Master's Theses

Graduate College

6-1962

Attempts in the Synthesis of T-Alkylhydrazines

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ATTEMPTS IN THE SYNTHESIS OF t-ALKYLHYDRAZINES

A Thesis
Presented to
The Faculty of the School of Graduate Studies
Western Michigan University

In partial fulfillment
of the requirement for
the degree of Master of Arts
in Chemistry

by
Richard A. Evans
Kalamazoo, Michigan
June 1962

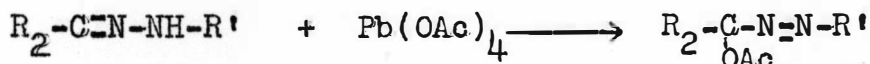## TABLE OF CONTENTS

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to his research director, Dr. Don C. Iffland, for his patience and very helpful guidance towards the organization of this problem.
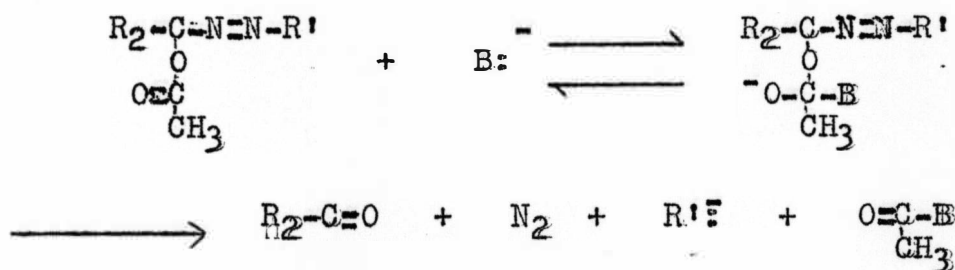
Acknowledgment is also given to the members of his committee for helpful suggestions and the National Science Foundation for financial assistance rendered on this project.

INTRODUCTION

Interest in t-alkylhydrazines has developed from the recent preparation of azoacetates (5) by the leadtetra-acetate oxidation of hydrazones:

$$R_2\text{-C=N-NH-R'} \quad + \quad Pb(OAc)_4 \longrightarrow R_2\text{-}\underset{\underset{OAc}{|}}{C}\text{-N=N-R'}$$

Of principle interest has been the base catalyzed decomposition of azoacetates in a protonic solvent to give a ketone, a hydrocarbon, nitrogen and an acetate salt. The following process has been proposed to account for these products.

$$R_2\text{-}\underset{\underset{\overset{|}{O=C}}{|}}{\underset{\overset{|}{O}}{C}}\text{-N=N-R'} \quad + \quad B: \quad \underset{\longleftarrow}{\overset{-}{\longrightarrow}} \quad R_2\text{-}\underset{\overset{|}{O}}{C}\text{-N=N-R'}$$

$$\underset{CH_3}{} \qquad\qquad \overset{-}{O}\text{-}\underset{\underset{CH_3}{|}}{C}\text{-B}$$

$$\longrightarrow \quad R_2\text{-C=O} \quad + \quad N_2 \quad + \quad R'\bar{:} \quad + \quad O=\underset{\underset{CH_3}{|}}{C}\text{-B}$$

$$R'\bar{:} \quad + \quad HB(\text{solvent}) \longrightarrow R'\text{-H} \quad + \quad B\bar{:}$$

It is anticipated that if the reaction were conducted in a non-protonic medium, reactions of the carbanion intermediate might be investigated. Furthermore, if the nitrogen atom is bonded to the group R' at an asymmetric carbon atom, an opportunity may be afforded to study the stereochemistry of carbanions. Determination of the stereochemical properties of the resultant R'-H will provide information pertinent to the configurational stability of the intermediate anion.

In order to examine the stereochemistry of carbanions derived from azoacetates, the need for hydrazines having the general structure $R^1-R^2-R^3C-NH-NH_2$ was recognized. After resolution via formation of diastereoisomeric salts, the optically active hydrazines would be converted to azoacetates and in turn into the hydrocarbon $R^1-R^2-R^3-CH$.

Previous studies (6) of the stereochemistry of carbanions have usually produced intermediates which might reasonably develop planar configuration through resonance participation stabilizing the ion. In these cases, only racemic reaction products were observed. In a recent report (2), either maintainance of asymmetry or racemization of carbanions depending upon the reaction medium has been indicated; however the reaction used to develop the carbanions and the carbanion structures was not as simple as that possible in the method proposed above. The approach to the study of stereochemistry of carbanions from azo-acetates will permit the formation of species free of resonance or strain interactions. The following is a description of attempts toward the synthesis of t-alkyl-hydrazines and discussion of limitations of the methods considered.
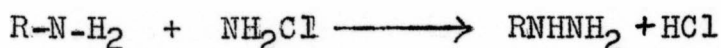
LITERATURE SURVEY

At the beginning of this study a search in <u>Chemical</u> <u>Abstracts</u> and Beilstein's <u>Handbuch der Organischen Chemie</u> revealed synthesis of only one simple t-alkylhydrazine, t-butylhydrazine (11). Current literature describes the preparation of t-butylhydrazine (1) and cumylhydrazine (7). The literature was also examined for methods of preparation of primary and secondary alkylhydrazines with the thought that such methods might be adapted to the synthesis of the desired t-alkylhydrazines.

The preparations of alkylhydrazines having possibility for application to the synthesis of t-alkylhydrazines may be classified into the following general procedures:

1. Alkylation of hydrazine (11)

$$NH_2N-H_2 + R-Cl \longrightarrow R-NHNH_2 + HCl$$

2. Amination of amines with chloramine (1)

$$R-N-H_2 + NH_2Cl \longrightarrow RNHNH_2 + HCl$$

3. Amination of amines with hydroxylamine-O-sulfonic acid (3)

$$R-NH_2 + NH_2-O-SO_3H + 2KOH \longrightarrow R-NHNH_2 + K_2SO_4 + 2H_2O$$

4. Acid or base hydrolysis of hydrazones (7) (8) (10)

$$R'_2C=N-NH-R + H_2O \longrightarrow R'_2C=O + H_2NNH-R$$

The alkylation of hydrazine with t-butyl chloride has been described by Westphal (11) with a 10-11 % yield reported. The method produces better yeilds with primary and secondary alkyl halides. The application of this procedure to the synthesis of t-heptylhydrazine was examined by Salisbury (9) who found the reaction produced exclusively heptenes.

Evidently, hydrazine reacted more effectively promoting elimination rather than the desired substitution.

The preparation of alkylhydrazines by reaction of primary amines with chloramine has been reviewed by Audrieth (1). The preparation of t-butylhydrazine in 72% yield and higher yields for primary and secondary alkylhydrazines is described. Salisbury investigated the application of Audrieth's procedure to the preparation of t-heptylhydrazine. In addition to difficulties in the preparation and handling of large amounts of chloramine, the yield of desired t-alkyl-hydrazine was negligible.

Smith (10) has described the synthesis of t-butyl-hydrazine through hydrochloric acid hydrolysis of benzo-phenone t-butylhydrazone. Synthesis of the parent hydra-zone from diphenyldiazomethane was also described and is reasonably convenient.

Gever and Hayes (3) have reported synthesis of primary and secondary alkylhydrazines in 10-60 % yields via the reaction of hydroxylamine-O-sulfonic acid (H-O-S) with primary and secondary alkyl amines. This procedure appears adaptable to the synthesis of tertiary alkylhydrazines.

Overberger (7) has described the synthesis of hydrazones via the reaction of Grignard reagents with azines and the subsequent hydrolysis of these hydrazones with oxalic acid to give the hydrazine oxalate salts. Although all of his syntheses involved addition of an aromatic Grignard reagent to azines, the procedure seemed applicable to the synthesis

of aliphatic hydrazones.

An evaluation of the limitations associated with these procedures in attempted syntheses of t-alkylhydrazines is described in the discussion section.

<center>EXPERIMENTAL</center>

Preparation of t-Alkylhydrazones

Benzophenone t-butylhydrazone was prepared in 71% yield according to the method described by Smith (10) by adding t-butyl magnesium chloride to diphenyldiazomethane. The t-heptyl homolog, a yellow, viscous liquid, was also obtained 74% yield via the same method; b.p. 194-196 @ 5 mm., n_D^{25} 1.5732. Analysis Calcd. for $C_{20}H_{26}N_2$: N, 9.52. Found: N, 9.50.

The necessary t-heptylchloride and its precursor, t-heptyl alcohol were prepared following the procedure developed by Salisbury (9).

The α-methyl-α-isobutylbenzylhydrazone of 4-methyl-2-pentanone was prepared in 32% yield by the method described by Overberger (7) by adding methylisobutylketazine to phenyl magnesium bromide.

Preparation of t-Butylhydrazine

The first attempts at acid catalyzed hydrolysis of t-alkylhydrazones duplicated the method presented by Smith. In this way, 50.4 g. (0.2 m.) of benzophenone t-butylhydrazone was dissolved in 150 ml. of chloroform, mixed with 27 ml. of conc. 36% hydrochloric acid and the two-phase system was stirred overnight at room temperature. During this time white crystals of t-butylhydrazine hydrochloride developed in the aqueous phase. After separation, the crystals weighed 9.8 g. (39%) and melted at 192°. Smith reported a 60% yield, m.p. 189°.

Preparation of t-Heptylhydrazine

A.   Substituting 0.2 m. of benzophenone t-heptylhydrazone
in the hydrochloric acid hydrolysis procedure failed to
yield crystalline t-heptylhydrazine hydrochloride.
Treatment of the aqueous phase with excess concentrated
sodium hydroxide produced an oil layer weighing 8.2 g.
Upon distillation, fractions boiling only in the 90-100°
range at 14 mm. were obtained. These fractions failed to
give Tollen's test but did decolorize bromine in carbon-
tetrachloride. It was concluded that this material was
a polymeric mixture of olefins produced by an elimination
reaction.

B.   The attempted hydrolysis of benzophenone t-heptyl-
hydrazone was repeated using chloroform-ether solvent
(2:1 volume ratio) for five days at room temperature.
The aqueous phase was removed daily and fresh concentrated
hydrochloric acid was added. The separated acid solution
was chilled in an ice bath, treated at once with concen-
trated sodium hydroxide solution and extracted with petroleum
ether (20-40°). The combined extracts were dried over
potassium hydroxide pellets and divided into two equal
portions. Distillation of the first portion yielded six
colorless fractions boiling between 100-176° at atmospheric
pressure (about 754 mm.) having a total weight of 1.90 g.
and n_D^{25} 1.3645 to 1.4379. Fractions 2-6 were soluble in
dilute hydrochloric acid and gave an immediate Tollen's
test. In the vacuum distillation of the second portion,

six fractions were collected boiling at 80-97° @ 34 mm.,
having a total weight of 5.96 g. and n_D^{25} 1.4338-1.4470.
All fractions were soluble in dilute hydrochloric acid
and gave instant Tollen's tests. The lower refractive
index values for fractions obtained in the atmospheric
distillation suggest ether or olefin impurities. Although
no material obtained was considered pure enough to warrant
elemental analysis, the vacuum distilled product was
assumed to be crude t-heptylhydrazine.

Preparation of α-Methyl-α-Isobutylbenzylhydrazine

Overberger's (7) procedure for the oxalic acid hydrolysis
of hydrazones was followed to give α-methyl-α-isobutyl-
benzylhydrazine oxalate, white crystals, m.p. 119-120°;
yield, 53%. The free base was obtained from the oxalate
by treatment with aqueous potassium hydroxide solution.
The oxalate salt (19 g., 0.062 m.) was introduced into
a separatory funnel containing 180 ml. of a 5% solution of
potassium hydroxide. The crude α-methyl-α-isobutyl benzyl-
hydrazine was extracted with petroleum ether and vacuum
distilled. The pure hydrazine gave the following properties:
b.p. 117-119° @ 1 mm.; n_D^{25} 1.5229-1.5235. Analysis. Calcd.
for $C_{12}H_{20}N_2$: N, 14.57%. Found: N, 14.41%.

Attempted Preparations of t-Heptylhydrazine

(1) Hydroxylamine-O-Sulfonic Acid Procedure

The method of Gever and Hayes (3) was utilized in
the following attempts. Their procedure was modified to

exclude precipitation of the alkylhydrazine as the oxalate salt. Instead, the reaction mixtures were steam distilled or extracted with petroleum ether and vacuum distilled to obtain the free alkylhydrazine.

In a 500 ml. round bottomed flask equipped with an addition funnel, stirrer and reflux condenser, 11.5 g. (0.1 m.) of t-heptylamine, 30 g. (0.5 m.) of potassium hydroxide and 100 ml. of water were mixed. This mixture was heated to reflux with stirring and a solution of 34.0 g. (0.3 m.) of hydroxylamine-O-sulfonic acid in 200 ml. of ice cold water was added over a period of one hour. This mixture was refluxed with stirring for three hours after which potassium carbonate was added to salt out alkyl-hydrazine. This solution was extracted with ethyl ether, concentrated and vacuum distilled. Only t-heptylamine was recovered. For the pure amine the following properties were observed and were identical to those previously reported (9). B.p. @ 740 mm. 129.5-130.5°; n_D^{25} 1.4170. This reaction was repeated incorporating the variations noted in Table I without success in isolating the desired hydrazine.

TABLE I

Variations in H -O-S Method

Solvent	M. RNH_2	M. H-O-S	M. KOH	Temp.	Time
100 ml. EtOH	0.1	0.3	0.5	reflux	3 hrs.
10 ml. EtOH 100 ml. H_2O	0.1	0.3	0.5	reflux	24
70 ml. H_2O	0.2	0.1	0.6	reflux	24
80 ml. H_2O	0.2	0.15	0.45	0-5°	1

(2). Alkaline Hydrolysis of Benzophenone t-Heptylhydrazone.

A. Potassium hydroxide

A solution of 5.6 g. (0.1 m.), of potassium hydroxide in 20 ml. of water was mixed with 100 ml. of diethylene glycol. Benzophenone t-heptylhydrazone (5.8 g., 0.02 m.) in 5 ml. of ethyl alcohol was added to the potassium hydroxide solution. Two layers formed. The solution became almost homogeneous after heating to 90° . The temperature was maintained at 112° for six days during which time the solution changed from yellow to dark brown. Tollen's tests for alkyl hydrazine proved negative on samples removed daily from the reaction mixture.

In a second hydrolysis attempt, the same amount of hydrazone (0.02 m.) was added to 50 ml. of 20% aqueous potassium hydroxide solution. To this solution, 1.5 g. of Dreft was added as an emulsifying agent. This mixture was heated for 24 hours with stirring. The mixture was steam distilled and the distillate was extracted with petroleum ether to separate t-heptylhydrazine. The petroleum ether extract gave a negative Tollen's test.

B. Sodium Hydrosulfide

In a 500 ml. flask equipped with a stirrer was placed a solution of 100 ml. of distilled water and 28 g. (0.5 m.) of sodium hydrosulfide. To this solution was added 20.58 g. (0.07 m.) of benzophenone t-heptylhydrazone which formed a layer on top. The layers were stirred and heated at 90-100° for five days. The reaction was terminated

after the fifth day and about 40 ml. of the liquid was distilled. The distillate was extracted with petroleum ether to isolate dissolved t-heptylhydrazine. This petroleum ether extract gave a negative test in alcoholic Tollen's reagent from which it was concluded that the reaction was unsuccessful.

This attempt was repeated with the following modifications. Sodium hydrosulfide was generated through the action of hydrochloric acid (0.2 m.) on sodium sulfide (0.2 m.) dissolved in 150 ml. of diethylene glycol. Benzophenone t-heptylhydrazone (29.4 g., 0.10 m.) was added to this solution and the mixture was heated between 160-170° for 24 hours. A cold finger attachment was employed using n-amyl alcohol (b.p. 148) with hopes that condensation of solvent would occur but any alkylhydrazine would be allowed to distill. About 5 ml. of distillate was collected and tested with Tollen's reagent. A negative test was obtained from which it was concluded that the reaction was unsuccessful.

(3) Oxalic Acid Hydrolysis of Benzophenone t-Heptylhydrazone

Solutions of 29.4 g. (0.1 m.) of benzophenone t-heptyl-hydrazone in 70 ml. of absolute ether and 23 g. (0.18 m.) of oxalic acid dihydrate in 70 ml. of absolute ethanol were prepared in separate flasks. The solutions were combined with cooling in a 500 ml. erlenmeyer flask. The solution was allowed to stir overnight at room temperature after which a very small amount of white precipitate formed. The precipitate weighed 0.32 g. and had a melting point of 125-

127°. Cooling of the reaction mixture below room temperature did not produce further precipitation. The precipitate, however, was not believed to be t-heptylhydrazine oxalate.*

In a second attempt, a solution of 2.35 g. (0.008 m.) of benzophenone t-heptyl hydrazone in 10 ml. of absolute ether was added to an equivalent amount of oxalic acid in 65 ml. of absolute ether. A turbidity formed immediately giving a small amount of a white, fluffy precipitate. The precipitate gave a melting range of 110-128°. Although the precipitate did give a very weak Tollen's test, the amount of impure material obtained was not enough to justify another similar hydrolysis attempt.

(4) Hydrazine Exchange Reactions

Benzophenone t-heptylhydrazone (8.82 g., 0.03 m.) and 19.2 g. (0.6 m.) of 95% hydrazine were mixed in a 200 ml. flask. To this mixture, 0.6 g. of acetic acid and 50 ml. of absolute alcohol were added. The solution was refluxed for 24 hours then added to 200 ml. of 0.05 molar sodium hydroxide. The yellow liquid which separated was extracted with petroleum ether and distilled. Only starting hydrazone was recovered (about 80%).

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* In an experiment using some crude t-heptylhydrazine from a previous hydrochloric acid hydrolysis attempt, a minute quantity of t-heptylhydrazine oxalate was precipitated by adding t-heptylhydrazine to a saturated solution of oxalic acid dihydrate in absolute ether. The oxalate salt melted sharply at 76-78°.

In a second attempt, 9.7 g. (0.33 m.) of benzophenone
t-heptylhydrazone and 19.2 g. (0.6 m.) of 95% hydrazine
were mixed in a 250 ml. erlenmeyer flask and allowed to
stir 60 hours. The reaction mixture was extracted on a
continuous extractor and the extract distilled. A 90%
recovery of starting material was obtained. The recovered
material in both attempts gave the following properties:
b.p. 160-170° @ 1 mm., n_D^{23} 1.5759-1.5800.

DISCUSSION

The first attempts to synthesize t-alkylhydrazines employed acid catalyzed hydrolysis of t-alkylhydrazones. At best only low yields were obtained. Acid catalyzed elimination to form alkenes appears to be the most serious limitation of this method and the presence of alkenes was demonstrated in most hydrolysis attempts. This course of the reaction may be summarized by the following sequence:

$$(C_6H_5)_2-C=N-NH-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-nC_3H_7 + H_2O \longrightarrow (C_6H_5)_2-C=O + H_2NNH-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-nC_3H_7$$

$$NH_2NH-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-nC_3H_7 + H^+ \longrightarrow NH_2\overset{+}{N}H_2-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-nC_3H_7 \longrightarrow$$

$$NH_2NH_2 + \overset{+}{\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}}-nC_3H_7 \longrightarrow H^+ + \underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}=CH-C_2H_5 \text{ (and isomers)}$$

It was realized that t-alkylhydrazines would be more prone to decomposition in this manner than the comparable primary or secondary alkylhydrazines because of the greater stability of the t-alkyl carbonium ion intermediate. However, it was not anticipated that this decomposition would be the fate of the bulk of the hydrolysis product. The greater yield of t-butylhydrazine obtained from benzophenone t-butylhydrazone compared to the lower yield of t-heptylhydrazine from the corresponding hydrazone may be a consequence of the separation of crystalline t-butylhydrazine hydrochloride from the acid reaction solution. Corresponding separation of t-heptylhydrazine hydrochloride did not occur and could not be made to
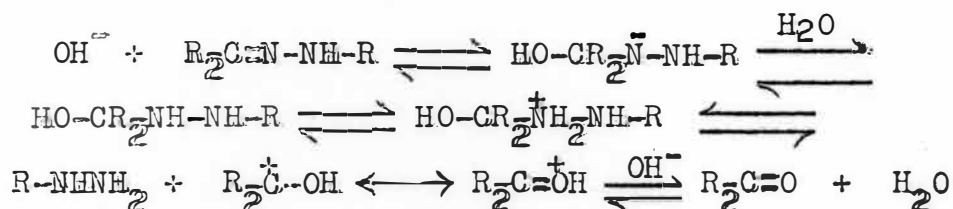
occur in the presence of concentrated aqueous hydrochloric acid.

An alternate arrangement might involve removal of the t-alkylhydrazine developed in the initial hydrolysis reaction by formation of a salt less soluble than the hydrochloride. This modification might possibly account for the success in oxalic acid hydrolysis of t-alkyl-hydrazones as reported by Overberger (7), as well as in the isolation of certain primary and secondary alkyl-hydrazines (3). Overberger has described oxalic acid catalyzed hydrolysis of the α-methyl-α-isobutylbenzyl-hydrazone of methyl isobutyl ketone in ether wherein forma-tion of the t-alkylhydrazine oxalate occurs. In spite of success in duplicating this particular reaction, applica-tion of the procedure to benzophenone t-heptylhydrazone failed to yield the hydrazine oxalate. The very low solubility of t-heptylhydrazine oxalate in ether was pre-viously demonstrated using some of the crude t-heptyl-hydrazine obtained in the aqueous hydrochloric acid hydro-lyses.

The formation of hydrazines in good yield by the method of Gever and Hayes, which involves the reaction of hydroxylamine-O-sulfonic acid with an alkylamine in an alkaline reaction medium, was of particular interest since it avoided an acid which promoted the elimination noted above. For the present purpose, no attempt was made to obtain the oxalate salt, instead, isolation of the free t-alkylhydrazine was sought. Therefore the oxalic acid

precipitation used in this method was omitted and the reaction mixtures were saturated with potassium carbonate and extracted with ether to collect the expected free base. In all cases, both in following the published procedure for the reaction and in the variations noted in Table I, no t-alkylhydrazine was obtained and unreacted t-alkylamine was recovered. Gever and Hayes have reported successful syntheses in 10-60% yields using primary and secondary amines.

In view of the elimination reaction associated with acid catalyzed hydrolysis of t-alkylhydrazones, interest turned to the use of base to promote the hydrolysis process. The following mechanistic steps appear to be a reasonable postulation for a base catalyzed hydrolysis:

$$OH^- + R_2C=N-NH-R \rightleftharpoons HO-CR_2\bar{N}-NH-R \xrightarrow{H_2O}$$

$$HO-CR_2NH-NH-R \rightleftharpoons HO-CR_2\overset{+}{N}H_2-NH-R$$

$$R-NHNH_2 + R_2\overset{+}{C}-OH \longleftrightarrow R_2C=\overset{+}{O}H \xrightarrow{OH^-} R_2C=O + H_2O$$

In spite of indications (4) that base does not catalyze hydrazone formation, two unsuccessful attempts were made to hydrolyze benzophenone t-heptylhydrazone with potassium hydroxide solution.

Powers and Westheimer (8) have discussed the reactivity of thiobenzophenone with phenyl hydrazine in alkaline reaction medium. They conclude that in the presence of base, thiobenzophenone reacts many times more rapidly with phenyl-hydrazine than does benzophenone and claim to have estab-lished evidence for base catalysis in the thiobenzophenone

reaction. Two alternate mechanisms were proposed for
the base catalyzed reaction as indicated in the following:

(1)

$$C_6H_5-\overset{\overset{S}{|}}{C}-C_6H_5 \quad \xrightarrow{\text{slow}} \quad C_6H_5-\overset{\overset{S^-}{|}}{\underset{NH}{C}}-C_6H_5$$
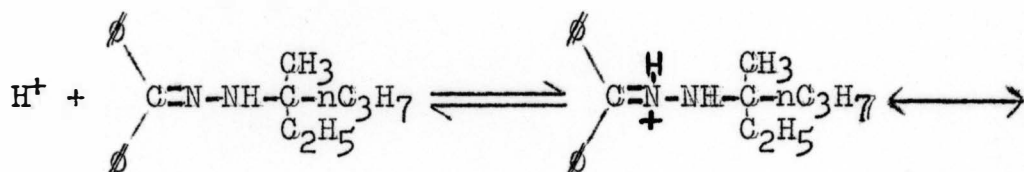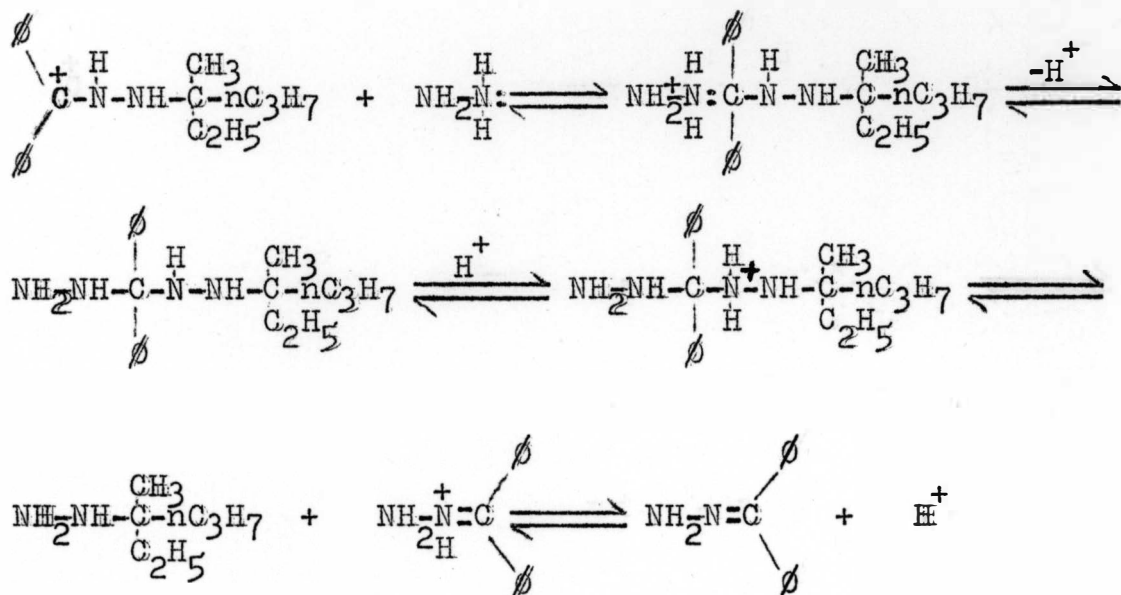$$\underset{HN-C_6H_5}{B:---HNH} \qquad\qquad\qquad HN-C_6H_5$$

$$\xrightarrow{\text{fast}} \quad (C_6H_5)_2C=N-NH-C_6H_5 + HS^-$$

(2)

$$C_6H_5-\overset{\overset{S}{|}}{C}-C_6H_5 + H_2NNH-C_6H_5 \rightleftarrows (C_6H_5)_2\underset{NH}{\overset{|}{C}}-SH +$$
$$\underset{HN-C_6H_5}{}$$

$$B: \longrightarrow (C_6H_5)_2C=N-NH-C_6H_5 + SH^- + BH^+$$

If this conversion is truly an equilibrium process, alkaline
 hydrolysis of a hydrazone in the presence of a great excess
of hydrosulfide base might reasonably be expected to reverse
the above process and provide a new source of substituted
hydrazine. However, an examination of this possibility
using a mixture of benzophenone t-heptylhydrazone and
excess aqueous sodium hydrosulfide led only to the isolation
of starting hydrazone.

Two acid catalyzed hydrazine exchange attempts were
tried using hydrazine and benzophenone t-heptyl hydrazone.
The following steps illustrate the postulated mechanism
for the reaction sought:

$$H^+ + \overset{\phi}{\underset{\phi}{>}}C=N-NH-\overset{\overset{CH_3}{|}}{\underset{C_2H_5}{C}}-nC_3H_7 \rightleftarrows \overset{\phi}{\underset{\phi}{>}}C=\overset{\overset{H}{|}}{\underset{+}{N}}-NH-\overset{\overset{CH_3}{|}}{\underset{C_2H_5}{C}}-nC_3H_7 \longleftrightarrow$$

$$\begin{array}{c}
\phi \\
\diagdown + \; H \quad\quad CH_3 \\
C-N-NH-C-nC_3H_7 \quad + \quad NH_2N: \\
\diagup \quad\quad\quad C_2H_5 \quad\quad\quad\quad H
\end{array}
\;\rightleftharpoons\;
\begin{array}{c}
\phi \\
H \;|\; H \quad CH_3 \\
NH_2^+N:C-N-NH-C-nC_3H_7 \\
H \;|\quad\quad C_2H_5 \\
\phi
\end{array}
\;\xrightleftharpoons{-H^+}$$

$$\begin{array}{c}
\phi \\
|\; H \quad\quad CH_3 \\
NH_2NH-C-N-NH-C-nC_3H_7 \\
|\quad\quad\quad C_2H_5 \\
\phi
\end{array}
\;\xrightleftharpoons{H^+}\;
\begin{array}{c}
\phi \\
|\; H_+ \quad CH_3 \\
NH_2NH-C-N-NH-C-nC_3H_7 \\
|\; H \quad\quad C_2H_5 \\
\phi
\end{array}
\;\rightleftharpoons$$

$$\begin{array}{c}
CH_3 \\
| \\
NH_2NH-C-nC_3H_7 \\
| \\
C_2H_5
\end{array}
\quad + \quad
\begin{array}{c}
+ \quad\quad \phi \\
NH_2-N=C \diagup \\
H \quad\quad \diagdown \phi
\end{array}
\;\rightleftharpoons\;
\begin{array}{c}
\phi \\
\diagup \\
NH_2-N=C \\
\diagdown \\
\phi
\end{array}
\quad + \quad H^+$$

In both reactions a twenty mole excess of hydrazine was
used to favor a shift of the equilibrium towards the
t-alkylhydrazine product. Trace amounts of acetic acid
or hydrochloric acid were used to promote the reaction
sequence and to avoid acid catalyzed elimination in the
t-alkylhydrazine if formed. Nevertheless, both attempts
resulted in isolation of only starting t-alkylhydrazone.

SUMMARY

A number of syntheses of t-alkylhydrazines were
attempted with special interest in the preparation of
t-heptylhydrazine. Only acid catalyzed hydrolysis of
benzophenone t-alkylhydrazones produced t-alkylhydrazines;
however, here decomposition of the product by acid cata-
lyzed elimination reaction resulted in isolation of only
a negligible amount of the desired compound. Four other
preparative methods were examined and found totally
unsuccessful or at best gave unisolatable trace amounts
of t-alkyl hydrazine.

BIBLIOGRAPHY

1. Audrieth, L.F. and Diamond, K.H., _J. Am. Chem. Soc._, 76, 4869 (1954).

2. Cram, D.J., Kopecky, K.R., Hauck, F. and Langemann, A., _J. Am. Chem. Soc._, 81, 5754 (1960).

3. Gever, G. and Hayes, K., _J. Org. Chem._, 14, 813 (1949).

4. Gould, E.S., _Mechanism and Structure in Organic Chemistry_, Henry Holt and Company, New York, 1959.

5. Iffland, D.C., Salisbury, L. and Schafer, W.R., _J. Am. Chem. Soc._, 83, 747 (1961).

6. Leffler, J.E., _The Reactive Intermediates of Organic Chemistry_, Interscience Publishers, Inc., New York, 1956.

7. Overberger, C.G. and DiGiulio, A.V., _J. Am. Chem. Soc._, 80, 6562 (1958).

8. Powers, J.C. and Westheimer, J.H., _J. Am. Chem. Soc._, 82, 5431 (1960).

9. Salisbury, L., Unpublished Work, Western Michigan University.

10. Smith, P.A.S., Clegg, J.M. and Lakritz, J., _J. Org. Chem._, 23, 1595 (1958).

11. Westphal, O., _Ber._, 74B, 759 (1941).

VITA

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