$
10:30 AM	3.0	0	v_1	0	1.000	62.9
10:40	7.3	10	v_2	4.3	1.048	60.0
10:50	11.9	20	v_3	8.9	1.105	56.8
11:00	16.8	30	v_4	13.8	1.173	53.1
11:10	21.2	40	v_5	18.2	1.242	50.0
11:20	25.2	50	v_6	22.2	1.311	47.3
11:30	29.2	60	v_7	26.2	1.389	44.5
11:40	33.0	70	v_8	30.0	1.471	41.7
11:50	36.3	80	v_9	33.3	1.55	39.4
12:00 N	39.4	90	v_{10}	36.4	1.64	37.3
12:10 PM	42.4	100	v_{11}	39.4	1.73	35.2
12:20	45.2	110	v_{12}	42.2	1.82	33.5
12:30	47.8	120	v_{13}	44.8	1.92	31.7

Table B cont.

time	vol. ml.	t min.	v	$V_{ml.}$	$\frac{V_\infty}{V_\infty - V_t}$	$v_i' - v_i$
12:40	50.4	130	v_{14}	47.4	2.02	29.9
12:50	52.6	140	v_{15}	49.6	2.13	28.3
1:00	54.8	150	v_{16}	51.8	2.24	26.8
1:10	56.9	160	v_{17}	53.9	2.36	25.4
1:20	58.9	170	v_{18}	55.9	2.48	24.1
1:30	60.8	180	v_{19}	57.8	2.61	22.9
1:40	62.7	190	v_{20}	59.7	2.76	21.5
1:50	64.4	200	v_{21}	61.4	2.91	20.4
2:00	65.9	210	v_1'	62.9	3.05	19.5
2:10	67.3	220	v_2'	64.3	3.19	
2:20	68.7	230	v_3'	65.7	3.36	
2:30	69.9	240	v_4'	66.9	3.51	
2:40	71.2	250	v_5'	68.2	3.69	
2:50	72.5	260	v_6'	69.5	3.88	
3:00	73.7	270	v_7'	70.7	4.09	
3:10	74.7	280	v_8'	71.7	4.27	
3:20	75.7	290	v_9'	72.7	4.48	
3:30	76.7	300	v_{10}'	73.7	4.70	
3:40	77.6	310	v_{11}'	74.6	4.93	
3:50	78.7	320	v_{12}'	75.7	5.23	
4:00	79.5	330	v_{13}'	76.5	5.48	
4:10	80.3	340	v_{14}'	77.3	5.74	
4:20	80.9	350	v_{15}'	77.9	5.96	
4:30	81.6	360	v_{16}'	78.6	6.24	

Table B cont.

time	vol. ml.	t min.	v	$V_{ml.}$	$\frac{V_\infty}{V_\infty - V_t}$
4:40	82.3	370	v_{17}'	79.3	6.55
4:50	83.0	380	v_{18}'	80.0	6.88
5:00	83.7	390	v_{19}'	80.7	7.26
5:10	84.2	400	v_{20}'	81.2	7.55
5:20	84.8	410	v_{21}'	81.8	7.93
5:30	85.4	420	v_{22}'	82.4	8.36
6:00	86.9	450		83.9	9.69
6:30	88.2	480		85.2	11.15
7:00	89.7	510		86.7	13.6
8:10 AM	97.2	1300		94.2;	p = 735 mm.
				93.6	corr. = V_∞

F. Absorption Spectra.

The infra-red absorption spectra were determined with an Infra-Red Recording Spectrophotometer, Model B, Baird Associates Inc. This is a double beam instrument with a sodium chloride prism. In one beam there was placed a sodium chloride blank, which approximately compensated for the absorption of the sodium chloride of the cell containing the sample. An 0.8 molar solution of the substance in carbon tetrachloride or chloroform was inserted into a 0.1 mm. cell, which was placed in the other beam. Since there is no compensation for absorption by the solvent in this procedure, the absorption curves for these solvents are included with the infra-red spectra for comparison purposes.

The ultraviolet absorption curves were determined with a Cary Recording Quartz Spectrophotometer, Model 11. This is a double beam instrument with a tungsten lamp and an hydrogen arc lamp as sources. These spectra were determined using the hydrogen arc. The instrument was balanced with one of a pair of matched 1 cm. quartz cells in each beam and both cells containing the solvent alone. The solvent in one cell was then replaced by a 2.52×10^{-3} molar solution of α-phenylazoisobutyronitrile and the absorption curves obtained. The solvents used were petroleum ether (b.p. 60-75°) and 50% by volume water-95% ethanol mixture. Optical density values were converted to molar extinction coefficients and replotted using the latter values.

G. Miscellaneous preparations and attempted reactions.

Hydrogenation of α-phenylazoisobutyronitrile. To show that no rearrangement had occurred on oxidation of the hydrazo

compound, α-phenylazoisobutyronitrile was catalytically reduced to α-(β-phenylhydrazino)-isobutyronitrile. With 0.8 gm. of 5% palladium on barium sulfate 4 gms. of the azo compound in 100 ml. of ether was shaken in an hydrogen atmosphere at room temperature and atmospheric pressure for about 16 hours. There was a definite hydrogen uptake but the volume change was not measured due to the vapor pressure of the ether. After filtration, evaporation of the solvent, and recrystallization, white crystals were obtained, m.p. 67-69.5°. Its infra-red curve was identical with that of α-(β-phenylhydrazino)-isobutyronitrile.

p-Methoxyphenylhydrazine. This compound was prepared by the procedure of Blaikie and Perkin[55]. By diazotization of 38 gms. of p-anisidine and reduction with stannous chloride, 17.5 gms. (41%) of brown crystals, m.p. 55-61°, was obtained.

Coupling of p-methoxyphenylhydrazine with acetone cyanohydrin. A solution of 16.6 gms. of p-methoxyphenylhydrazine, 55 ml. of ether, and 10.5 gms. of acetone cyanohydrin was allowed to stand at room temperature for two weeks. No water separated. After drying over sodium sulfate, the ether was removed under reduced pressure. The oil, which remained, crystallized upon standing in the refrigerator for a few days. After recrystallization from ether and petroleum ether (b.p. 30-40°) mixture, and charcoal treatment, there was obtained 9.7 gms. of white crystals, m.p. 51-53.5°.

Anal.: Found: C, 68.76; H, 7.60; N, 14.18

The analysis does not correspond to any expected coupled product.

The infra-red curve showed a doublet N-H band between 2.9 and 3.0 microns and a C≡N band at about 4.45 microns. Whereas the hydrazo nitriles had a very strong band at about 6.25 microns, this material had two relatively weak bands at 6.2 and 6.3 microns.

This material was surprizingly unreactive towards oxidation. Reaction with silver oxide in ether solution required a few days shaking whereupon the solution became red; however, no crystalline substance could be isolated. Oxidation with permanganate or manganese dioxide in acid solution did not produce a crystalline material.

Attempts to prepare α-(β-phenylhydrazino)-α-phenyl propionitrile. Two procedures were tried: (1) coupling of the cyanohydrin of acetophenone with phenylhydrazine and (2) addition of hydrogen cyanide to the phenylhydrazone of acetophenone. In both cases the materials isolated were acetophenone phenylhydrazone and hydrogen cyanide. It is believed that an equilibrium is involved which does not favor the addition compound, but the hydrazone and hydrogen cyanide.

The cyanohydrin of acetophenone was formed by bubbling hydrogen cyanide into acetophenone containing a small amount of sodium cyanide to a stoichiometric gain in weight. Ether was added and the sodium cyanide filtered off before adding the phenylhydrazine. The phenylhydrazone of acetophenone was formed by warming a solution of phenylhydrazine and acetophenone in alcohol-water mixture in the presence of a trace of acetic acid.

Attempt to condense p-nitrophenylhydrazine with acetone cyanohydrin. Several such attempts were made but only one is mentioned here. p-Nitrophenylhydrazine was dissolved in a minimum amount of dioxane and an equimolecular amount of acetone cyanohydrin added. After one year of standing at room temperature, no reaction had occurred, since evaporation of the solvent and recrystallization of the solid gave p-nitrophenylhydrazine.

α-Chloroisobutyronitrile. Isobutyramide was prepared from isobutyric acid through isobutyryl chloride by the method of Organic Syntheses. This was converted to isobutyronitrile by phosphorus pentoxide dehydration according to the Organic Syntheses procedure[56]. Phosphorus pentachloride chlorination by the method of Stevens[57] gave the α-chloroisobutyronitrile.

Attempted coupling of p-nitrophenylhydrazine and α-chloroisobutyronitrile. It was thought that the α-chloro nitrile might be enough more reactive to couple even though the α-hydroxy nitrile would not. In one attempt, p-nitrophenylhydrazine in methanol solution was refluxed for 6 hours with a slight excess of α-chloroisobutyronitrile and an excess of pyridine. On concentrating and cooling, crystals separated which after recrystallization were shown to be unchanged p-nitrophenylhydrazine.

α-Aminoisobutyronitrile. This compound was made by a modified Strecker synthesis. A mixture of ammonium chloride, water, acetone, and sodium cyanide was allowed to stand at room temperature. After two days concentrated aqueous ammonia was added and the

mixture allowed to stand two more days. After ether extraction, drying, and distillation, the product was collected at 60-62.5°/23mm.

Attempted condensation of p-nitroso-dimethylaniline with α-aminoisobutyronitrile. Since it was known that aromatic nitroso compounds react with primary aromatic amines to give azo compounds,[58] it was thought that this reaction might be used to give mixed azo nitriles. This was checked rather superficially by attempts to condense p-nitroso-dimethylaniline with α-aminoisobutyronitrile. In refluxing alcohol with acetic acid, in dibutyl ether at 100° with acetic acid, or on long standing in ether with or without acetic acid no reaction appeared to take place.

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