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THE NITROUS ACID DEAMINATION
OF
1,1-DISUBSTITUTED HYDRAZINES

by

MICHAEL DE ROSA

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirement for the degree of Doctor of Philosophy, The City University of New York.

1974

This manuscript has been read and accepted for the University Committee in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

5/17/74
date

Paul Haberfield
Chairman of Examining Committee

5/21/74
date

Leonard H. Schwartz
Executive Officer

Herbert Meislich

Robert A.

Supervisory Committee

The City University of New York

DEDICATION

To

SUSAN

With Love

Acknowledgment

I wish to thank Professor Paul Haberfield for his guidance during the course of this work.

ABSTRACT

THE NITROUS ACID DEAMINATION OF 1,1-DISUBSTITUTED HYDRAZINES

Adviser: Professor Paul Haberfield

The nitrous acid deamination of N-methyl-N-phenylhydrazine, N-tert-butyl-N-phenylhydrazine, 1,1-diphenylhydrazine and 9-aminocarbazole was studied. Reactions were carried out in methanol, n-butanol and benzene using isoamylnitrite/HBF_4 and isoamylnitrite/acetic acid as deamination reagents.

The deamination of N-methyl-N-phenylhydrazine, 1,1-diphenylhydrazine and 9-aminocarbazole gave as products N-methylaniline, diphenylamine and carbazole respectively. N-tert-Butyl-N-phenylhydrazine gave N-tert-butyl-aniline and phenylazide as products.

In addition, nitrous oxide was produced in all reactions. The yield of nitrous oxide is much less than that of the secondary amine formed in each reaction. It is shown that secondary amines are produced by at least two processes, but only one of which produces nitrous oxide.

The cleavage reaction which gives phenylazide from N-tert-butyl-N-phenylhydrazine produces, in methanol, comparable amounts of methyl tert-butyl ether. An N-diazonium ion is proposed to explain the formation of phenylazide and methyl tert-butyl ether.

The N-tert-butyl-N-phenylhydrazine deamination was studied in detail. Authentic N-tert-butyl-*p*-anisidine was prepared. No trace of this material was found when reactions were run in methanol. This indicates that no singlet product was formed in this reaction. O-Acetyl-N-tert-butyl-N-phenylhydroxylamine and O-methyl-N-tert-butyl-N-phenylhydroxylamine were prepared. They were not detected as products. This indicates that no reaction took place between a positive nitrogen and available nucleophiles.

It has been proposed that the initially formed singlet nitrenium ion quickly spin inverts to a triplet species. The triplet abstracts hydrogen atoms to give secondary amines.

A mechanism is proposed to explain the products.

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INTRODUCTION

1. General Statement

Trivalent electron-deficient carbon species (carbonium ions) have been extensively studied under a variety of experimental conditions. The literature of organic chemistry amply attests to the interest in trivalent carbon cations.[1] This is in marked contrast to the chemistry of the electron-deficient divalent nitrogen analog, the nitrenium ion.[2]

Prior to 1965 very little had been published on the formation and reactivity of nitrenium ions. Since then P. Gassman and co-workers have published data which have helped to elucidate the chemistry of this interesting class of intermediates.[3-8]

This thesis presents evidence for the formation of nitrenium ions in the nitrous acid deamination of 1,1-disubstituted hydrazines: ($PhRNNH_2$; R=CH_3,$C(CH_3)_3$, Ph and 9-aminocarbazole).

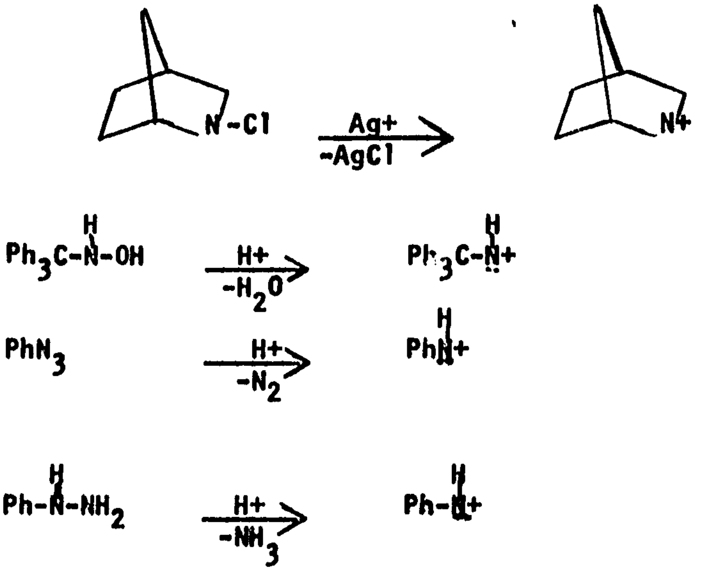
Evidence is presented for the formation of an N-diazonium ion ($PhRN-N_2+$) which can lose nitrogen to give a nitrenium ion. This N-diazonium ion can undergo, in the case of N-tert-butyl-N-phenylhydrazine, alkyl cleavage to give phenylazide and methyl tert-butyl ether. The N-diazonium ion can undergo cleavage to either a nitrenium ion and a neutral fragment (N_2) or a carbonium ion and a neutral fragment (phenylazide). No other example of this type has yet been reported.

This work also shows that the decomposition of the N-diazonium ion gives a very unstable nitrenium ion which quickly undergoes intersystem crossing to a triplet state. The chemistry of the nitrenium ion generated by nitrous acid deamination is that associated with a triplet nitrenium ion.

This thesis postulates a reaction pathway which has heretofore not been reported for the reaction of 1,1-disubstituted hydrazines with nitrous acid.

2. Formation of Nitrenium Ions

Nitrenium ions have been obtained from a variety of N-chloroamines.[4, 8, 9] They have also been postulated as intermediates in the reaction of hydroxylamines,[10] azides,[11-14] and mono-substituted hydrazines with acids.[15]



$$Ph_3C\text{-}\overset{H}{N}\text{-}OH \xrightarrow[-H_2O]{H+} Ph_3C\text{-}\overset{H}{\ddot{N}}+$$

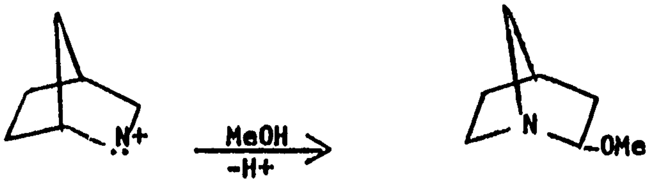
$$PhN_3 \xrightarrow[-N_2]{H+} Ph\overset{H}{\ddot{N}}+$$

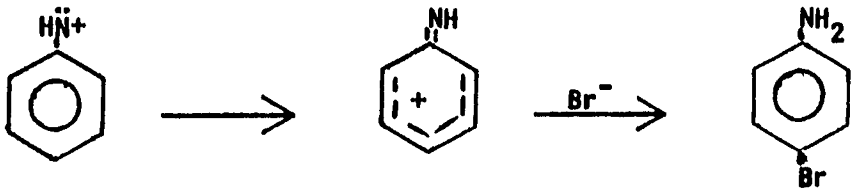
$$Ph\text{-}\overset{H}{N}\text{-}NH_2 \xrightarrow[-NH_3]{H+} Ph\text{-}\overset{H}{\ddot{N}}+$$

3. Reactivity of Nitrenium Ions

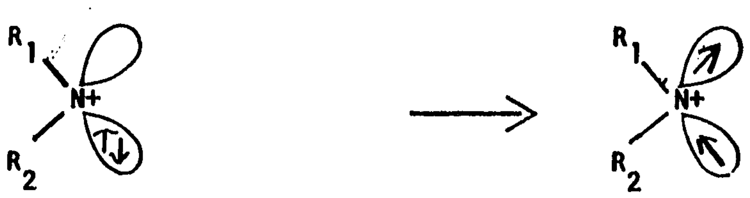
A nitrenium ion differs from a carbonium ion in two ways:

(I) Nitrogen is more electronegative than carbon; as a result a nitrenium ion is more reactive than a carbonium ion.[2] No case has been reported in which the electron-deficient nitrogen reacts directly with nucleophile. The positive charge is quickly shifted to a suitable carbon atom either by a skeletal rearrangement or electronic redistribution. The carbonium ion formed then reacts with a nucleophile.





(II) Unlike the carbonium ion a nitrenium ion contains a pair of non-bonded electrons. As a consequence the nitrenium ion can exist in either a singlet or triplet state.[7, 16]



Singlet Triplet

By its mode of formation a nitrenium ion is a singlet.[2] Intersystem crossing between singlet and triplet states has been found to be catalyzed by heavy atoms,[17-19] and paramagnetic substances.[20]

P. Gassman has been able to catalyze the conversion of singlet to triplet.[7] Each spin state has a different chemistry; the singlet has "carbonium ion" like properties (it rearranges and then reacts with a nucleophile); the triplet behaves as a radical cation (abstracts hydrogen atoms). The ability to catalyze this interconversion is also evidence for the existence of a discrete nitrenium ion, instead of a concerted mechanism in which a full positive charge is not generated at the nitrogen atom.[7]

A study of the thermal rearrangement of *p*-substituted-N-tert-butylanilines indicated that as the electron withdrawing power of the substituent increased so did the yield of starting *para*-substituted-N-tert-butylaniline.[21] The following table summarizes the data:

Table I

Para Substituent	% Yield of Starting Aniline
CH_3	1
F	8
H	16
Cl	17
$CO_2C_2H_5$	19
$C\equiv N$	29

Electron withdrawing substituents on the ring lead to greater positive charge on the nitrogen. It appears that as the nitrogen becomes more positive relative to the ring, the rate of singlet to triplet conversion increases relative to the rate of reaction of the singlet state with nucleophile. This leads to enhanced yields of triplet product, *i.e.*, *para*-substituted-N-tert-butylanilines. The reason(s) for this are not immediately obvious. Similar results have been obtained from the silver catalyzed reaction.[22] This work will be discussed more fully in the main body of this work.

Two independent theoretical molecular orbital calculations for the simplest nitrenium ion (N^+H_2) have been published. The first indicates that the triplet state is linear or almost linear and is 45 kcal/mol lower in energy than the singlet state.[23] The singlet state has an HNH angle $\theta \sim 115°$. The second calculation gives the energy difference between triplet and singlet as being 38 kcal/mol and minimum energy angles of 140° and 120° respectively.[24]

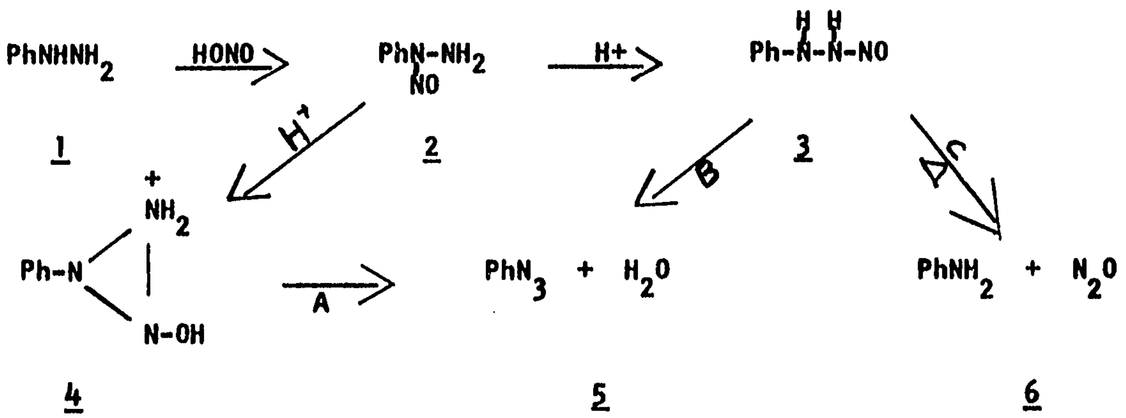
The following sections are reviews of the literature pertinent to this thesis.

4. Reactions of Hydrazines with Nitrosating Agents

A. Mono-Substituted Hydrazines

Mono-substituted alkyl and aryl hydrazines react with nitrosating agents in similar ways to give azides.[25, 26] The hydrazine is initially nitrosated on the substituted nitrogen to give: $R\text{-}\overset{NO}{N}\text{-}NH_2$.[25] This has been substantiated by trapping the species with a ketone to give an

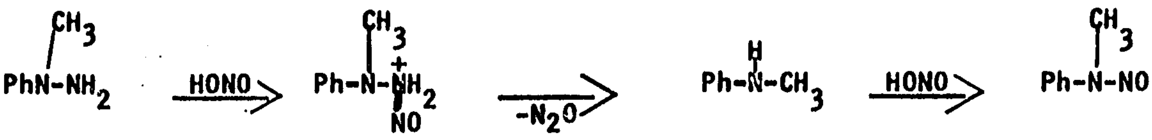
N-nitrosohydrazone: $R-\overset{NO}{N}-N=CR_2$.[25] In the presence of acid the initially formed N-nitrosohydrazine rearranges to the isomeric N-nitrosohydrazine: $R\overset{H}{N}-\overset{H}{N}-NO$. The following is a proposed scheme for the formation of phenylazide from phenylhydrazine:[27, 28]



As yet no evidence has been presented in the literature to substantiate the existence of any of the intermediates in the above scheme.

B. 1,1-Disubstituted Hydrazines

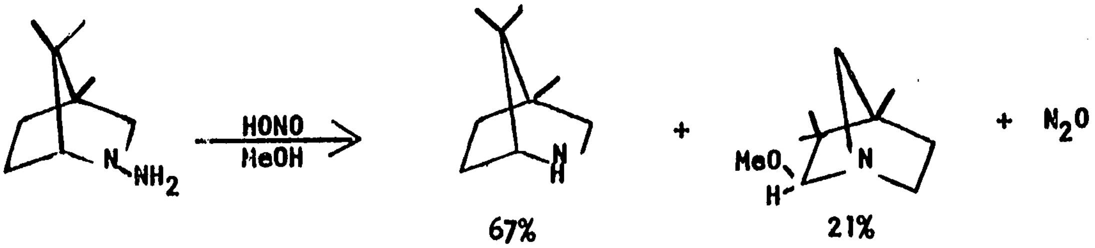
Originally the reaction of N-methyl-N-phenylhydrazine with nitrous acid was found by E. Fisher to give N-nitroso-N-methlyaniline.[29] Closer examination by J. Thiele revealed the following reaction scheme:[30]



The N-nitroso-N-methylaniline is formed in the presence of excess nitrous acid. It has also been found that 1-aminobenzimadozole is deaminated by nitrous acid to give benzimadozole.[31]

The rocket engines of the lunar landing module utilize a fuel consisting of 1,1-dimethylhydrazine and nitrogen tetroxide.[32] The exhaust gases contain trace amounts (less than 0.1%) of the following compounds: NH_3, CH_3N_3, $C_2H_5N_3$; $CH_5\overset{H}{N}-\overset{H}{N}-NO$ and $C_2H_5-N=N-NO$. The system was studied by mass spectroscopy.

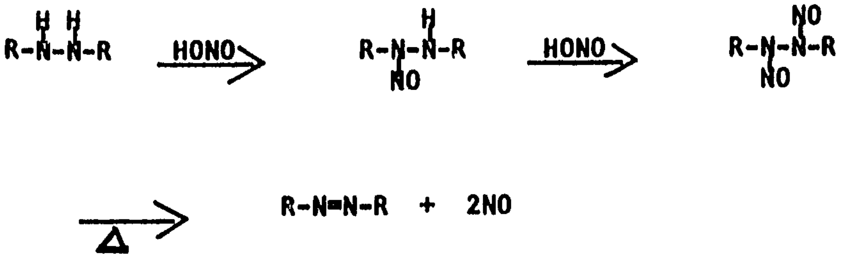
Subsequent to the start of this study P. Gassman reported the results of the nitrous acid deamination of an aliphatic 1,1-disubstituted hydrazine: 2-amino-3,3,4-trimethyl-2-azabicyclo-(2.2.1)heptane.[33]



He reported a large yield of secondary amine and isolated nitrous oxide as the major gaseous product.

C. 1,2-Disubstituted Hydrazines

This class of compounds react with nitrous acid to give isolable compounds containing one or two N-nitroso groups.[30, 34] The N,N^1-dinitroso hydrazine formed readily loses nitric oxide giving an azo compound.



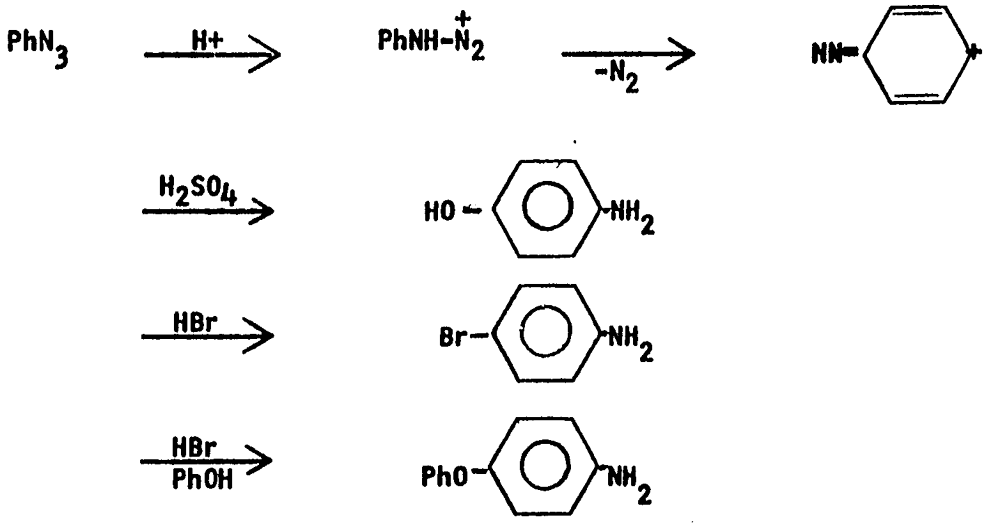
$$R-\overset{H}{N}-\overset{H}{N}-R \xrightarrow{HONO} R-\underset{NO}{N}-\overset{H}{N}-R \xrightarrow{HONO} R-\underset{NO}{N}-\overset{NO}{N}-R$$

$$\xrightarrow[\Delta]{} R-N=N-R + 2NO$$

5. Reactions in which the N-Diazonium Ion has been Proposed to Explain Products or Kinetics

A. Reaction of Arylazides with Strong Mineral Acids

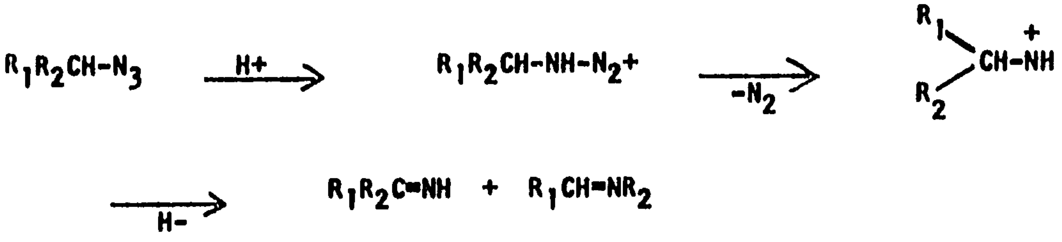
Phenylazide and substituted arylazides decompose in the presence of strong acid to give basic products and nitrogen.[11-14] A kinetic investigation showed the rate law for the decomposition of phenylazide to be: rate = $k(PhN_3)H°$.[13] This suggests the formation, in the rate determining step, of the conjugate acid of phenylazide ($(\mathrm{Ph}\overset{H}{\mathrm{N}}\text{-}\overset{H}{\mathrm{N}}_2{}^{+}$, an N-diazonium ion). The following is a proposed scheme which accounts for the products obtained and some examples.[11]



Para-substituted azides can be converted to 2,4-disubstituted anilines, para-substituted anilines and polymers with the general formula $(X\text{-}C_6H_4\text{-}N)_n$.[14]

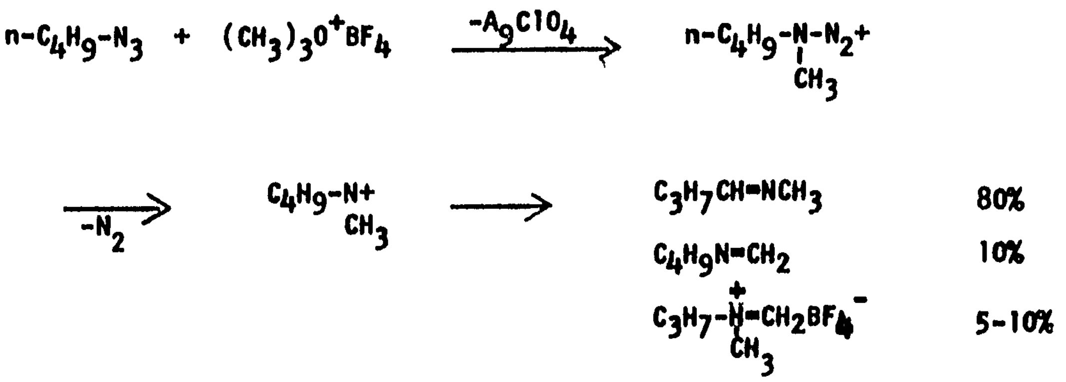
B. Reactions of Alkylazides with Acid

The following is a proposed mechanism for the reaction of alkylazides with acid:[35]



C. The Reaction of Alkylazides with Alkylating Agents

Alkylazides can be alkylated by powerful alkylating agents such as trimethyl oxonium fluoroborate.[36] An N-diazonium ion has been proposed as a possible intermediate.



$$n\text{-}C_4H_9\text{-}N_3 + (CH_3)_3O^+BF_4 \xrightarrow{-AgClO_4} n\text{-}C_4H_9\text{-}\underset{\displaystyle CH_3}{\underset{|}{N}}\text{-}N_2{+}$$

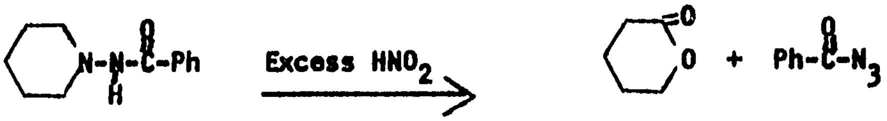
$$\xrightarrow[-N_2]{} \begin{matrix} C_4H_9\text{-}N{+} \\ \quad CH_3 \end{matrix} \longrightarrow \begin{array}{ll} C_3H_7CH{=}NCH_3 & 80\% \\ C_4H_9N{=}CH_2 & 10\% \\ C_3H_7\text{-}\overset{+}{\underset{\displaystyle CH_3}{N}}{=}CH_2BF_4^- & 5\text{-}10\% \end{array}$$

D. As an Intermediate in the Schmidt Rearrangement

The Schmidt rearrangement is a series of reactions employing as a reagent hydrazoic acid in sulfuric acid.[37] One can effect the conversion of a carboxylic acid to an amine containing one carbon less or a ketone to an amide. One of the intermediates proposed in the rearrangement is an N-diazonium ion.

6. Reactions of Hydrazine Derivatives with Nitrous Acid

A. Nitrosative Cleavage of Dialkylhydrazines[38]

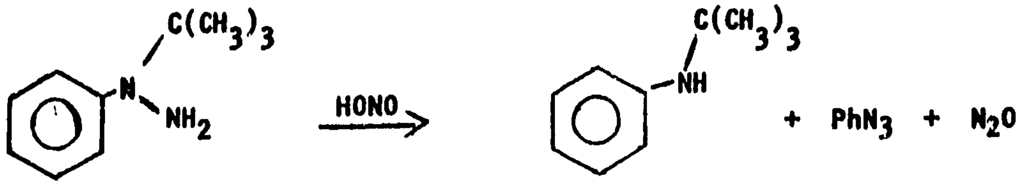


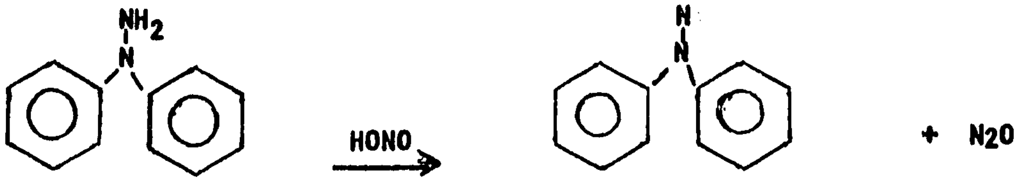
B. Conversion of Unsubstituted Amidazones to Amidines[39]

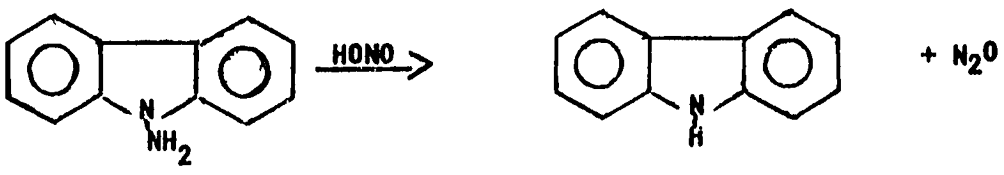
The above reaction is analogous to the deamination of 1,1-disubstituted hydrazines.

RESULTS

The nitrous acid deamination of 1,1-disubstituted hydrazines has been studied. The following equations illustrate the hydrazines used and their respective products.







The following tables give products and yields obtained when the reactions were run using isoamylnitrite/fluoroboric acid in methanol and isoamylnitrite/acetic acid/lithium acetate in methanol, n-butanol and benzene.

Table II

Deamination of 1,1-Disubstituted Hydrazines with Isoamylnitrite/HBF_4 in Methanol

Product Yields (%) [a]

Hydrazine	Run No.	PhN_3	$Ph\overset{H}{N}R$ [b]	$Ph\overset{H}{N}NO$	N_2O
N-Methyl-N-phenylhydrazine	28	trace	58	5	10
N-tert-Butyl-N-phenylhydrazine	32	8	78		20
1,1-Diphenylhydrazine	36		80		20
9-Aminocarbazole	40		65		14

a. Product yields as given in Tables II to VI are based on unrecovered starting material.

b. Carbazole from 9-aminocarbazole.

Table III

Deamination of N-Methyl-N-Phenylhydrazine with Isoamylnitrite/Acetic Acid/Lithium Acetate

Product Yields (%)

Solvent	Run Number	$Ph\overset{H}{N}CH_3$	N_2O
Methanol	29	61	16
n-Butanol	31	68	22
Benzene	30	90	15

Table IV

Deamination of N-tert-Butyl-N-Phenylhydrazine
with
Isoamylnitrite/Acetic Acid/Lithium Acetate

Product Yields (%)

Solvent	Run Number	PhN_3	$Ph\overset{H}{N}C(CH_3)_3$	N_2O
Methanol	33	12	45	21
n-Butanol	35	16	63	21
Benzene	34	16	57	14

Table V

Deamination of 1,1-Diphenylhydrazine
with
Isoamylnitrite/Acetic Acid/Lithium Acetate

Product Yields (%)

Solvent	Run Number	Ph_2NH	N_2O
Methanol	37	62	13
n-Butanol	39	71	21
Benzene	38	87	31

Table VI

Deamination of 9-Aminocarbazole
with
Isoamylnitrite/Acetic Acid/Lithium Acetate

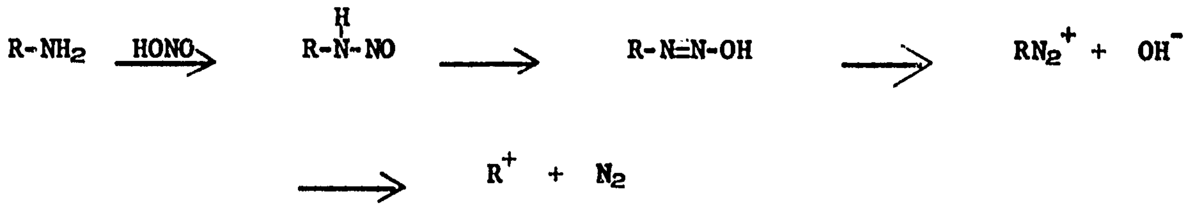
Product Yields (%)

Solvent	Run Number	Carbazole	N_2O
Methanol	41	52	15
n-Butanol	43	75	28
Benzene	42	72	44

DISCUSSION

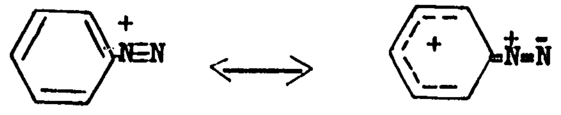
1. Introduction

The reaction of primary amines with nitrous acid can be summarized by the following scheme:[40]



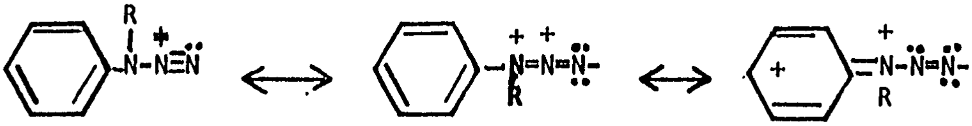
$$R\text{-}NH_2 \xrightarrow{HONO} R\text{-}\overset{H}{N}\text{-}NO \longrightarrow R\text{-}N{=}N\text{-}OH \longrightarrow RN_2^+ + OH^- \longrightarrow R^+ + N_2$$

Primary aromatic amines give diazonium ions which can be isolated, secondary amines yield N-nitroso compounds and primary aliphatic amines a variety of deamination products. The stability of the aromatic diazonium ion has been attributed to resonance structures such as:



No comparable resonance structures can be written for aliphatic diazonium ions. No aliphatic diazonium ion with N_2^+ bound to an sp^3 carbon has as yet been isolated. Its existence has been proposed to explain the nitrous acid deamination of aliphatic primary amines. The diazonium ion is thought to quickly decompose to give a carbonium ion and nitrogen. The formation of a carbonium ion intermediate has been confirmed by comparing the nature and stereochemistry of products obtained by nitrous acid deamination to those obtained from similar carbonium ions generated by other reaction paths.

The analogous reaction of a 1,1-disubstituted hydrazine with nitrous acid should lead to an N-diazonium ion. On the basis of the resonance contributors shown below, the N-diazonium ion should be intermediate in stability between an aliphatic and aromatic diazonium ion. Resonance contributor II would not be expected to contribute much to the stability of the N-diazonium ion.



I II III

Similarly it might be predicted that an N-diazonium ion could decompose to give a nitrenium ion plus nitrogen. The formation of a nitrenium ion could be demonstrated by showing that the products obtained were similar to those obtained from nitrenium ions generated by alternate routes.

Tables II through VI in the preceding section indicate that the deamination of 1,1-disubstituted hydrazines leads exclusively to unsubstituted secondary amines. This is in contrast to systems studied by P. Gassman and coworkers where ring substituted products were obtained and explained using nitrenium ions.[8, 21, 22] In some cases, the nitrenium ion was identical to that expected in this study. Only with N-tert-butyl-N-phenylhydrazine was the pattern broken. Here a small yield of non-basic compound, phenylazide, was obtained (pp 72-74).

The succeeding sections will discuss the mechanistic implications of the data presented in the preceding tables. These tables indicated that three types of products were obtained: nitrous oxide, phenylazide and unsubstituted secondary amines. Nitrous oxide and secondary amines can be envisioned to come from N-N bond cleavage and phenylazide from C-N cleavage. Each type of product will be discussed separately and a unified mechanism presented in the final section.

2. Formation of Nitrous Oxide

J. Thiele was the first to proposed nitrous oxide as one of the products obtained from the nitrous acid deamination of 1,1-disubstituted hydrazines.[30] This was confirmed by P. Gassman and K. Shado in their study of the nitrous acid deamination of dialkylhydrazines.[33] They trapped and identified nitrous oxide as the major gaseous product. No data were given to indicate how much of the secondary amine was produced in the same process which formed nitrous oxide.

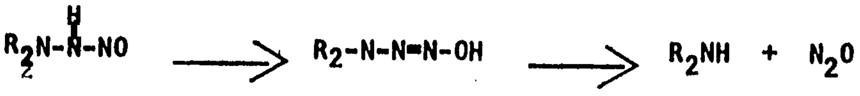
In our work a vacuum system was developed to trap and determine quantitatively the yield of nitrous oxide produced under the reaction conditions employed in this study. The vacuum system had a trapping efficiency of at least 80-90% and could be used to determine if nitrous oxide and secondary amine were produced in a molar ration of 1:1. (pp 62-65)

An Infrared Spectrometer was used to determine both the trapping efficiency of the vacuum line and the yield of nitrous oxide in a reaction (pp. 62-65). Infrared spectroscopy can be used to detect from 0.003-3% by volume of nitrous oxide in a mixture.[41] Nitrous oxide and similar diatomic and triatomic gases do not obey Beer's law at all concentrations.[42] Absorbance is found to be a function of both the partial pressure of the gas and the total pressure of the gas mixture. To get accurate quantitative results, it is necessary to use a calibration curve. This curve is obtained by plotting absorbance versus partial pressure of the gas (keeping a constant total pressure by adding a non-absorbing gas). Using this method accuracies of better than 10% have been obtained for simple gases.[42]

Tables II through VI summarize the data obtained from nitrous oxide trapping experiments using a variety of hydrazines substances and reaction conditions.

These tables indicate that the formation of nitrous oxide, while a significant process, does not account for the bulk of amines observed. The results indicate that there are at least two distinct pathways which lead to secondary amines.

It has been suggested that nitrous oxide is formed by the following processes[33, 43]

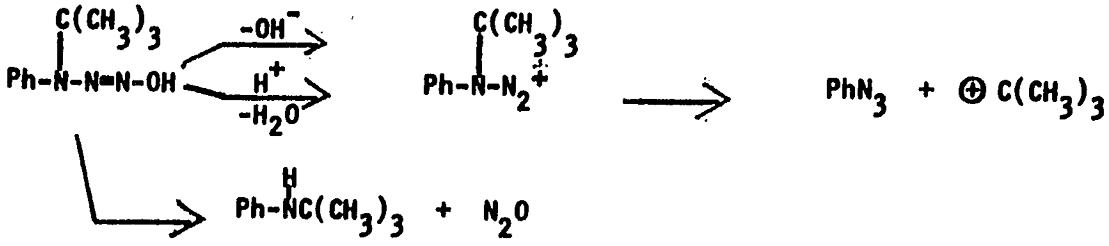


$$R_2N\overset{H}{N}\text{-}NO \longrightarrow R_2\text{-}N\text{-}N\text{=}N\text{-}OH \longrightarrow R_2NH + N_2O$$

The formation of $R_2N\text{-}N\text{=}N\text{-}OH$ is analogous to the formation of R-N=N-OH (diazotic acid) in the diazotization of aromatic primary amines. No diazotic acid has as yet been isolated but spectroscopic evidence indicates its existence in solution. Also sodium salts of diazotic ion ($R\text{-}N\text{=}N\text{-}O^-$) have been isolated.[44]

3. Formation of Phenylazide

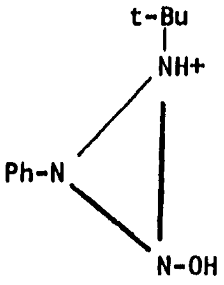
The deamination of N-tert-butyl-N-phenylhydrazine gives N-tert-butylaniline and a small yield of phenylazide. Formation of phenylazide is direct evidence of an N-diazonium ion as one of the intermediates in the nitrous acid deamination of N-tert-butyl-N-phenylhydrazine and by analogy other 1,1-disubstituted hydrazines. Its formation can be envisioned to come from the same diazotic acid intermediate which leads to nitrous oxide.



In the analogous deamination of aliphatic amines, a diazonium ion has been proposed but direct evidence for its existence has not been published.

The cleavage reaction which produces phenylazide also gives a carbonium ion fragment. The nature of this carbonium ion (free or otherwise) is not known.

It is possible that another intermediate might be responsible for the formation of phenylazide and a carbonium ion fragment. One possibility is given below. A similar intermediate has been proposed for the formation of phenylazide from phenylhydrazine (p 6). The analogous reactions of primary aromatic and aliphatic amines seem to suggest that the N-diazonium ion is the more attractive intermediate.



A tert-butyl carbonium ion can give both substitution and elimination (isobutylene) products.[45] Formation of an ether has been shown to be the chief product in ethanol $\frac{S_N1}{E1} = 4.$[45] In methanol the major product should be methyl tert-butyl ether. Gas chromatographic analysis of the products of a reaction run in methanol indicated that the yields of phenylazide and ether are comparable $\frac{\text{ether}}{PhN_3} = 1.2$ (p 92). The ether was identified by comparing the mass spectrum of authentic ether to that of material having the same retention time as methyl-tert-butyl-ether (p 94). Isolation of both azide and ether strongly indicates the intermediacy of an N-diazonium ion.

Phenylazide can be expected only from an N-diazonium ion which can cleave to give a stable carbonium ion. The following table of carbonium ion stabilities indicates that methyl and phenyl carbonium ions are much less stable than tert-butyl carbonium ions.[46]

Table VII

Heats of Formation of Carbonium Ions

Ion	ΔH_f (kcal/mole)[a]
CH_3 +	258
tert-C_4H_9+	174
Ph +	285-288

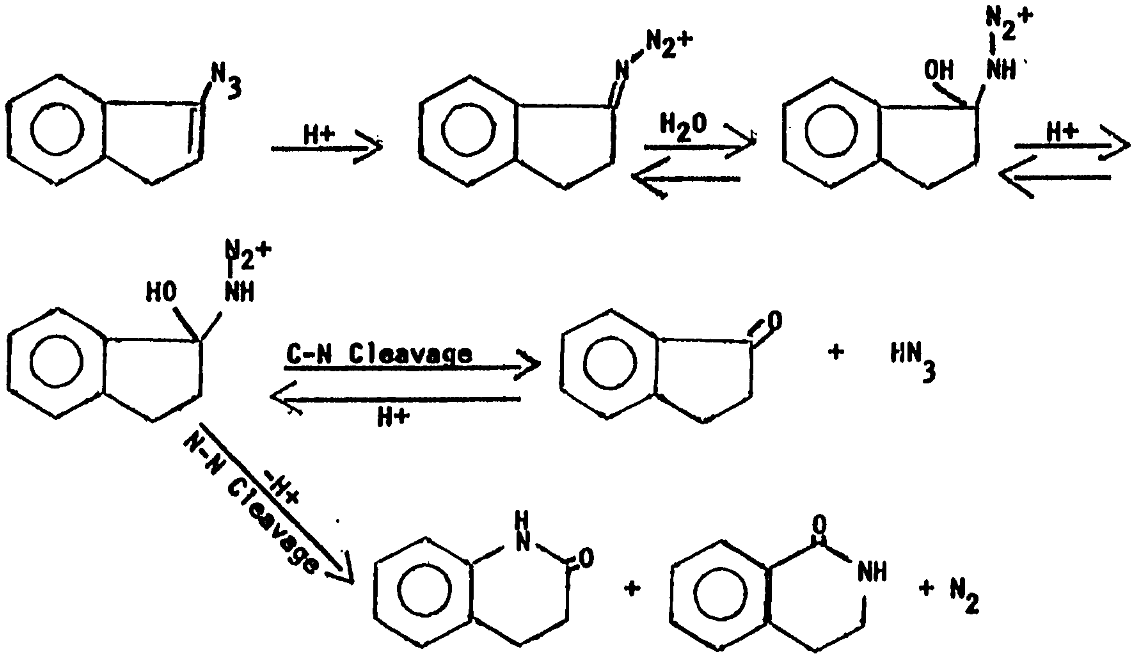
a. ΔH_f (ion) = ΔH_f (radical) + I_p (radical)

Consequently little or no phenylazide is to be expected when the carbonium ion fragment is either methyl or phenyl cation. The experimental evidence confirms this.

Mono-substituted alkyl and aryl hydrazines react with nitrous acid to give azides, primary amines and nitrous oxide.[25, 26] This reaction is remarkably similar to the reaction under study. In the reaction of phenylhydrazine with nitrous acid it has been suggested that $Ph\text{-}\overset{H}{N}\text{-}\overset{H}{N}\text{-}NO$

is formed and decomposes to give as products phenylazide, aniline and nitrous oxide. There is no evidence to substantiate this mechanism.

An interesting example has been published in which an intermediate similar to that in our proposed mechanism has been found to cleave to give an azide as one of the products. The acid catalyzed hydrolysis of vinyl azides can give as one of the products a ketone with concomitant formation of hydrazoic acid (NH$_3$).[47]



The formation of a ketone and hydrazoic acid is similar to the C-N cleavage observed in the deamination of N-tert-butyl-N-phenylhydrazine. In addition N-N cleavage can take place to give a lactam. The intermediate leading to the lactam is a positive species but not a nitrenium ion.

It thus appears that the N-diazonium ion proposed in the acid catalyzed hydrolysis of vinyl azides can undergo two different modes of cleavage. This is similar to what we have proposed in our work. In addition it should be noted that in the reaction of indanone with hydrazoic acid and sulfuric acid (Schmidt rearrangement), a lactam is isolated which is identical to that obtained from the acid catalyzed hydrolysis of the above vinyl azide.[47] Here too, an N-diazonium ion has been proposed as one of the intermediates.

It is of interest that the reverse of C-N cleavage has been reported. N-diazonium ions have been obtained by protonation[11-14] or alkylation of azides.[36]

The following evidence strongly indicates the formation of N-diazonium ions during the deamination of 1,1-disubstituted hydrazines:

(i) Formation of phenylazide and methyl tert-butyl ether.

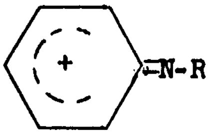
(ii) Absence of phenylazide where an unstable carbonium ion would also be formed.

(iii) Analogous reactions in the literature.

4. Formation of Secondary Amines: Introduction

It has been noted previously that the only deamination products isolated have been secondary amines containing no substitution on the benzene nucleus. Also the data show that changes in solvent polarity from methanol to benzene or the addition of a stronger nucleophile (acetate ion) have had no effect on the number of products observed. There have been changes only in the relative yields of the various products. The results are not what are predicted for nitrenium ions.

The nitrenium ions expected from N-methyl-N-phenylhydrazine have been obtained by other workers via the silver ion catalized methanolysis of the appropriate N-chloroaniline.[8] Methanolysis of N-chloro-N-tert-butylaniline gave *o* and *p*-methoxy-N-tert-butylaniline, *o* and *p*-chloro-N-tert-butylaniline and N-tert-butylaniline as products. N-chloro-N-methylaniline gave similar results. These results have been explained in terms of a delocalized nitrenium ion:



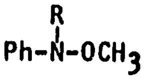
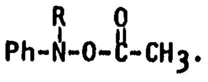
The isolation of 4-methoxy-4-methyl-2,5-cyclohexadienone from the thermal rearrangement of N-chloro-N-tert-butyl-*p*-toludine is additional evidence for the existence of delocalized nitrenium ions.[21]

Since products of these types are not observed in our system, it is reasonable to doubt the formation of a delocalized nitrenium ion under the reaction conditions employed. This does not preclude the formation of a non-delocalized nitrenium ion, *i.e.*, nitrogen bearing a full positive charge. A non-delocalized nitrenium ion might be expected to have properties not shared by a delocalized and more stable nitrogen cation. This is analogous to the so called "hot" carbonium ions obtained from the nitrous acid deamination of aliphatic amines. Carbonium ions formed by this process have unique properties which are attributed to their mode of formation.

The rate determining step in the diazotization of amines is the formation of an N-nitroso compound. Formation of a diazonium ion from the N-nitroso compound is rapid and probably does not require much activation energy. The decomposition of the diazonium ion simultaneously produces a carbonium ion and nitrogen. It appears that the carbonium ion contains most of the energy contained in the transition state common to both products.[46] This results in a carbonium ion which has been labeled "hot" or "unsolvated". Products are then formed which are not normally obtained by simple heterolysis. In addition, the lifetime of the ion can be very short, the solvent shell of the cation being essentially the same as that of the diazonium ion.

A nitrenium ion formed by the decomposition of an N-diazonium ion might be expected to have different properties than one obtained by the heterolysis of an N-chloroamine. Nitrenium ions are formed as singlet species but can undergo intersystem crossing to a triplet state. Triplet nitrenium ions have been shown to be good hydrogen atom abstractors and give unsubstituted secondary amines.[7] It is possible that a nitrenium ion produced by the nitrous acid deamination of a di-substituted hydrazine undergoes intersystem crossing much faster than it reacts with an available nucleophile. This would result in larger yields of unsubstituted amines. This possibility will be further explored in a subsequent section.

Before we can completely rule out a delocalized nitrenium ion as an intermediate, it is necessary to establish that small yields of product derived from this species could have in fact been detected. It is also necessary to preclude the existence of N-substituted products resulting from the direct attack of nucleophile on the positive nitrogen,

e.g.,  $\mathrm{Ph{-}\overset{R}{\overset{|}{N}}{-}OCH_3}$ or  $\mathrm{Ph{-}\overset{R}{\overset{|}{N}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$.

5. Search for Substituted Secondary Amines

Only the methyl and tert-butyl compounds gave any evidence of producing small amounts of unidentified minor components. P. Gassman has reported that side reactions took place in the silver catalyzed methanolysis of N-chloro-N-methylaniline which lowered the total yield of recovered material.[8] The nitrenium ion obtained from N-chloro-N-methylaniline can undergo elimination to give an imine. The imine can undergo hydrolysis or possibly react with nitrous acid (olefins are known to react in this fashion). This is not possible for the tert-butyl compound. To simplify the analysis of side products the N-tert-butyl compound was chosen for further study.

The substituted amines expected from the deamination of N-tert-butyl-N-phenylhydrazine in methanol are o and p-methoxy-N-tert-butylaniline. Previous work, by P. Gassman, on N-chloroanilines indicates that the p-methoxy compound is the major product. Therefore, p-methoxy-N-tert-butylaniline was prepared (p 51).

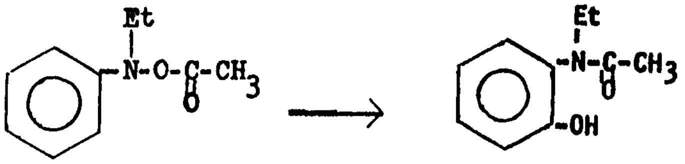
An analytical procedure was developed which could detect a 1% yield of the p-methoxy compound (p 84). Analysis of the product mixture under the same conditions as a standard indicated that, within the limits of detectability previously established, no p-methoxy-N-tert-butylaniline is formed (p 87). This indicates that no product is obtained from a singlet nitrenium ion.

6. Search for N-Substituted Products

The compounds expected from direct attack on the positive nitrogen of N-tert-butylanilenium ion are O-acetyl-N-tert-butyl-N-phenylhydroxylamine and O-methyl-N-tert-butyl-N-phenylhydroxylamine. Neither compound has been previously reported in the literature. They were prepared from the corresponding hydroxylamine (p 49). The hydroxylamine was synthesized in 2% yield by a route previously used to make N-ethyl-N-phenylhydroxylamine.[48] The O-acetyl compound (p 51) was obtained pure while the O-methyl compound (p 53) was obtained 90% pure.

It was necessary to determine if these compounds were stable to the reaction conditions employed in the deamination procedure. The scant information in the literature indicated the possibility of rearrangement under the reaction conditions used.

Hydroxylamine derivatives analogous to the O-acetyl compound have been previously prepared only from N-ethyl-N-phenylhydroxylamine.[49] This compound in refluxing benzene rearranges to:



Attempts to prepare similar derivatives from other phenylhydroxylamines resulted in the isolation of phenolic compounds.[49] Aliphatic derivatives are isolable and well known.[50]

Similarly very little has been published on O-alkyl derivatives of N-substituted phenylhydroxylamines. A. C. Cope has prepared O-s-butyl-N-methyl-N-phenylhydroxylamine.[51] Hydrolysis of this compound in hydrochloric acid gave s-butylalcohol, N-methylaniline and p-chloro-N-methylaniline as products.

In our work it was found that the O-acetyl-N-tert-butyl-N-phenylhydroxylamine was completely stable to the reaction conditions (p 80). In contrast 21% of the O-methyl-N-tert-butyl-N-phenylhydroxylamine did not survive the reaction conditions (p 82). The main decompostion product was N-tert-butylaniline. If formed, enough of the O-methyl compound would have remained to be detected.

An analytical procedure was developed to detect a1% yield of either the O-acetyl or O-methyl compound (p 83). Analysis of the product mixtures under the same conditions as the standard solutions indicated that, within the limits of detectability previously established, no O-methyl or O-acetyl compound was formed (pp 86-87). This would seem to indicate that if a localized nitrenium ion is formed, spin inversion is much faster than direct attack on the positive nitrogen.

7. Effect of Solvent

Our initial work was in methanol. No evidence was obtained in this medium of singlet nitrenium ion. The reaction was studied in the presence of an added nucleophile (acetate ion). This should lead to an increase in the rate of reaction of singlet nitrenium ion with a nucleophile relative to the process which produces unsubstituted secondary amines. Np new products were observed in methanol when this was done (p 87).

The reaction was run in three different solvents: methanol, butanol and benzene. As one goes from methanol to benzene the degree of association of a nitrenium ion and its counter ion (acetate) should increase. This should have the effect of increasing the relative nucleophile concentration (acetate ion) around the nitrenium ion. An increase in the rate of a reaction involving the nucleophile might be expected relative to the process which produces secondary amines. No new products were obtained when the solvent was changed.

The only effect noted was that diphenylhyrazine (4 hr) reacted faster relative to the other hydrazines (20 hr). This might be caused by a difference in basicity. In the diazotization of anilines it has been noted that the weaker bases react faster.[52] The attacking species in the diazotization of anilines is usually NO^+. This reaction is faster when a greater proportion of the amine remains unprotonated. In the absence of complete basicity data for the four hydrazines used, no order of reactivity can be proposed.

8. Formation of Secondary Amines: Mechanism

The following processes could each be responsible for the formation of secondary amines:

(i) Hydrogen atom abstraction by a triplet nitrenium ion.
(ii) Hydrogen abstraction by a nitrogen free radical.
(iii) Hydride abstraction by an extremely reactive singlet nitrenium ion.

Each will be discussed in turn.

P. Gassman has demonstrated that triplet nitrenium ions can lead to unsubstituted or unrearranged amines. He has catalyzed the inter-system crossing from the singlet to the triplet state by the addition of heavy atom solvents (halogenated hydrocarbons).[7]

The thermal and silver catalyzed rearrangements of <u>para</u>-substituted N-chloro-N-tert-butylanilines has been studied.[21, 22] The products have been explained in terms of nitrenium ion intermediates. The following are tables based on data published by P. Gassman and co-workers.

Table VIII

Product Distribution for Silver Ion Promoted Methanolysis of N-Chloro-N-tert-Butylaniline[a]

Para Substituent	Yield (%) of Products due to Nucleophilic Attack[b]	Yield (%) of o-Chloro-N-tert-Butylaniline	Yield (%) of Starting Aniline
CH_3	70	17	2
Ph	62	5	c
H	45	28	6
Cl	36	25	12
CO_2Et	0	58	26
NO_2	0	65	d

a. P. G. Gassman, G. A. Campbell and R. C. Frederick, J. Amer. Chem. Soc., **94**, 3884 (1972).

b. Para-substituted amines give 2,5-cyclohexadienone imine as the initial product. This product hydrolyzes to give the appropriate 2,5-cyclohexadienone.

c. No data available.

d. *p*-NO_2-N-tert-butylaniline reported but no yield is given.

Table IX

Thermal Rearrangement of N-Chloro-N-*tert*-Butylaniline in Buffered Ethanol[a]

Para Substituent	Yield (%) of o-Chloro-Aniline	Yield (%) of Starting Amine	Yield (%) of Products due to Nuchleophilic Attack
CH_3	85	1	10
F	84	8	
H	64	16	
Cl	72	17	
CO_2Et	78	19	
C≡N	64	29	

a. P. G. Gassman and G. A. Campbell, J. Amer. Chem. Soc., **94**, 3891 (1972)

These data indicate a change in product distribution as the para substituent becomes more electron withdrawing. As the para substituent is changed from H to electron withdrawing groups, the following occurs:

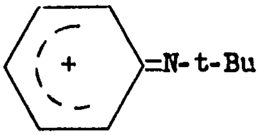
(i) Charge density on the nitrogen increases.

(ii) Yield of triplet product increases (using P. Gassman's criteria for triplet product[7]).

Electron donating substituents have opposite effects and produce increased amounts of singlet product.

It is possible that changes in the charge density on nitrogen and intersystem crossing are related. Increased charge density on the nitrogen might be lowering the energy difference between the singlet and triplet states. This would tend to increase the rate of intersystem crossing.

The transition state for the silver catalyzed solvolysis of N-chloro-N-tert-butylaniline has been depicted by P. Gassman as follows:[8]



The above indicates delocalization of the positive charge into the ring. Decomposition of an N-diazonium ion would put the positive charge directly on the nitrogen (this is analogous to the formation of a "hot" carbonium ion), and intersystem crossing is enhanced. We conclude that secondary amines are derived from the triplet state.

In the absence of theoretical work on nitrenium ions as complex as the ones proposed in this study, the above statement must be considered as a working hypothesis.

There has been some criticism of Gassman's nitrenium ion mechanism. It is felt that not all of the products come from the nitrenium ion precursors--particularly the o-chloroanilines. This criticism is based on a study by P. Haberfield and D. Paul on the thermal rearrangement of N-chloroanilines in polar and non-polar aprotic solvents.[53] The results, for N-chloro-N-tert-butylanilines, are briefly stated below:

(i) Rearrangement is acid catalyzed and the N-chloroaniline is stable in base.

(ii) N-Chloro-N-tert-butylaniline can ring chlorinate other anilines.

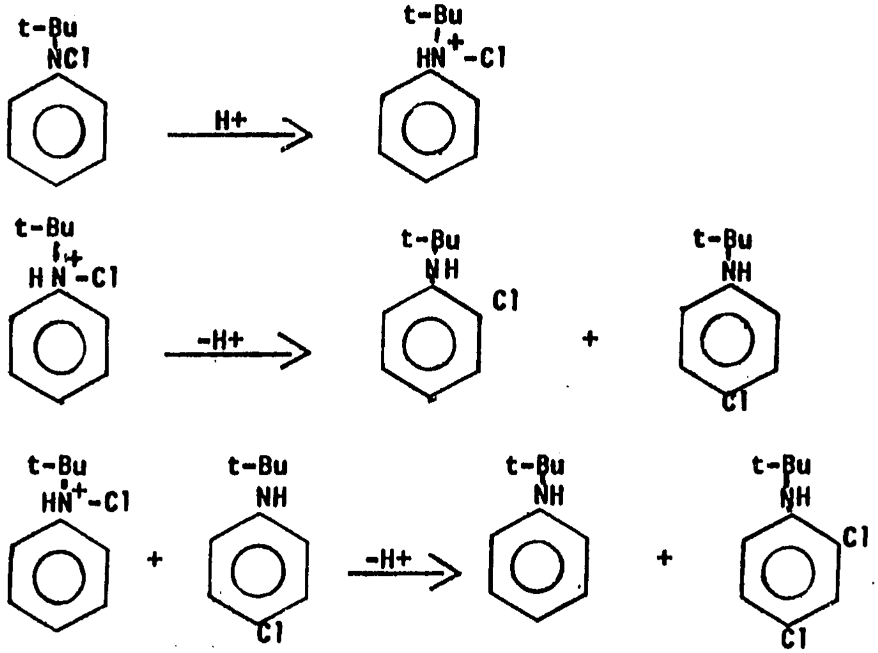
(iii) Products are o and p-chloro-N-tert-butylanilines, 2,4-dichloro-N-tert-butylaniline and N-tert-butylaniline.

(iv) Yields of N-tert-butylaniline and dichloro-N-tert-butylaniline are about the same.

(v) There is no appreciable change in the yield of N-tert-butylaniline when the rearrangement is carried out in carbon tetrachloride or in dichlorobenzene.

The data indicate an acid catalyzed electrophilic reaction in which no nitrenium ions appear to be involved. N-tert-butylaniline results from the chlorination of mono-chloro-N-tert-butylaniline by a molecule of N-chloro-N-tert-butylaniline.

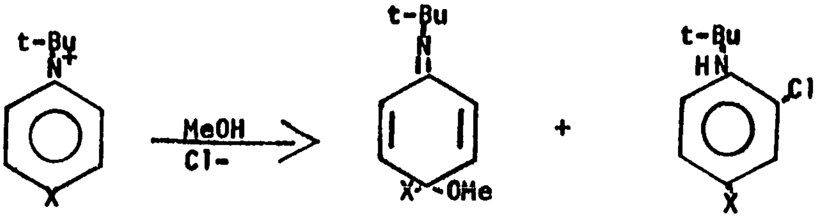
The following equations summarize the above results:



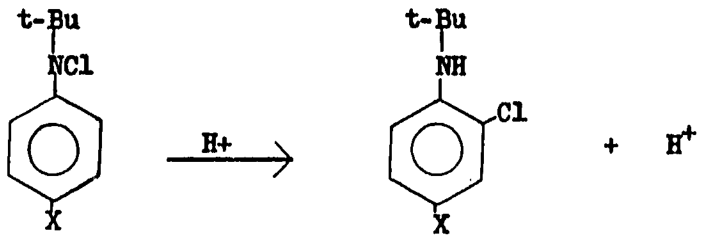
The above reactions need a catalytic amount of acid to start. The acid can be added or it maybe present as an impurity. In addition, it is not yet known whether ring chlorination is an inter- or intra-molecular process.

The above data would seem to indicate that more than one process is responsible for the products observed by Gassman in the rearrangement of <u>para</u>-substituted-N-chloro-N-butylaniline. There appears to be three different reaction pathways:

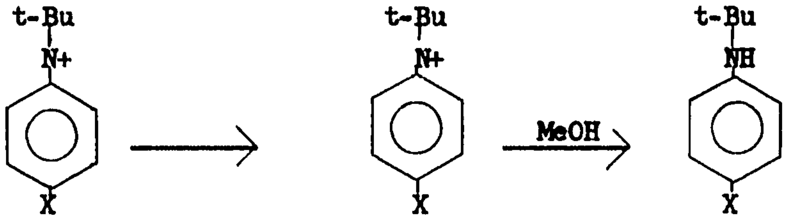
(I) A singlet nitrenium ion giving products incorporating solvent and possibly ring chlorinated products.



(II) An electrophilic reaction giving ring chlorinated products.



(iii) A process which produces starting para-substituted-N-tert-butylanilines.



Singlet Triplet

The unpublished data of P. Haberfield and D. Paul indicates that starting anilines can not be produced by an electrophilic mechanism. An electrophilic process would also produce comparable amounts of dichloroanilines. Dichloroanilines have not been reported as products by P. Gassman.

There is published evidence for the intermediacy of triplet nitrenium ions in the formation of unsubstituted amines.[7] P. Gassman has been able to catalize intersystem crossing between singlet and triplet states by the use of heavy atom solvents. The ratio of triplet to singlet product is 0.0885 in pure methanol and 45.9 in a 50:50 mixture of bromoform and methanol.

A free radical mechanism can also be used to explain the formation of secondary amines. It has been reported that the nitrous acid deamination of strained bridgehead amines results in products which can be explained in terms of free radical intermediates.[54] Formation of a bridgehead ion is unlikely in the above case. These workers envision radical formation as follows:

$$R{-}N{=}N{-}OH \xrightarrow{NOCl} R{-}N{=}N{-}ONO \longrightarrow R\cdot + N_2 + NO_2$$

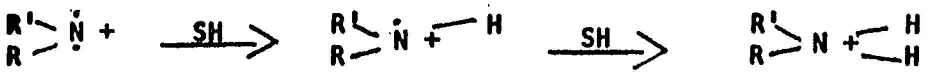
A similar mechanism could be proposed for the deamination of hydrazines. The driving force would be the formation of a more stable (compared to a nitrenium ion) intermediate.

Nitrogen radicals of the type expected in our reaction have been prepared by the thermolysis of tetrazenes.[55]

$$R_2N{-}N{=}N{-}NR_2 \longrightarrow 2\ R_2N\cdot + N_2$$

They give secondary amines as products but most of the products come from the coupling of two or more radicals. No products of this type were encountered in this study for reactions run in a nitrogen atmosphere. (compare results in experiment 36 to those in experiment 54). The absence of coupling products would seem to rule out nitrogen radicals such as: $R_2N\cdot$.

The following equation traces the path from triplet nitrenium ion to secondary amine:

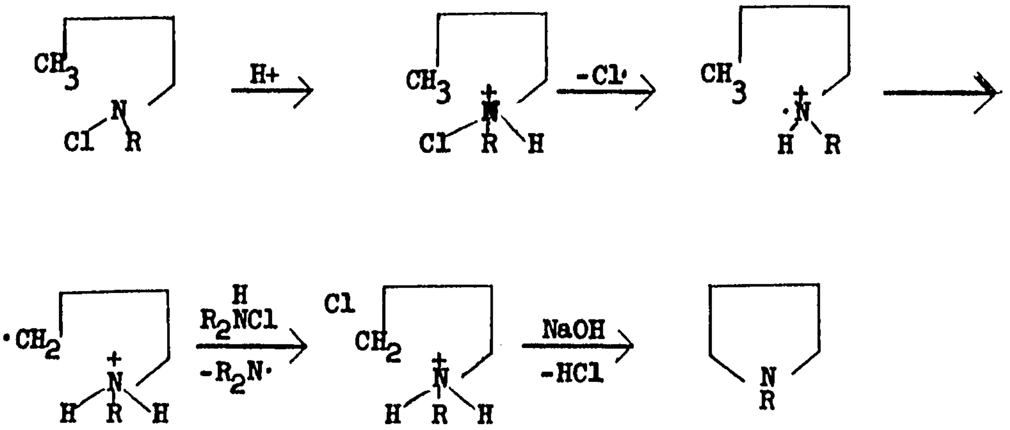


Triplet Nitrenium Ion

Aminium Ion

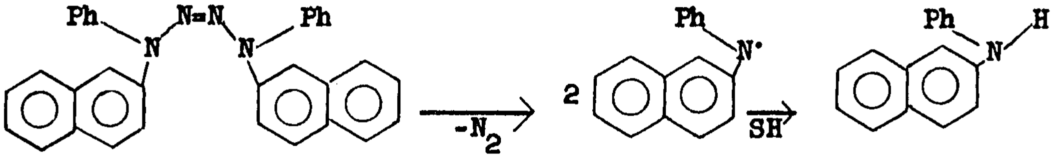
Product

As can be seen two different radical like species are involved in hydrogen atom abstraction. Evidence for the existence and chemistry of triplet nitrenium ion has been published by Gassman.[7] The aminium radical cation has been proposed as the intermediate in the Hoffman-Löffler reaction.[56] This reaction is a rearrangement in which N-chloro-aliphatic amines are cyclized to pyrrolidine derivatives in the presence of trifluoroacetic acid and sulfuric acid (preferred reaction conditions). A free radical mechanism has been proposed.[57, 58]



An experiment was designed to determine the extent of radical chemistry associated with a triplet nitrenium ion. The deamination of N-tert-butyl-N-phenylhydrazine was carried out in cumene. If the triplet nitrenium ion behaved in the same manner as a carbon free radical, it could abstract a hydrogen atom from cumene and give bicumyl. No bicumyl was found when the reaction was run in cumene (p 89). This result does not rule out a triplet nitrenium ion as an intermediate. It would only seem to indicate that a triplet nitrenium ion does not behave like a carbon radical.

This result is similar to results reported for some nitrogen free radicals. The thermal decomposition of N,N^1-diphenyl-N,N^1-di-2-napthyltetrazene gives nitrogen free radicals:[55]



In benzene there is a 5% yield of secondary amine resulting from hydrogen atom abstraction from solvent. In cumene a 6% yield of amine is obtained. There is no noticeable change even though cumene is much more readily oxidizable than benzene. In ethanol, a 9% yield of amine is obtained and in 1,4-cyclohexadiene, a 90% yield. R. Bridger concluded that the stereochemistry of the transferred hydrogen atom was the determing factor not the degree of activation. Similarly E. J. Cory has proposed two factors to explain the propensity of an aminium radical to intramolecular δ-hydrogen abstraction:[58]

(i) The tendency of the hydrogen transfer to be linear in the transition state, i.e., for the $\overset{+}{N}\cdots H\cdots C$ angle to be about 180°.

(ii) The minimization of angle strain and steric replusions involving non-bonded atoms in the transition state for rearrangement.

There is evidence in the literature that hydrogen atom transfers to nitrogen radicals and radical cations are sensitive to steric effects. Whether the triplet nitrenium ion (diradical cation) is sensitive to the steric environment of the transferred hydrogen is as yet unknown; however, this is not an unlikely possibility. The steric effect should be most evident for anilenium ions derived from 1,1-diphenylhydrazine and N-tert-N-phenylhydrazine. The steric requirements for these ions should be similar to that of the radicals obtained from the thermal decomposition of N,N'-diphenyl-N,N'-di-2-napthyltetrazene.

A problem in our work is to explain the source of hydrogen atoms abstracted by the radical like species, when the reactions are run in benzene or cumene. The reaction mixtures also contain acetic acid. In a solution containing benzene and acetic acid the N-diazonium ion would be expected to be solvated preferentially by acetic acid. The solvent cage would probably not be altered when the N-diazonium ion decomposes to give a nitrenium ion and nitrogen.

Cases have been reported in which the Hoffman-Löffler reaction was used in the attempted preparation of conanines (azasteriods) using a 5 N solution of sulfuric acid in acetic acid.[59] No product was isolated. Only starting amine was recovered. The data led to the conclusion that acetic acid itself might be chlorinated, i.e., it was serving as a source of hydrogen atoms. It would appear that at least in some instances the hydrogens in acetic acid have the proper steric requirements for successful hydrogen transfer to a radical cation.

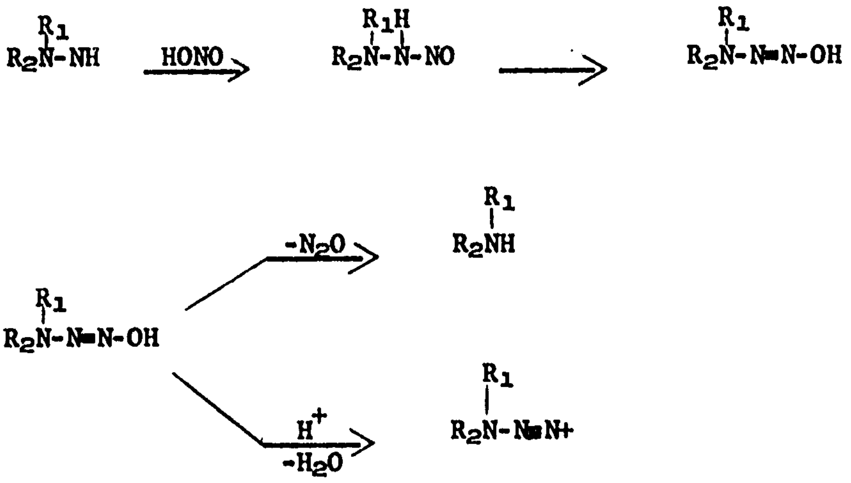
We feel that in a solution containing benzene and acetic acid, the latter is probably the source of hydrogen atoms. This would also explain why no bicumyl was observed when the reaction was run in cumene.

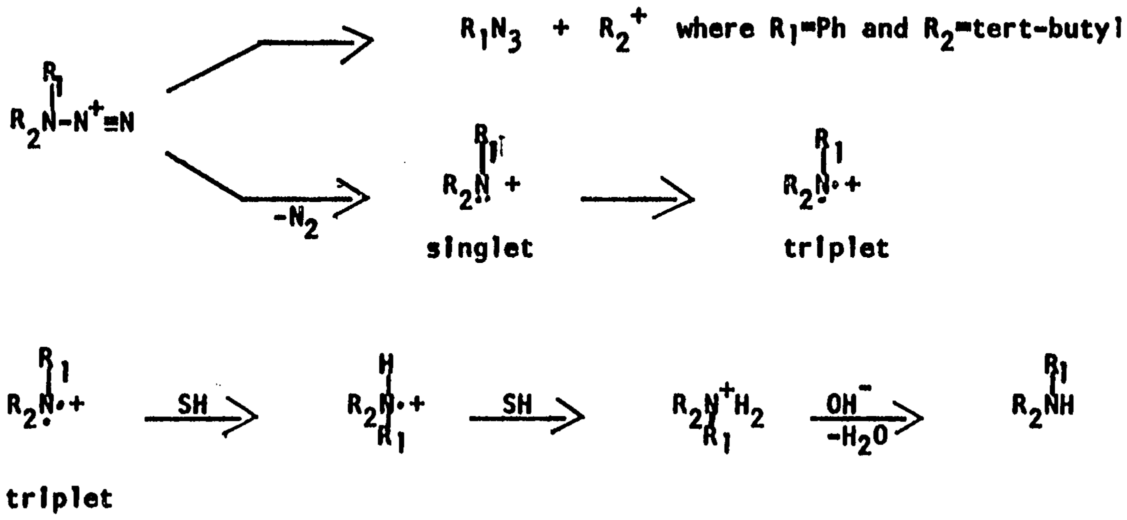
It is harder to dismiss the possiblity of hydride abstraction by a singlet nitrenium ion. Carbonium ions are known to abstract hydride ions and the rate increases as the life time of the carbonium ion decreases.[60] The carbonium ion also gives substitution products. It is difficult to picture a nitrenium ion which could abstract a hydride but not react with nucleophile.

We feel that the bulk of the experimental and literature data indicate that a triplet nitrenium ion is responsible for the formation of secondary amine. It is possible, but much less likely, that hydride abstraction leads to the formation of some of the amine.

9. Conclusion

We propose the following scheme to explain our results:





To support this scheme, we report the following experimental observations:

(I) Nitrous oxide has been quantitatively trapped and identified. In all cases the yield of nitrous oxide is less than the yield of secondary amine. At least two pathways are responsible for formation of secondary amine, only one of which leads to nitrous oxide concurrently.

(II) Isolation of phenylazide and methyl-tert-butylether strongly indicates the formation of an N-diazonium ion in the deamination of N-tert-butyl-N-phenylhydrazine. The absence of phenylazide in the other cases is expected if the mechanism for its formation is correct.

(III) Within the limits set, no incoporation of solvent has taken place to give ring substituted products. This argues against the formation of delocalized nitrenium ions.

The only intermediate which appears to explain the formation of secondary amine satisfactorily is a triplet nitrenium ion. The evidence in the literature supports the belief that this type of intermediate gives unsubstituted products.

To conclude, this study has:

(i) Reported a cleavage reaction not previously reported. for 1,1-disubstituted hydrazines.

(ii) Found direct evidence for an N-diazonium ion.

(iii) Described some of the properties of a non-delocalized singlet nitrenium ion--a species which appears to have a very short life time.

(iv) Proposed a mechanism for the nitrous acid deamination of 1,1-disubstituted hydrazines.

EXPERIMENTAL

1. Instruments

Infrared spectra were taken on a Perkin Elmer 236 spectrometer, nmr spectra on a Varian A60-P spectrometer and HA-100 spectrometer and mass spectra on a Varian M66 spectrograph. Quantitative analysis of reaction mixtures was done on a Hewlett Packard 5750 gas chromatograph and a Varian 1520 Autoprep gas chromatograph. The Varian Autoprep was also used for preparative purposes.

2. Purification of Solvents

Methanol (Fisher Spectronalized), benzene (Fisher Spectronalized), and anhydrous ether were used without further purification. Anhydrous tetrahydrofuran was obtained by distilling Baker reagent grade tetrahydrofuran from lithium aluminium hydride under a btabketblanket of nitrogen.[61] Cumene (Eastman yellow label) was purified by washing with small portions of concentrated sulfuric acid until the washings were colorless to light yellow. The cumene was washed with two 100-ml portions of water, 100 ml of 10% sodium bicarbonate, 100 ml of water, dried over anhydrous potassium carbonate, filtered and distilled from lithium aluminium hydride under a static blanket of nitrogen, bp 151°, lit.[62] bp 151-52°.

3. Purification of Anilines

N-Methylaniline was obtained from Aldrich. Prior to use it was distilled from zinc dust, bp 60-61° (3.5 mm), lit.[63] bp 81-82° (14 mm). Diphenylamine was obtained from Baker (reagent grade) and used without further treatment, mp 52°, lit.[64] mp 53°.

Similarly carbazole was commerically available and used withiut further purification, mp 243-46°, lit.[65] mp 246°.

4. Synthesis of N-tert-Butylaniline[66]

A 67.0 g (0.354 mol) sample of tert-butyl iodide was combined with 16.5 g (0.177 mol) of aniline (Baker reagent grade). The mixture was stirred for 12 hr. To the resulting solid mass there was added 200 ml of a concentrated sodium hydroxide solution. The basic mixture was extracted with three 250-ml portions of benzene. Benzene was removed under reduced pressure using a rotary evaporator. Analysis of the crude mixture by gas chromatography (using the relative peak areas of the two components) indicated the presence of ca. 40% starting aniline. To the crude mixture there was added 50 ml water and 20.0 ml (0.14 mol) of acetic anhydride. The mixture was stirred for 15 min, basified with sodium carbonate and product isolated by steam distillation. Vacuum distillation gave a 12.1 g (46%) yield of N-tert-butylaniline, bp 30° (0.2 mm), lit.[66] bp 97° (19 mm); nmr ($CDCL_3$) δ 1.33 (s,9), 3.23 (s,1), 6.73 (m,5); ir (neat) 3410, 3060, 2980, 750, 695 cm^{-1}.

5. Synthesis of tert-Butyl Iodide[67]

A 100.0 g (1.35 mol) sample of tert-butyl alcohol (Baker reagent grade) was combined with 907.2 g (4.00 mol) of 48-50% hydroiodic acid.

The solution was refluxed for 2 hr. The layers were separated and the tert-butyl iodide was washed twice with an equal volume of cold concentrated hydrochloric acid and dried over sodium carbonate. A 87.0 g (32%) yield was obtained. The iodide was used without further purification.

6. Synthesis of N-Nitroso-N-Methylaniline[63]

A 35.03 g (0.328 mol) sample of freshly distilled N-methylaniline was added to 48.0 ml (0.58 mol) of concentrated hydrochloric acid and 100 g of ice water was added to the mixture. To the cooled mixture, there was added a solution containing 22.6 g (0.328 mol) of sodium nitrite in 10000 ml of water. Addition took 15 min. The reaction mixture was extracted with 200 ml of benzene. The benzene phase was distilled under reduced pressure to give a 41.96 g (94%) yield of N-nitroso-N-methylaniline, bp 83°,(1.3 mm), lit.[63] bp 133-35°(13 mm); nmr ($CDCl_3$) δ 3.45,(s,3), 7.50 (m,5); ir (neat) 3020, 2960, 1600, 820, 760, 690 cm^{-1}.

7. Synthesis of N-Nitroso-N-tert-Butylaniline[66]

A 12.1 g (0.0812 mol) sample of N-tert-butylaniline was combined with 8.0 ml (0.096 mol) of concentrated hydrochloric acid and 50 ml water. The solution was cooled to 0° in an ice-salt bath. To the cooled solution there was added, in a 5 min period, a solution of 5.61 g (0.0812 mol) of sodium nitrite in 50 ml of water. The mixture was stirred for 30 min and then filtered. The product was washed with water, air dried and left overnight in a desiccator containing phospherous pentoxide. There was obtained a 11.25 g (79%) yield of N-nitroso-N-tert-butylaniline, mp 59-60°, lit.[66] mp 60-61°.

8. Synthesis of N-Nitroso-1,1-Diphenylamine[68]

To a 17.0 g (0.10 mol) sample of 1,1-diphenylamine in 100 ml of boiling ethanol, there was added 38.0 ml (0.46 mol) of concentrated hydrochloric acid. This mixture was cooled to -5° in an ice-salt bath. To the cooled mixture, with vigorous stirring, was added 6.9 g (0.10 mol) of sodium nitrite in 40 ml of water. Addition took 30 min. The crude product was isolated by filtration and recrystallized from petroleum ether to give a yield of 16.7 g (83%) of N-nitroso-1,1-diphenylamine, mp 60-61°, lit.[68] mp 61°.

9. Synthesis of N-Nitrosocarbazole[65]

A 17.0 g (0.10 mol) sample of carbazole was dissolved in 250 ml of glacial acetic acid. The solution was quickly cooled and gave a precipitate of very fine white crystals of carbazole. To this stirred mixture there was added 12.0 g (0.15 mol) sodium nitrite in 100 ml of water. The mixture was cooled in an ice-salt bath, stirred for 2 hr and 200 ml of water added. The product was transferred to a Büchner funnel, washed with water and sucked dry to give a 15.5 g (81%) yield of N-nitrosocarbazole, mp 80-82°, lit.[65] mp 82°.

10. Synthesis of N-Methyl-N-Phenylhydrazine[63]

To 85.0 g (1.30 g atoms) of zinc dust there was added 100 ml water and sufficient ice to lower the temperature to 10-20°. To the stirred mixture there was added, over a 30 min period, a solution containing 41.96 g (0.309 mol) of N-nitroso-N-methylaniline in 80.0 ml (1.38 mol) of glacial acetic acid. Temperature during addition was kept between 10-20° by the addition of ice. The reaction was stirred for an additional hour. The mixture was heated to 80° on a steam bath and filtered hot. The zinc residue was washed with three 50-ml portions of warm 6 N hydrochloric acid. The filtrate was cooled and solid sodium hydroxide pellets added until all the zinc hydroxide initially precipitated dissolved. The mixture was extracted with three 200-ml portions of benzene. The benzene was removed by evaporative distillation and the residue was distilled under reduced pressure to give a yield of 14.02 g (40%) of N-methyl-N-phenylhydrazine, bp 55-57° (0.35 mm), lit.[63] bp 106-09° (13 mm); nmr ($CDCl_3$) δ 300 (s,9), 3.52 (s,2), 6.99 (m,5); ir (neat) 3420, 3025, 2950, 760, 690 cm^{-1}.

11. N-tert-Butyl-N-Phenylhydrazine: Method A

A 4.0 g (0.023 mol) sample of N-nitroso-N-tert-butylaniline in 100 ml of anhydrous tetrahydrofuran was added slowly to 200 ml of gently refluxing tetrahydrofuran containg 1.7 g (0.045 mol) of lithium aluminium hydride (98+%, Alpha Inorganics). The reaction mixture was refluxed for 16 hr. Tetrahydrofuran was partially removed by evaporative distillation and excess lithium aluminium hydride destroyed by the careful addition of water. The reaction mixture was filtered and the solid residue washed with benzene. The benzene phase was removed by evaporative distillation and the residue was distilled to give a 2.1 g (62%) yield of N-tert-butyl-N-phenylhydrazine, bp 91-93° (5.0 mm), lit.[69] bp 47-48° (0.3 mm); nmr δ 1.12 (s,9), 134 (s,2), 7.10 (s,5); ir (neat) 3325, 3050, 2960, 770, 700 cm^{-1}.

12. Synthesis of N-tert-Butyl-N-Phenylhydrazine: Method B

In 500 ml of water there was combined 216.0 (2.0 mol) of phenylhydrazine (Baker reagent grade), 106.0 g (1.0 mol) of sodium carbonate and 116.0 g (1.0 mol) of tert-butyl bromide (Aldrich). The reaction mixture was stirred for 5 days at room temperature. Material boiling below 100° was distilled off. The residue was extracted with three 200-ml portions of benzene. The benzene was removed by evaporative distillation and the residue was distilled to give a 6.92 g (4%) yield of N-tert-butyl-N-phenylhydrazine, bp 91-93° (5.0 mm). Spectral properties were identical to those of material obtained by method A.

13. Synthesis of 1,1-Diphenylhydrazine[68]

A 20.0 g (0.10 mol) sample of N-nitroso-diphenylamine was combined with 32.0 g (0.5 g atoms) of zinc dust and 100 ml of absolute ethanol (Rossville Gold Shield). The mixture was cooled in an ice-salt bath. To the cooled mixture there was added 83.0 g (1.40 mol) of glacial acetic acid over a 2 hr period. During the addition of solid the reaction mixture was stirred vigorously and the temperature kept at 0-5°. The reaction mixture was filtered and the filtrate diluted with an equal volume of water. The aqueous solution was cooled and 500 ml of concentrated hydrochloric acid added giving blue white needles of 1,1-diphenylhydrazine hydrochloride. The salt was filtered, basified with 30% sodium hydroxide solution and extracted with three 150-ml portions of benzene. The benzene was removed by evaporative distillation and the residue was distilled to give a 9.2 g (50%) yield of 1,1-diphenylhydrazine, bp 121-23° (0.5 mm), lit.[68] bp 220° (40-50 mm); ir (neat) 3320, 3090, 1600, 760, 700 cm^{-1}.

14. Synthesis of 9-Aminocarbazole[65]

A 10.09 g (0.051 mol) sample of N-nitrosocarbazole was dissolved in 115 ml of ether (previously saturated with water) and 25.0 ml (0.44 mol) of glacial acetic acid added. The solution was cooled in an ice-water bath and 40.0 g (0.62 g atoms) of zinc dust added to the vigorously stirred solution. The reaction mixture was stirred for 1 hr, filtered and the zinc residue washed with ether. Filtrate and ether washings were combined, stirred with 60 g sodium carbonate, filtered and dried with calcium chloride. To the ethereal solution 50 ml of concentrated hydrochloric acid was added and 6.4 g of the hydrochloride salt was isolated by filtration. The salt was dissolved in the minimum amount of ethanol and the calculated amount (2.0 ml) of concentrated ammonium hydroxide added. The solution was cooled and the product precipitated out. The crude product was transferred to a Büchner funnel, sucked dry and recrystallized from ethanol to give a 5.4 g (50%) yield of 9-aminocarbazole, mp 150°, lit.[65] mp 151° (dec); ir (KBr) 3430, 3025, 1600, 750, 700 cm^{-1}.

15. Nitrosobenzene[70]

A mixture of 100.0 ml (0.68 mol) of nitrobenzene (Baker reagent grade) and a solution of 60.0 g (1.12 mol) of ammonium chloride in 2 ℓ of water in a 5 ℓ 3-necked flask was stirred vigorously, and 149.0 g (2.20 g atoms) of zinc dust was added in small portions over 5 min periods. After the addition of zinc was completed the temperature rose. When the temperature reached 60-65° enough ice was added to lower the temperature to 50-55°. Stirring was continued for 20 min after the addition of zinc. The solution was filtered and the zinc oxide residues were washed with 1 ℓ of boiling water. The filtrate and washings (containing phenylhydroxylamine) are combined in a 8 ℓ battery jar and quickly cooled to -2-0° by the addition of ice. Enough ice was added to leave approximately 500 g of ice unmelted.

To this cooled and vigorously stirred suspension there was added a solution of 300 ml concentrated sulfuric acid and sufficient ice to lower the tempprature to -5°. An ice-cold solution of 68.0 g (0.23 mol) of sodium dichromate dihydrate in 300 ml of water was added as quickly as possible into the stirred mixture. After 2-3 min the yellow precipitate of nitrosobenzene was collected on a Büchner funnel and washed with 1 ℓ of water.

The reaction sequence was repeated and the crude nitrosobenzene from both reactions was combined and steam distilled. The distillate was collected in a receiver cooled by ice. The product obtained was transferred to a Büchner Funnel and washed with water until the filtrate was no longer brown. Product was sucked as dry as possible and then pressed between layers of filter paper. The crude nitrosobenzene was finely ground in a mortar and recrystallized from a small amount of ethanol (with good cooling) to give a 109.0 g (75%) yield of pure nitrosobenzene, mp 64-66°, lit.[70] mp 64-67°.

16. N-tert-Butyl-N-Phenylhydroxylamine[48]

A mixture of 200 ml of absolute ether and 18.4 g (0.79 g atoms) of magnesium turnings in a 2 ℓ 3-necked flask was stirred vigorously and

10 ml of a solution of 86.0 ml (0.76 mol) of 2-bromo-2-methylpropane in 200 ml of absolute ether was added. The mixture was stirred vigorously until reaction begins (5-10 min) and the balance of the ethereal solution was added at such a rate as to maintain a gentle reflux of ether. Stirring was continued for an additional 30 min after all the alkyl halide had been added.

To the stirred solution of tert-butyl magnesium bromide there was added a solution of 36.0 g (0.34 mol) of nitrosobenzene in 500 ml of absolute ether. The ethereal solution was added as such a rate as to maintain a gentle reflux of ether. The reaction mixture was stirred overnight and then cooled in an ice-water bath and an ice-water mixture was added to the reaction mixture. Sufficient ice-water was added so that the magnesium hydroxide forms a thick paste and a clear ether solution was obtained. The layers were separated and the aqueous fraction was extracted twice with 200-ml portions of ether. The combined ether fractions were dried over calcium chloride, filtered and reduced in volume under reduced pressure. The concentrated ethereal solution was cooled in an ice-water bath and extracted three times with 15-ml portions of ice-cold 1 N hydrochloric acid solution. The aqueous layer was quickly basified with a 50% sodium hydroxide solution and then extracted with three 200-ml portions of ether. The combined ether extracts were dried over calcium chloride, filtered and concentrated under reduced pressure to give a solid residue of crude hydroxylamine. Crude product was transferred to a sublimator and sublimed at 50° and 0.05 mm. The sublimed material was collected, transferred to a Buchner funnel, washed with a small amount of petroleum ether (cooled to -72° in a dry-ice-2-

propanol bath) and sucked dry to give 1.1 g (2%) of pure N-tert-butyl-N-phenylhydroxylamine, mp 115-17°, lit.[71] mp 115-17°.

17. N-tert-Butyl-p-Anisidine[21]

A mixture of 12.5 g (0.084 mol) of p-anisidine hydrochloride and 25 ml of tert-butyl alcohol was sealed in a steel bomb and heated for 24 hr. The bomb was cooled to -72° in a dry-ice-2-propanol bath and opened. The reaction mixture was dissolved in 250 ml of water, made basic with aqueous ammonium hydroxide solution and extracted with three 200-ml protions of ether. Ether extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to leave a red oil. To the oil there was then added a solution of 5 g of acetic anhydride in 75 ml of water and stirred for 3 hr. Excess sodium bicarbonate was added, and the mixture was steam distilled until the distillate was neutral to lithmus paper.

The distillate was extracted with three 100-ml portions of ether. The ethereal extracts were combined, dried over anhydrous magnesium sulfate, fractionally distilled to give a 3.2 g (21%) yield of pure N-tert-butyl-p-anisidine, bp 59° (0.09 mm), lit.[21] bp 54-56° (0.05 mm); nmr ($CDCl_3$) 1.52 (s,9), 3.25 (s,1), 4.00 (s,3), 7.05 (s,5).

18. O-Acetyl-N-tert-Butyl-N-Phenylhydroxylamine[49]

A mixture of 2.07 g (10.0 mmol) of N-tert-butyl-N-phenylhydroxylamine, 0.83 ml (10.2 mmol) of pyridine and 25 ml of absolute ether was cooled in an ice-water bath and a similarly cooled solution of 0.72 ml (10.1 mmol) of acetyl chloride in 25 ml of absolute ether added to it. The reaction was kept at 0° for 48 hr. The reaction mixture was washed with two 50-ml portions of ice-cold 1 N hydrochloric acid solution and two 50-ml portions of ice-cold 10% sodium hydroxide solution. The acidic aqueous solution was basified with 10% sodium hydroxide solution and starting hydroxylamine precipitated out. This material was collected on a Büchner funnel, washed with water and sucked dry to give 0.41 g (20%) of recovered starting material.

The ethereal solution was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to a dark oil. The oil was recrystallized by adding five times its volume of petroleum ether, cooled in an dry-ice-2-propanol bath, filtered, washed with cold petroleum ether, cooled to -72°and sucked dry to give 0.89 g (54%) yield of pure O-acetyl compound, mp 35-37°; nmr ($CDCl_3$) δ 8.77 (s,9), 7.90 (s,3), 2.68 (s-broad, 5); ir (neat) 2960, 1790, 800, 695 cm^{-1}.

19. Attempted Synthesis of O-Methyl-tert-Butyl-N-Phenylhydroxylamine[72]

A mixture of 1.04 g (6.4 mmol) of N-tert-butyl-N-phenyhydroxylamine, 75 ml of ethanol and 75 ml of 20% sodium hydroxide solution was cooled and 1.40 ml (15.0 mmol) of dimethyl sulfate (Eastman practical grade) was added. The heterogenous mixture was stirred and heated at 37°for 24 hr. The reaction mixture was diluted with 500 ml water and extracted with three 100-ml portions of ether. The combined extracts were washed twice with an equal volume of water, dried over anhydrous sodium carbonate, filtered and concentrated under reduced pressure to give 0.77 g (81%) of a red oil whose nmr and ir spectra were identical to that of authentic

N-tert-butylaniline.

20. O-Methyl-N-tert-Butyl-N-Phenylhydroxylamine

A 0.0756 g (0.63 mmol) sample of potassium hydride (33% oil dispersion) was placed in a sintered glass funnel and washed with two 50-ml portions of dry hexane, sucked dry under an atmosphere of dry nitrogen, transferred with 50 ml of dry methyl sulfoxide into a flask and 0.0981 g (0.55 mmol) of N-tert-butyl-N-phenylhydroxylamine added. To this oil free solution there was added 0.17 ml (1.02 mmol) of dimethyl sulfate. Upon addition of dimethyl sulfate, the reaction mixture turned red. The mixture was let stand at room temperature for 30 min, then diluted with 500 ml water and extracted with three 100-ml portions of ether. The combined ethereal extracts were extracted twice with 50-ml portions of ice-cold 1 N hydrochloric acid solution, twice with equal volumes of water, dried over anhydrous sodium carbonate, filtered and concentrated under reduced pressure to give a red oil. The red oil was purified by molecular distillation at 0.10 mm and 20° to give 0.0357 g (36%) of a red liquid containg O-methyl-N-tert-butyl-N-phenylhydroxylamine, nmr ($CDCl_3$) δ 8.88 (s,9), 6.55 (s,3), 2.73 (s-broad, 5); ir (neat) 2970, 1205, 770, 700 cm^{-1}.

The nmr spectrum of this liquid indicated the presence of several unidentified minor components. The ratio of aromatic to methoxy protons was 47:25. The expected ratio is 47:28 (5:3) and the purity is equal to $\frac{25}{28}$ X 100 = 90%.

21. Synthesis of Bicumyl

A mixture of 100 ml of purified cumene and 6.0 g (0.041 mol) of di-tert-butylperoxide was heated at reflux for 18 hr. The bulk of the cumene and tert-butanol was distilled off at atmospheric pressure. The residue was cooled in an ice-water bath and 10 ml of ethanol added. The addition of ethanol precipitated out the product. Product was collected on a Büchner funnel, washed with cold ethanol and sucked dry. A 5.5 g (57% based on peroxide used) yield of bicumyl was obtained, mp 113-14°, lit.[73] mp 115°.

22. Synthesis of Methyl tert-Butylether[74]

In a 500 ml 3-necked flask equiped with an addition funnel, a fraction cutter and a thermometer, there was combined 100 ml of water, 10 ml of concentrated sulfuric acid and 30.0 ml (0.74 mol) of methanol. The mixture was heated to 70° and 35.0 ml (0.37 mol) of tert-butyl alcohol added in 5 ml portions over a 30 min period. The temperature of the reaction vessel was kept at <u>ca.</u> 70° so that only the ether distilled off (49-50°). The product was slowly collected in this manner over a 3 hr period. The product was washed ten times with 10-ml portions of water. The organic phase was dried over sodium carbonate and distilled to give a 3.63 g (6%) yield of methyl tert-butylether, bp 54-56°, lit.[74] bp 55°; nmr ($CDCl_3$) δ 1.15 (s,9), 3.22 (s,3); mass spectrum m/e (relative intensity) 87(2), 74(2), 73(40), 59(4), 58(1), 57(25), 56(4), 55(5), 45(15), 44(2), 43(48), 42(10), 41(100), 40(6), 39(35), 31(18). The parent peak (88) was of the same magnitude as the background noise.

23. Product Analysis by Gas Chromatography

The products obtained in the reactions of N-methyl-N-phenylhydrazine, N-tert-butyl-N-phenylhydrazine and 1,1-diphenylhydrazine with isoamylnitrite and acid were separated using a Varian 1520 Autoprep and a Hewlett Packard 5750. Product mixtures contained components of widely varying volatility. The resulting large differences in retention times made isothermal operation of the gas chromatograph impractical in the analysis of N-methyl-N-phenylhydrazine and N-tert-butyl-N-phenylhydrazine product mixtures. Sharp peaks and reasonable retention times were obtained using temperature programming.

The 1,1-diphenylhydrazine system was analyzed using a solid support consisting of 5% by weight potassium hydroxide on chromosorb/W (HP), the liquid phase was 5% by weight carbowax 20 M.

The N-methyl-N-phenylhydrazine and N-tert-butyl-N-phenylhydrazine reaction mixtures were analyzed on 5'X¼" aluminium column packed with 20% SE-30 on Diataport S. Suitable conditions were not found to effect a successful gas chromatographic separation of the compounds obtained from the deamination of 9-aminocarbazole. Solid supports and liquid phases were obtained from Varian Aerograph.

The quantitative determination of each component was made by the method of internal standards. The analyses were carried out in the following manner:

A calibration mixture containing a known weight of standard (naphthalene or chlorobenzene) and each of the expected components was prepared in 1.00 ml of benzene. The calibration mixture was analyzed under the same conditions as the reaction mixture. An intergration constant (Kx) was determined for each component in the mixture using the following formula:

$$\frac{Ax}{As} = K\left(\frac{Wx}{Ws}\right)$$

Where Ax was the area of the peak of compound x in the calibration mixture, As the area of the internal standard peak, Wx the weight of the compound x in the calibration mixture and Ws the weight of the internal standard in the calibration mixture. Several calibration mixtures were prepared and an average intergration constant (Kx) obtained.

A known amount of standard was added to a previously worked up reaction mixture. The mixture was chromatographed and the weight of each component obtained by solving for Wx in the formula previously given. Yields were obtained from the weight.

24. Conditions for Gas Chromatographic Analysis of Reaction Mixtures

A. N-Methyl-N-Phenylhydrazine Reaction Series

Analyzed using a 5'x1/4" aluminium column packed with 20% SE-30 on Diataport S using the following instrument parameters:

Injection port temperature 200°, carrier flow 60 cc/min, column temperature (Programming) initial temperature 110° held 3 min, and then raised 10°/min until column reached 150° and held there.

B. N-tert-Butyl-N-Phenylhydrazine Reaction Series

Analyzed using same column as methyl series. Also injection port and flow conditions identical. Column temperature (Programming) held at 110° for 3 min then raised 10°/min until column reached 160° and held there.

C. 1,1-Diphenylhydrazine Reaction Series

Analyzed on a 6'X¼" aluminium column packed with 5% carbowax 20 M and 5% potassium hydroxide on chromosorb/W (HP) using the following conditions:

Injection port 250°, carrier gas flow 100 cc/min and column (isothermal) at 190°.

Table X

Relative Retention Times[a] Obtained in a Typical Gas Chromatographic Analysis:

N-tert-Butyl-N-Phenylhydrazine Reaction Series

Compound	Retention Time (min)	Peak Width at Half Height (min)
Chlorobenzene[b]	1.57	0.27
Phenylazide	3.73	0.54
N-tert-Butylaniline	5.68	0.40
N-tert-Butyl-N-Phenylhydrazine	7.36	0.62
Other[c]		

a. Relative to air.

b. Internal standard.

c. Unknown small peaks at 8.47, 9.95 and 11.04.

Table XI

Analytical Data Obtained in a Typical
Gas Chromatographic Analysis:
N-tert-Butyl-N-Phenylhydrazine Reaction Series

1) Calibration Mixture

Compound	Weight of Sample (g)	Area Ratio $\left(\frac{Ax}{As}\right)^a$	Weight Ratio $\left(\frac{Ws}{Wx}\right)^b$	Intergration Constant K^c
Chlorobenzene	0.0436	------	------	------
Phenylazide	0.0438	1.18	0.995	1.17
N-tert-Butyl-aniline	1.0363	1.04	1.20	1.25
N-tert-Butyl-N-phenylhydrazine	0.0376	0.535	1.16	0.620

a. Ax = area of component
As = area of standard

b. Wx = weight of component
Ws = weight of standard

c. $K = \left(\frac{Ax}{As}\right)\left(\frac{Ws}{Wx}\right)$

Table XII

Analytical Data Obtained in a Typical
Gas Chromatographic Analysis
N-tert-Butyl-N-Phenylhydrazine in
Methanol/Acetic Acid/Lithium Acetate

2) Reaction Mixture

Compound	Area Ratio $\left(\frac{Ax}{As}\right)$	Weight of^a Component (mg) $Wx = \left(\frac{Ax}{As}\right)\left(\frac{Ws}{K}\right)$	Yield (%)^b
Phenylazide	0.140	5.9	5
N-tert-Butylaniline	0.644	25.6	19
N-tert-Butyl-N-Phenylhydrazine	1.04	85.4	57

a. Based on 49.3 mg of added internal standard (chlorobenzene).

b. Based on 149.9 mg (0.91 mmol) of starting hydrazine.

25. Isolation Procedures

The products obtained from reactions run in the same solvent were isolated in the same manner.

A. Benzene

At the conclusion of the reaction time the mixture was basified by the addition of 2 g of anhydrous sodium carbonate. The mixture was stirred over sodium carbonate for 30-60 min. The benzene phase was decanted and the sodium carbonate dissolved in a small amount of water and extracted with two 25-ml portions of benzene. The benzene fractions were combined and the volume reduced to approximately 5 ml by distillation on a steam bath using a 10 cm column packed with glass helices. The internal standard was added and the mixture analyzed by gas chromatography.

B. Methanol

The reaction mixture was basified as previously described. The methanol phase was decanted and the sodium carbonate was washed twice with small volumes (10-20 ml) of methanol. The methanol fractions were combined and 300 ml of water added. The aqueous solution was extracted five times with 50-ml portions of benzene. The benzene phase was washed twice with an equal volume of water and reduced in volume and analyzed by gas chromatography as previously described.

C. n-Butanol

Procedure was identical to that used for methanol.

These procedures were used for the methyl, tert-butyl and phenyl series which were analyzed by gas chromatography. The 9-aminocarbazole reaction series was analyzed by isolatingthe products. Isolation procedures were modified as described below.

D. 9-Aminocarbazole

Isolation procedures were identical to those described above except that the benzene solution containing the product mixtures was first dried by azeotropic distillation of water and then the volume reduced to 75 ml. HCl gas was slowly bubbled through the benzene solution for 300 sec where upon a white solid precipitated. The hydrochloric salt was dissolved in 50 ml of water. The benzene phase was separated and washed with 25 ml of water. The benzene phase containing neutral material was concentrated to dryness under reduced pressure using a rotary evaporator. The residue was transferred to a semi-micro sublimator and sublimed at 60° and 0.1 mm. Material was obtained whose melting point and infrared spectrum indicated it was carbazole.

The aqueous phase containing basic material was cooled in an ice-salt bath and basified with a concentrated sodium hydroxide solution and extracted with two 25-ml portions of benzene. The benzene was removed under reduced pressure to give a crystalline residue whose melting point and infrared spectrum indicated it was 9-aminocarbazole.

Table XIII

Results Obtained in a Typical Isolation
Procedure: 9-Aminocarbazole in
Benzene/Acetic Acid/Lithium Acetate

Compound	Weight (mg)	Yield (%)[a]	mp (°)
Carbazole	56.1	36	242-45
9-Aminocarbazole	79.8	50	148-50

a. Based on 161.2 mg (0.88 mmol) of starting hydrazine

In subsequent descriptions the phrase "products isolated" will mean one of the procedures described in this section.

26. Proof of Structure

The products obtained in the deamination of N-methyl-N-phenylhydrazine, N-tert-butyl-N-phenylhydrazine and 1,1-diphenylhydrazine were isolated as follows:

> A deamination reaction run in methanol/HBF_4 was concentrated to a volume of ca. 0.5 ml by evaporating the excess benzene with a stream of dry nitrogen. The compounds were isolated using a Varian 1520 Autoprep. Infrared spectra were taken of the following trapped materials and compared to spectra of authentic materials:

N-Methylaniline
N-tert-Butylaniline
Diphenylamine
N-Methyl-N-Phenylhydrazine
N-tert-Butyl-N-Phenylhydrazine
1,1-Diphenylhydrazine
N-Nitroso-N-Methylaniline

in other solvents a peak with the same retention time as a sample of authentic material was assumed to be identical to the authentic sample.

The following were isolated as previously described and identified by their melting points and infrared spectra:

Carbazole
9-Aminocarbazole

A. Phenylazide[75]

It was first identified by its relative retention time. Phenylazide was unstable to high temperatures and decomposed on the vpc detector (300°). The peak with the same retention time as authentic phenylazide was collected and an infrared spectrum taken. The spectrum of the decomposed material was identical to that obtained from authentic phenylazide which had been injected and collected under identical conditions.

The reaction mixture obtained from the deamination of N-tert-butyl-N-phenylhydrazine in benzene was concentrated by rotary evaporation. A drop was put on a salt plate and any further traces of solvent were removed by evaporation. An infrared spectrum was taken of the residue. The spectrum contained a strong doublet at 2090 cm^{-1}. A peak in this region has been shown to be characteristic for azides.[76]

27. Nitrous Oxide: Isolation and Analysis

Authentic nitrous oxide was obtained from Matheson. Samples of gas were obtained by the displacement of water in a graduate cylinder whose bottom had been cut and replaced by a rubber septum. Samples were removed through the septum with a gas tight syringe.

The identification and analysis of nitrous oxide was done by infrared spectroscopy. Nitrous oxide has intense peaks at 1300 and 2250 cm^{-1}. These peaks were used for the quantitative determination of nitrous oxide. Nitrous oxide does not follow Beer's Law and calibration curves were needed (Fig 1 and 2). (Note: It was necessary every 6-8 weeks to plot new calibration curves.)[77]

Spectra were taken by injecting known volumes of nitrous oxide into a 10.0 cm gas cell which had been previously evacuated to less than 1.0 mm. The cell was brought to atmospheric pressure by syringing in air. Infrared spectra were taken of known volumes in this fashion and absorbance was plotted against volume.

A vacuum system was devised for the quantitative trapping of nitrous oxide (Fig 3). A 250 ml flask containing a magnetic stirring bar was connected to the vacuum line at male joint A with stop cock I closed. The line was evacuated to 1μ or better with a two stage mercury diffusion pump. Trap B was cooled in liquid nitrogen and the reaction flask in dry-ice-2-propanol. The reaction was slowly evacuated and condensible material was trapped in B. Stopcock I was closed and the reaction flask warmed up to room temperature with stirring. The flask was then cooled to -72° and evacuated. Freeze-thaw cycles were continued until the vacuum gauge showed little or no change when stopcock I was opened. Three cycles were usually necessary to get complete degassing. Condensible material was then in trap B. Trap B was warmed up to room temperature and brought back to atmospheric pressure by introducing air through a septum at socket C. The trap was equilibrated overnight. Gas was transferred from trap B to an evacuated (less than 1.0 mm) ir gas cell, connected to the trap at point C. The gas cell was brought to atmospheric pressure and a spectrum taken of the gaseous products.

From the known volumes of gas cell and trap it was possible to calculate what fraction of trapped gas was transferred to the ir cell. The volume of the gas cell was calculated to be 152 ml. Trap B was filled completely with water and its contents weighed. It had a volume of 194 ml. Hence % transfer was equal to:

$$\frac{152}{346} \times 100 = 44\%$$

It was necessary to gauge the trapping efficiency of the vacuum line. This was done as follows:

In a 250 ml flask there was put 50.00 ml of benzene and a magnetic stirring bar. The flask was covered with a septum and 5.00 ml of authentic nitrous oxide introduced through the septum with a 10 ml gas tight syringe. The solution was frozen in a dry-ice-2-propanol bath and the flask was attached to the vacuum line at point A. The partial vacuum in the flask prevents gas from escaping when the septum was removed prior to attachment at point A. The flask was degassed and an ir spectrum taken of the condensed material.

A. Sample Calculation: Trapping Efficiency in Benzene

Absorbance at 2250 cm^{-1} = 0.68

Volume from calibration curve = 1.9 ml

$$\text{Percent recovery} = \frac{1.9 \times 100}{(5.0)(0.44)} = 86\%$$

This was repeated and trapping efficiences of 80-90% obtained for benzene. Values for alcohols were 90-100% recovery. Reaction mixtures were degassed and analyzed in this manner.

B. Sample Calculation: Nitrous Oxide Obtained from the Deamination of N-tert-Butyl-N-Phenylhydrazine in Benzene/Acetic Acid/Lithium Acetate

Absorbance = 0.45

Volume from calibration curve = 0.65 ml

$$\text{Total volume} = \frac{0.65}{0.44} = 1.48 \text{ ml}$$

$$\text{Volume of 1.0 mmol of } N_2O \text{ at } 20^\circ C = \left(22.4\ \frac{\text{ml}}{\text{mmol}}\right)\left(\frac{298^\circ K}{273^\circ K}\right) = 24.4\ \frac{\text{ml}}{\text{mmol}}$$

$$\text{Volume for 100\% yield of } N_2O = \left(24.4\ \frac{\text{ml}}{\text{mmol}}\right)\left(0.93 \text{ mol}\right) = 22.7 \text{ ml}$$

$$\text{Percent Yield} = \frac{1.48}{22.7} \times 100 = 7\%$$

In the descriptions of reaction conditions the phrase "gaseous products collected and analyzed" will mean procedures described in this section have been followed.

28. Deamination of N-Methyl-N-Phenylhydrazine: Methanol/HBF_4

In a 250 ml flask there was combined 0.2191 g (1.79 mmol) of N-methyl-N-phenylhydrazine, 0.2421 g (1.96 mmol) of isoamylnitrite

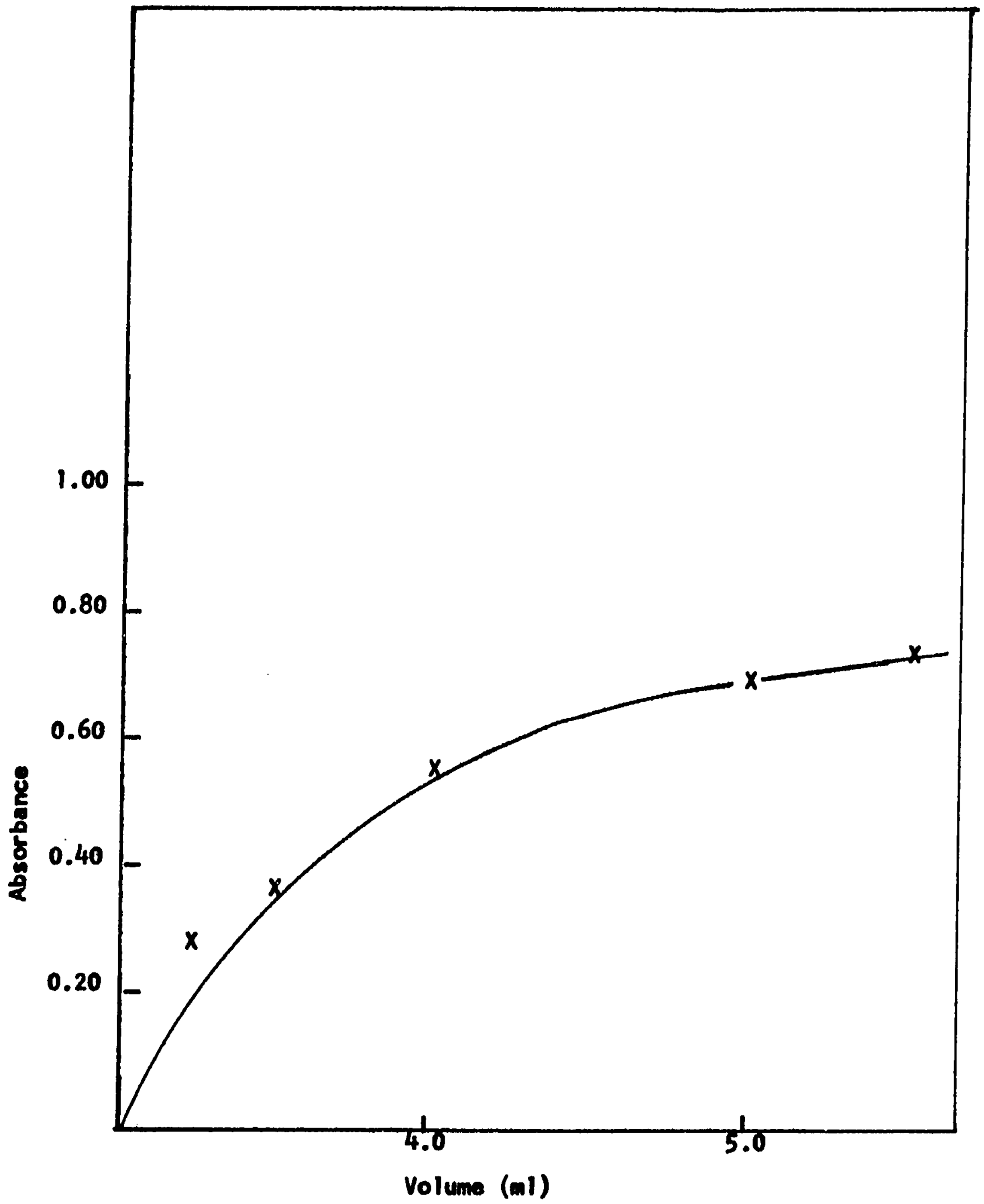


Figure 1

Absorbance of Nitrous Oxide at 2250 cm^{-1}

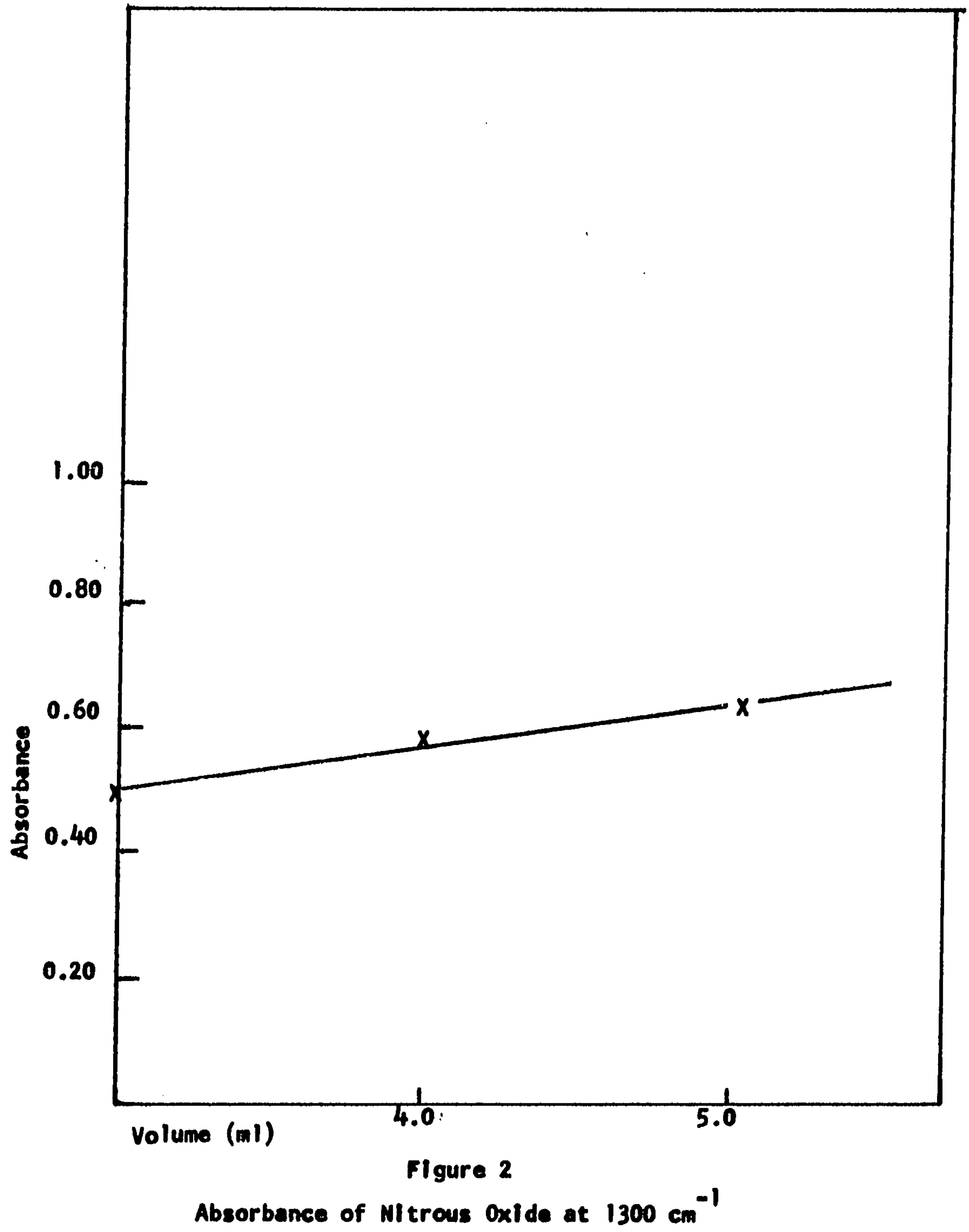
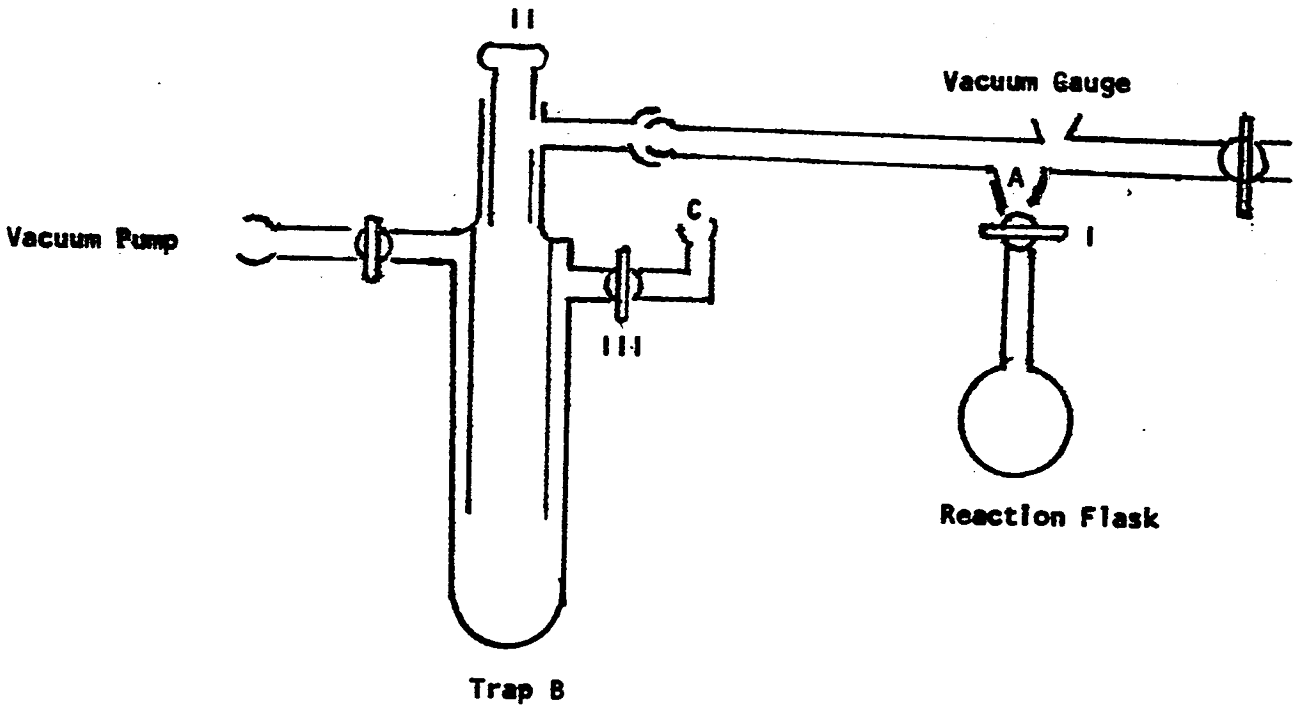


Figure 2

Absorbance of Nitrous Oxide at 1300 cm^{-1}

Figure 3

Trapping Apparatus for Nitrous Oxide



(Eastman yellow label - 95% minimum purity), 1.00 ml (12.0 mmol) of fluoroboric acid (50% - 12 M our analysis) and 50.00 ml of reagent grade methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and then heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate. Products isolated and analyzed by gas chromatography with the following results.

Table XIV

Product Yields for the Deamination of N-Methyl-N-Phenylhydrazine in Methanol/HBF_4

Compound	Yield (%)
Phenylazide	trace
N-Methylaniline	35
N-Methyl-N-phenylhydrazine	40
N-Nitroso-N-methylaniline	5
Nitrous Oxide	6

29. Deamination of N-Methyl-N-Phenylhydrazine: Methanol/Acetic Acid/ Lithium Acetate

In a 250 ml flask there was combined 0.2200 g (1.80 mmol) of N-methyl-N-phenylhydrazine, 0.241 g (1.97 mmol) of isoamylnitrite, 12.00 g of lithium acetate, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and then heated for

20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g anhydrous sodium carbonate; products isolated and analyzed by gas chromatography with the following results.

Table XV

Product Yields for Deamination of N-Methyl-N-Phenylhydrazine in Methanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
N-Methylaniline	20
N-Methyl-N-phenylhydrazine	51
N-Nitroso-N-methylaniline	10
Nitrous oxide	8

30. Deamination of N-Methyl-N-Phenylhydrazine: Benzene/Acetic Acid/ Lithium Acetate

In a 250 ml flask there was combined 0.2196 g (1.80 mmol) of N-methyl-N-phenylhydrazine, 0.2391 g (1.94 mmol) of isoamylnitrite, 0.20 g of lithium acetate, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of benzene. The solution was deaerated by bubbling dry nitrogen through it for 5 min. The solution was frozen in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The reaction mixture was heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate and products isolated and analyzed by gas chromatography with the following results.

Table XVI

Product Yields for Deamination of N-Methyl-N-Phenylhydrazine in Benzene/Acetic Acid/Lithium Acetate

Compound	Yield (%)
N-Methylaniline	50
N-Methyl-N-phenylhydrazine	41
N-Nitroso-N-methylaniline	3
Nitrous Oxide	9

31. Deamination of N-Methyl-N-Phenylhydrazine: n-Butanol/Acetic Acid/ Lithium Acetate

In a 250 ml flask there was combined 0.2187 g (1.80 mmol) of N-methyl-N-phenylhydrazine, 0.2407 g (1.96 mmol) of isoamlynitrite, 1.00 g of lithium acetate, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of n-butanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate; products isolated and then analyzed by gas chromatography with the following results.

Table XVII

Product Yields for Deamination of N-Methyl-N-Phenylhydrazine in n-Butanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
N-Methylaniline	22
N-Methyl-N-phenylhydrazine	50
N-Nitroso-N-methylaniline	12
Nitrous oxide	11

32. Deamination of N-tert-Butyl-N-Phenylhydrazine: Methanol/HBF_4

In a 250 ml flask there was combined 0.1500 g (0.91 mmol) of N-tert-butyl-N-phenylhydrazine, 0.1261 g (1.02 mmol) of isoamylnitrite, 0.50 ml (6.00 mmol) of fluoroboric acid and 25.00 ml of methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.50-1.0 mm and then heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate, products isolated and analyzed by gas chromatography with the following results.

Table XVIII

Product Yields for Deamination of N-tert-Butyl-N-Phenylhydrazine in Methanol/HBF_4

Compound	Yield (%)
Phenylazide	3
N-tert-Butylaniline	31
N-tert-Butyl-N-phenylhydrazine	60
Nitrous oxide	8

33. Deamination of N-tert-Butyl-N-Phenylhydrazine: Methanol/Acetic Acid/Lithium Acetate

In a 250 ml flask there was combined 0.1499 g (0.91 mmol) of N-tert-butyl-N-phenylhydrazine, 0.1238 g (1.01 mmol) of isoamylnitrite, 6.00 g of lithium acetate, 0.34 ml (6.0 mmol) of glacial acetic acid and 25.00 ml of methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.501.0 mm and then heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate; products isolated and analyzed by gas chromatography with the following results.

Table XIX

Product Yields for Deamination of
N-tert-Butyl-N-Phenylhydrazine in
Methanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Phenylazide	5
N-tert-Butylaniline	19
N-tert-Butyl-N-phenylhydrazine	57
Nitrous Oxide	9

34. Deamination of N-tert-Butyl-N-Phenylhydrazine: Benzene/Acetic Acid/Lithium Acetate

In a 250 ml flask there was combined 0.1523 g (0.93 mmol) of N-tert-butyl-N-phenylhydrazine, 0.1299 g (1.05 mmol) of isoamylnitrite, 0.20 g of lithium acetate, 0.34 ml (6.0 mmol) of glacial acetic acid and 25.00 ml of benzene. The solution was deaerated by bubbling dry nitrogen through it for 5 min. The solution was frozen in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The reaction mixture was heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of sodium carbonate. Products were isolated and anlyzed by gas chromatography with the following results.

Table XX

Product Yields for Deamination of N-tert-Butyl-N-Phenylhydrazine in Benzene/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Phenylazide	8
N-tert-Butylaniline	28
N-tert-Butyl-N-phenylhydrazine	51
Nitrous oxide	7

35. Deamination of N-tert-Butyl-N-Phenylhydrazine: n-Butanol/Acetic Acid/Lithium Acetate

In a 250 ml flask there was combined 0.1439 g (0.88 mmol) of N-tert-butyl-N-phenylhydrazine, 0.1204 g (0.98 mmol) of isoamylnitrite, 0.50 g of lithium acetate, 0.34 ml (6.0 mmol) of glacial acetic acid and 25.00 ml of n-butanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm.and heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate. Products were isolated and analyzed by gas chromatography with the following results.

Table XXI

Product Yields for Deamination of N-tert-Butyl-N-Phenylhydrazine in n-Butanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Phenylazide	7
N-tert-Butylaniline	27
N-tert-Butyl-N-phenylhydrazine	57
Nitrous oxide	9

36. Deamination of 1,1-Diphenylhydrazine: Methanol/HBF_4

In a 250 ml flask there was combined 0.3312 g (1.80 mmol) of 1,1-diphenylhydrazine, 0.2435 g (1.97 mmol) of isoamylnitrite, 1.00 ml (12.0 mmol) of fluoroboric acid and 50.00 ml of methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and then heated for 30 min at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate. Products were isolated and analyzed by gas chromatography with the following results.

Table XXII

Product Yields for Deamination of
1,1-Diphenylhydrazine in
Methanol/HBF_4

Compound	Yield (%)
Diphenylamine	53
1,1-Diphenylhydrazine	34
Nitrous oxide	13

37. Deamination of 1,1-Diphenylhydrazine: Methanol/Acetic Acid/ Lithium Acetate

In a 250 ml flask there was combined 0.3363 g (1.83 mmol) of 1,1-diphenylhydrazine, 0.2400 g (1.94 mmol) of isoamylnitrite, 12.00 g of lithium acetate, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through it for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and then heated for 4 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate. Products were isolated and analyzed by gas chromatography with the following results.

Table XXIII

Product Yields for Deamination of
1,1-Diphenylhydrazine in
Methanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Diphenylamine	33
1,1-Diphenylhydrazine	47
Nitrous oxide	7

38. Deamination of 1,1-Diphenylhydrazine: Benzene/Acetic Acid/Lithium Acetate

In a 250 ml flask there was combined 0.3359 g (1.83 mmol) of 1,1-diphenylhydrazine, 0.2430 g (1.89 mmol) of isoamylnitrite, 0.20 g of lithium acetate, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of benzene. The solution was deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was frozen in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The reaction mixture was heated for 4 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of sodium carbonate. Products were isolated and analyzed by gas chromatography with the following results.

Table XXIV

Product Yields for Deamination of
1,1-Diphenylhydrazine in
Benzene/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Diphenylamine	28
1,1-Diphenylhydrazine	68
Nitrous oxide	12

39. Deamination of 1,1-Diphenylhydrazine: n-Butanol/Acetic Acid/Lithium Acetate

In a 250 ml flask there was comined 0.3382 g (1.84 mmol) of 1,1-diphenylhydrazine, 0.2409 g (1.98 mmol) of isoamylnitrite, 1.00 g of lithium acetate, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of n-butanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and heated for 4 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate. Products were isolated and analyzed by gas chromatography with the following results.

Table XXV

Product Yields for Deamination of
1,1-Diphenylhydrazine in
n-Butanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Diphenylamine	34
1,1-Diphenylhydrazine	52
Nitrous oxide	10

40. Deamination of 9-Aminocarbazole: Methanol/HBF_4

In a 250 ml flask there was combined 0.1644 g (0.90 mmol) of 9-aminocarbazole, 0.1230 g (1.05 mmol) of isoamylnitrite, 0.50 ml (6.0 mmol) of fluoroboric acid and 25.00 ml of methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and then heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate and products were isolated with the following results.

Table XXVI

Product Yields for Deamination of
9-Aminocarbazole in
Methanol/HBF_4

Compound	Yield (%)
Carbazole	27
9-Aminocarbazole	58
Nitrous oxide	6

41. Deamination of 9-Aminocarbazole: Methanol/Acetic Acid/Lithium Acetate

In a 250 ml flask there was combined 0.1622 g (0.89 mmol) of 9-aminocarbazole, 0.1219 g (0.99 mmol) of isoamylnitrite, 6.00 g of lithium acetate, 0.34 ml (6.0 mmol) of glacial acetic acid and 25.00 ml of methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and then heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate. Products were isolated with the following results.

Table XXVII

Product Yields for Deamination of
9-Aminocarbazole in
Methanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Carbazole	25
9-Aminocarbazole	52
Nitrous oxide	7

42. Deamination of 9-Aminocarbazole: Benzene/Acetic Acid/Lithium Acetate

In a 250 ml flask there was combined 0.1612 g (0.88 mmol) of 9-aminocarbazole, 0.1242 g (1.00 mmol) of isoamylnitrite, 0.20 g of lithium acetate, 0.34 ml (6.0 mmol) of glacial acetic acid and 25.00 ml of benzene. The solution was deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was frozen in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The reaction mixture was heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate and the products were isolated with the following results.

Table XXVIII

Product Yields for Deamination of
9-Aminocarbazole in
Benzene/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Carbazole	36
9-Aminocarbazole	50
Nitrous oxide	22

43. Deamination of 9-Aminocarbazole: n-Butanol/Acetic Acid/ Lithium Acetate

In a 250 ml flask there was combined 0.1627 g (0.90 mmol) of 9-aminocarbazole, 0.1251 g (1.01 mmol) of isoamylnitrite, 0.50 g of lithium acetate, 0.34 ml (6.0 mmol) of glacial acetic acid and 25.00 ml of n-butanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through the solution for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and heated for 20 hr at 50±2° in an oil bath. Gaseous products were collected and analyzed. The reaction mixture was basified with 2 g of anhydrous sodium carbonate and the products were isolated with the following results.

Table XXIX

Product Yields for Deamination of
9-Aminocarbazole in
n-Butanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Carbazole	27
9-Aminocarbazole	64
Nitrous oxide	10

44. Attempted Solvolysis of O-Acetyl-N-tert-Butyl-N-Phenylhydroxylamine: Methanol

A mixture of 0.0936 g (0.45 mmol) of O-acetyl-N-tert-butyl-N-phenylhydroxylamine, 1.75 g of lithium acetate, 0.17 ml (3.00 mmol) of acetic acid and 12.5 ml of methanol (reagent grade) was deaerated by bubbling dry nitrogen through it for 5 min. The solution was cooled in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The evacuated flask was heated for 20 hr at 50±2°. The mixture was cooled to room temperature, basified with 10% sodium hydroxide solution, diluted with 250 ml of water and extracted with three 100-ml portions of benzene. The combined benzene extracts were dried over anhydrous sodium carbonate, filtered and reduced in volume by evaporative distillation (on a steam bath using a 10 cm column packed with glass helices). Any benzene remaining in the residue was evaporated using a stream of dry nitrogen gas. There was obtained 0.0909 g (97% recovery) of a yellow residue whose nmr and ir spectra showed it to be pure starting O-acetyl compound.

45. Attempted Solvolysis of O-Acetyl-N-tert-Butyl-N-Phenylhydroxylamine: Benzene

A mixture of 0.0929 g (0.45 mmol) of O-acetyl-N-tert-butyl-N-phenylhydroxylamine, 0.0250 g of lithium acetate, 0.17 ml (3.00 mmol) of acetic acid and 12.5 ml of benzene was deaerated by bubbling dry nitrogen gas through it for 5 min. The solution was frozen in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The evacuated flask was heated for 20 hr at 50±2°. The mixture was cooled to room temperature, basified with 10% sodium hydroxide solution and the benzene layer separated. The aqueous fraction was extracted twice with 25-ml portions of benzene. The combined benzene fractions were dried over anhydrous sodium carbonate, filtered and reduced in volume by evaporative distillation (on a steam bath using a 10 cm column packed with glass helices). Any benzene remaining in the residue was evaporated under a stream of dry nitrogen. There was obtained 0.0889 g (96% recovery) of a yellow residue whose nmr and ir spectra showed it to be pure starting O-acetyl compound.

46. Solvolysis of O-Methyl-N-tert-Butyl-N-Phenylhydroxylamine: Methanol

A mixture of 0.1153 g (0.66 mmol) of O-methyl-N-tert-butyl-N-phenylhydroxylamine, 0.50 g lithium acetate, 0.26 ml (4.60 mmol) of acetic acid and 20.00 ml of methanol was deaerated by bubbling dry nitrogen through it for 5 min. The solution was cooled in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The evacuated flask was heated for 20 hr at 50±2°. The mixture was cooled to room temperature and basified with 10% sodium hydroxide, diluted with 250 ml of water and extracted with three 100-ml portions of benzene. The combined benzene extracts were dried over anhydrous sodium carbonate, filtered and reduced in volume by evaporative distillation (on a steam bath using a 10 cm column packed with glass helices). Any benzene remaining in the residue was evaporated under a stream of dry nitrogen. The residue was diluted with deuterochloroform (1% v/v TMS) and examined by nmr spectroscopy.

The nmr spectrum of starting material contained peaks corresponding to aromatic and methoxy protons in a ratio of 30:19 or 5:3 respectively. A broad singlet was obtained in the aliphatic region but its integral (81) was larger than expected from a single tert-butyl group. From its integral the material appeared to be ca. 70% pure, with the impurity being non-basic and neutral. The impurity appears to be an oil which was not completely washed out with the pentane.

The nmr spectrum of the product showed an increase in the ratio of aromatic to methoxy protons from the value of 30:19 (5:3) for starting material to 23:11 (5:2.4). This indicated a disappearance of 21% of starting material. The expected ratio was 23:14 (5:3) so that the loss of methoxy equals $\frac{14-11}{14} \times 100 = 21\%$. The stability of this compound may be greater than indicated. Small traces of unremoved benzene would lead to an increase in the ratio of aromatic to methoxy protons.

The deuterochloroform solution containing the product mixture was diluted with 100 ml benzene and extracted with two 50-ml portions of ice-cold 1 N hydrochloric acid solution. The benzene fraction containing the neutral products was dried over sodium carbonate, filtered, reduced in volume under reduced pressure, diluted with deuterochloroform and its nmr spectrum taken. The nmr of the neutral material has a value of 5:3.5 for the ratio of aromatic to methoxy protons. The aqueous fraction was basified with 10% sodium hydroxide solution and extracted with two 50-ml portions of benzene. The combined benzene extracts were dried over anhydrous sodium carbonate, filtered and reduced in volume under reduced pressure. The benzene free residue was diluted with deuterochloroform and its nmr spectrum taken. The spectrum of basic material had no peaks indicative of the presence of methoxy protons and hence no N-tert-butyl-*p*-anisidine was formed in the reaction. The bulk of the material appeared to be N-tert-butylaniline.

The spectra of both neutral and basic fractions indicated the formation of small quantities of other unidentified products.

47. Detection Limits of Gas Chromatography

Standard solutions were prepared (as described below) and analyzed by gas chromatography on a 5'X¼" aluminium column packed with 20% SE-30 on Diataport S (80-100 mesh) using temperature programming (initial temperature of 110° for three min and then raised 10°/min until 160° reached and kept there until analysis was completed).

A. N-tert-Butyl-p-Anisidine

A solution containing 0.0166 g (0.093 mmol) of N-tert-butyl-p-anisidine, 0.0535 g of chlorobenzene and 5.00 ml of benzene was prepared and 10 μl of solution analyzed by gas chromatography with the following results.

Table XXX

Compound	Retention Time (min)	Attenuation Factor	Peak Height (cm)	Width at Half Height (cm)	Area (cm^2)
Chlorobenzene	1.56	4	11.8	0.40	18.9
N-tert-Butyl-p-anisidine	11.00	1	5.2	1.05	5.25

Reactions were run using 1.8 mmol hydrazine. A 1% yield of any product would be 0.018 mmol. The N-tert-butyl-p-anisidine contains the equivalent of 5% yield. A 1% yield would give a peak of 1.0 cm and could be easily detected. A peak as small as 0.5 cm can be detected.

B. O-Acetyl-N-tert-Butyl-N-Phenylhydroxylamine

A solution containg 0.0174 g (0.085 mmol) of O-acetyl-N-tert-butyl-N-phenylhydroxylamine, 0.0531 g of chlorobenzene and 5.00 ml of benzene was prepared and 10 μl of solution analyzed by gas chromatography with the following resutls.

Table XXXI

Compound	Retention Time (min)	Attenuation Factor	Peak Height (cm)	Width at Half Height (cm)	Area (cm^2)
Chlorobenzene	1.56	4	11.5	0.40	18.9
O-Acetyl-N-tert-butyl-N-phenylhydroxylamine	11.70	1	1.4	2.90	1.26

In the case of O-acetyl compound extensive decomposition was observed as evidence by the higher area ratio of chlorobenzene to O-acetyl compound when compared to that of the anisidine.

Using a peak height of 0.5 cm as the minium detectable vpc peak, only 2-3% of the O-acetyl compound can be detected under the same conditions as 1% of the anisidine. To observe a 1% yield of O-acetyl compound an injection of 20-30 μl would be required.

C. O-Methyl-N-tert-Butyl-N-Phenylhydroxylamine

A sample of O-methyl-N-tert-butyl-N-phenylhydroxylamine, dissolved in benzene, decomposes when analyzed under conditions identical to those used for N-tert-butyl-p-anisidine and the O-acetyl compound. The chromatogram shows four major peaks plus several minor components. This indicates extensive decomposition at the temperatures utilized for gas chromatographic analysis.

48. Detection Limits of Nuclear Magnetic Resonance Spectroscopy

A. Methoxy Group

A solution containing 0.0045 g of N-tert-butyl-p-anisidine in 1.00 ml of deuterochloroform (1% v/v TMS) was prepared. The spectrum of the solution was taken using a Varian Instrument T-60 Nuclear Magnetic Spectrograph. The following results were obtained.

Table XXXII

Spectrum Amplitude	Peak Height (cm)
50	2.7
100	5.1
160	8.8
200	10.4
250	12.8

The standard solution corresponds to a 1.5% yield of methoxy containing compound. The above table indicates that as little as one-fifth of this amount could be detected.

49. Detection of Minor Products

A. Benzene

A previously analyzed reaction mixture obtained from the reaction of N-tert-butyl-N-phenylhydrazine with isoamylnitrite/acetic acid in the presence of benzene and added acetate ion, was rechromatographed under the same conditions as the standard containing O-acetyl-N-tert-butyl-N-phenylhydroxylamine. The chromatogram revealed no peak whose retention time matched that of the authentic O-acetyl compound. From this it can be concluded that within the limits of detectability previously established, no O-acetyl compound was formed in this reaction.

B. Methanol

A previously analyzed reaction mixture obtained from the reaction of N-tert-butyl-N-phenylhydrazine with isoamylnitrite/acetic acid in the presence of methanol and added acetate ion, was rechromatographed employing the same experimental conditions as the standard solution containing O-acetyl-N-tert-butyl-N-phenylhydroxylamine and N-tert-butyl-p-anisidine. The chromatogram revealed no peaks whose retention time was identical to that of either known compound.

A stream of dry nitrogen was used to remove the benzene in which the reaction products were dissolved. The benzene free residue was diluted with 1.00 ml of deuterochloroform (1% V/v TMS) and an nmr spectrum taken using instrument settings identical to that employed for the standard solution of N-tert-butyl-p-anisidine. The nmr spectrum revealed a small broad peak with a chemical shift in the same region as the methoxy group of the anisidine. From its broad shape, it appeared to be that of N-H protons present in the reaction mixture. A few crystals of trichloroacetic acid were added to the deuterochloroform solution and the spectrum retaken. The broad peak previously described had disappeared and a small multiplet was found in this region. The peak heights (1.3 cm) indicated very little (less than 1%) of a compound which could contain a methoxy group.

C. Butanol

A previously analyzed reaction mixture obtained from the reaction on N-tert-butyl-N-phenylhydrazine with isoamylnitrite/acetic acid, in the presence of butanol and added ion, was rechromatographed under the same conditions as the standard containing 0-acetyl-N-tert-butyl-N-phenylhydroxylamine. The chromatogram revealed no peak whose retention time matched that of the authentic 0-acetyl compound. From this it can be concluded that within the limits of detectability previously established, no 0-acetyl compound was formed in this reaction.

The following table summarizes the gas chromagraphic data obtained from the above reactions.

Table XXIII

Detection of Minor Products
Gas Chromatographic Data

Benzene Compound	Retention Time (min)
Chlorobenzene	1.56
Phenylazide	3.65
N-tert-Butylaniline	5.40
N-tert-Butyl-N-phenylhydrazine	7.02
Unknown	9.40
Unknown	10.71
O-Acetyl-N-tert-butyl-N-phenylhydroxylamine	11.70

Methanol Compound	Retention Time (min)
Chlorobenzene	1.57
Phenylazide	3.73
N-tert-Butylaniline	5.68
N-tert-Butyl-N-phenylhydrazine	7.36
Unknown	8.47
Unknown	9.95
Unknown	11.04
N-tert-Butyl-p-anisidine	11.42[a]
O-Acetyl-N-tert-butyl-N-phenylhydroxylamine	11.96[b]

a. Separate injection
b. Separate injcetion

Table XXIII (cont)

n-Butanol Compound	Retention Time (min)
Chlorobenzene	1.52
Phenylazide	3.65
N-tert-Butylaniline	5.36
N-tert-Butyl-N-phenylhydrazine	7.00
Unknown	9.12
Unknown	10.71
O-Acetyl-N-tert-butyl-N-phenylhydroxylamine	11.70
Unknown	12.40

50. Bicumyl Recovery Control

A mixture containing 50.00 ml of cumene and 0.1113 g of bicumyl was prepared. The cumene was distilled off leaving a residue of 1-2 ml. The residue was tranferredcto a vial and the distillation flask was washed with 2-3 ml of benzene. The benzene and cumene fractions were combined and 0.1021 g of chlorobenzene added (internal standard). The distillation residue was analyzed by gas chromatography using a 5'X$\frac{1}{4}$'' aluminium column packed with 20% SE-30 on Diataport S and using temperature programming (initial temperature of 120° held for 3 min and then raised 50°/min until 190°reached and held there). A 95% recovery of bicumyl was effected.

51. Deamination of N-Methyl-N-Phenylhydrazine in Cumene/Acetic Acid

A. Reaction Conditions

In a 250 ml flask there was combined 0.2184 g (1.78 mmol) of N-methyl-N-phenylhydrazine, 0.2359 g (1.93 mmol) of isoamylnitrite, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of cumene. The solution was deaerated by bubbling dry nitrogen through it for 5 min.

The mixture was frozen in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The heterogenous mixture was stirred and heated for 20 hr at 50±2°. The solution was cooled and extracted three times with 50-ml portions of 10% sodium hydroxide solution. The cumene phase was extracted with three 50-ml portions of 1 N hydrochloric acid. The organic fraction, containing neutral material, was washed with an equal volume of water, dried over anhydrous sodium carbonate and distilled. The residue was analyzed by gas chromatography for bicumyl. The aqueous phase, containing basic products, was basified with 10% sodium hydroxide solution and extracted with three 50-ml portions of benzene. The benzene phase was dried over sodium carbonate and concentrated by evaporative distillation. The residue was analyzed by gas chromatography.

Table XXXIV

Product Yields for Deamination of
N-Methyl-N-Phenylhydrazine in
Cumene/Acetic Acid

Compound	Yield (%)
N-Methylaniline	21
N-Methyl-N-phenylhydrazine	68
Bicumyl	0

B. Cumene Control

In a 250 ml flask there was combined 0.2318 g (1.88 mmol) of isoamylnitrite, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of cumene. The control reaction was carried out, products isolated and analyzed in a manner identical to the previous reaction. No trace of bicumyl was detected in the control reaction.

52. Deamination of N-Methyl-N-Phenylhydrazine in Cumene/Benzene/Acetic Acid

A. Reaction Conditions

In a 250 ml flask there was combined 0.2297 g (1.87 mmol) of N-methyl-N-phenylhydrazine, 0.2540 g (2.06 mmol) of isoamylnitrite, 0.68 ml (12.0 mmol) of glacial acetic acid, 10.00 ml of benzene and 40.00 ml of cumene. The solution was deaerated by bubbling dry nitrogen through it for 5 min. The mixture was frozen in a dry-ice-2-propanol bath and evacuated to a pressure of 0.5-1.0 mm. The homogenous solution was heated for 20 hr at 50±2°. The products were isolated and analyzed in the same manner as the previous reaction in pure cumene.

Table XXXV

Product Yields for Deamination of
N-Methyl-N-Phenylhydrazine in
Cumene/Benzene/Acetic Acid

Compound	Yield (%)
N-Methylaniline	42
N-Methyl-N-phenylhydrazine	47
Bicumyl	0

B. Cumene/Benzene Control

In a 250 ml flask there was combined 0.2511 g (2.03 mmol) of isoamylnitrite, 0.68 ml (12.0 mmol) of glacial acetic acid, 10.00 ml of benzene and 40.00 ml of cumene. The control was carried out, products isolated and analyzed in the same manner as the deamination reaction in the same solvent mixture. A trace (less than 1%) of bicumyl was detected in the control reaction.

53. Isolation and Identification of Methyl tert-Butyl Ether from the Deamination of N-tert-Butyl-N-Phenylhydrazine: Methanol/Acetic Acid/Lithium Acetate

A. Reaction Conditons

In a 250 ml flask there was combined 0.3035 g (1.85 mmol) of N-tert-butyl-N-phenylhydrazine, 0.2436 g (1.98 mmol) of isoamylnitrite, 12.00 g lithium acetate, 0.68 ml (12.0 mmol) of glacial acetic acid and 50.00 ml of methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through it for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and then heated for 20 hr at 50±2° in an oil bath. The reaction mixture was basified with 2 g of anhydrous sodium carbonate and analyzed for methyl tert-butyl ether. The nitrogenous products were isolated and analyzed by gas chromatography.

Table XXXVI

Product Yields for Deamination of
N-tert-Butyl-N-Phenylhydrazine in
Methanol/Acetic Acid/Lithium Acetate

Compound	Yield (%)
Methyl tert-Butyl Ether	6
Phenylazide	5
N-tert-Butylaniline	19
N-tert-Butyl-N-phenylhydrazine	61

B. Gas Chromatographic Analysis of Methyl tert-Butyl Ether

The yield of ether could not be readily determined using the method of internal standards. A calibration curve (Fig 4) was used to obtain the yield of ether from the peak height. The calibration curve was obtained by dissolving a known amount of ether in 100.00 ml of methanol and plotting weight of ether versus height obtained when 50 μl of solution was injected.

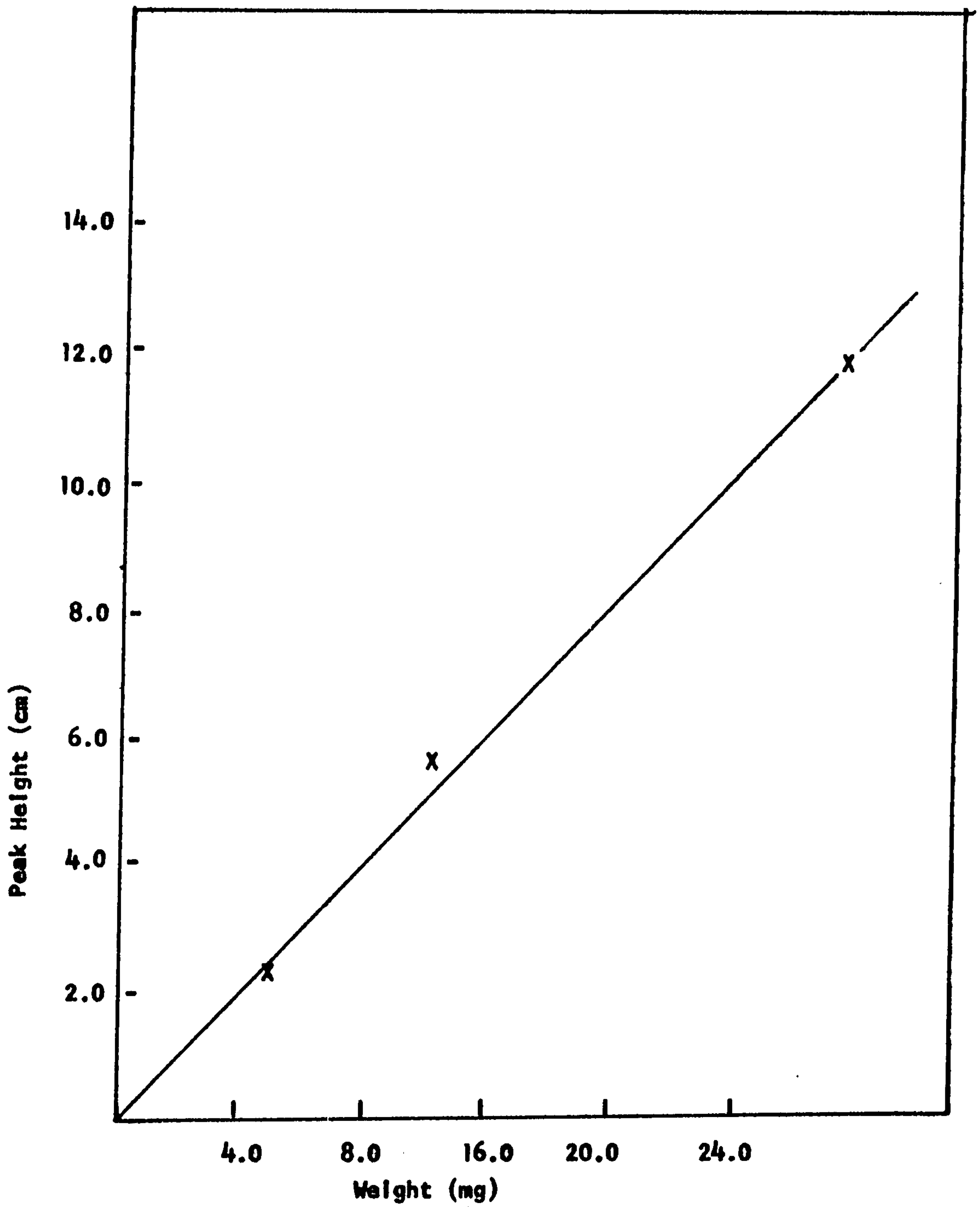


Figure 4

Calibration Curve for the Gas Chromatographic Determination of Methyl tert-Butyl Ether

The yield of ether, in a reaction, was obtained by injecting 50μl of the basified reaction mixture; this was done prior to the isolation procedures described in section 25. The weight of ether was read off the calibration curve. (The reaction was run in 50.00 ml of methanol and peak heights were obtained using anaattenuation factor of two.)

C. Structure Proof of Methyl tert-Butyl Ether

The basified methanol solution was distilled and 1-2 ml collected in a cooled flask. The material was analyzed on a Varian Aerograph 2700 series gas chromatograph connected to a Varian CH7 mass spectrometer. A 5'X1/8" column packed with 5% carbowax 20 M and 5% KOH on chromosorb P was used with the column temperature at 65°, the injection port at 95° and the flow at 20 ml/min. The methanol solution contained two components:

> A major component with a retention time of 50 sec and a minor component at 80 sec. The major component had the same retention time and mass spectrum as an authentic sample of methyl tert-butyl ether. There was not enough of the minor component to analyze in the mass spectrograph.

D. Methyl tert-Butyl Ether Reaction Control

In a 250 ml flask there was combined 0.0167 g (0.19 mmol) of methyl tert-butyl ether, 24.00 g of lithium acetate, 1.36 ml (24.00 mmol) of glacial acetic acid and 100.00 ml methanol. The solution was cooled in a dry-ice-2-propanol bath and deaerated by bubbling dry nitrogen through it for 5 min. The solution was evacuated to a pressure of 0.5-1.0 mm and then heated for 20 hr at 50±2° in an oil bath. The reaction was basified with

4 g of anhydrous sodium carbonate and analyzed for recovered ether. A 93% recovery of methyl tert-butyl ether was effected.

54. Deamination of 1,1-Diphenylhydrazine: Methanol/HBF$_4$ In Air

In a 250 ml flask there was combined 0.6549 g (3.56 mmol) of 1,1-diphenylhydrazine, 2.00 ml (24.0 mmol) of fluoroboric acid, 0.4422 g (3.59 mmol) of isoamylnitrite and 100.00 ml of methanol. The solution was heated for 15 min at 50±2° in an oil bath. The reaction mixture was basified with 4 g of anhydrous sodium carbonate. The products were isolated and analyzed by gas chromatography with the following results.

Table XXXVII

Product Yields for Deamination of 1,1-Diphenylhydrazine in Methanol/HBF$_4$ In Air

Compound	Yield (%)
Phenylazide	1
Diphenylamine	60
1,1-Diphenylhydrazine	7
N,N^1,N^1-Triphenyl-phenylenediamine[a]	21

a. This compound was isolated by preparative gas chromatography and identified on the basis of the following spectral data:

nmr (100 Mh$_z$/CDCl$_3$) 5.28 (s,1), 6.90 (m,19)

ir 3400, 1600, 1500, 855 cm^{-1}

mass spectrum m/e (relative intensity) 336(5), 260(1), 245(15), 244(4), 182(52), 167(100)

There is some uncertainty as to whether the compound isolated is the *ortho*-or *para*-phenylenediamine derivative.

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