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LOWER ALIPHATIC DERIVATIVES OF HYDRAZINE

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Aerojet-General CORPORATION
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY
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THE GENERAL TIRE

THE LOWER ALIPHATIC DERIVATIVES OF HYDRAZINE

Contract N7onr-462
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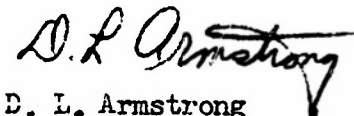E. M. Wilson

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CONTRACT FULFILLMENT STATEMENT

This literature compendium is issued as a special report in partial fulfillment of Contract N7onr-462, Task Order III.

I.   INTRODUCTION

A.   Tonnage quantities of hydrazine were being produced for use as a rocket fuel in Germany in 1944. Although theoretically capable of producing specific impulses considerably greater than fuels such as aniline or ethyl alcohol (because of its heat of formation of +12.0 Kcal/mole and the low mean molecular weight of its combustion products), hydrazine has a freezing point that requires the use of additives to depress it to the Service requirement of -65°F (-54°C). The freezing point of methylhydrazine, on the other hand, is -52.4°C, and mixtures of this compound with hydrazine or other alkylhydrazines might have freezing points well below the Service requirement. Since the addition of a limited number of carbon atoms to an otherwise acceptable molecule does not seriously affect specific impulse, these derivatives should be outstanding fuels for rocket propulsion.

B.   During an investigation at Aerojet, an extensive collection of references on the general subject of alkyl hydrazines was assembled. While this list is by no means to be considered complete, it does contain a large part of the fundamental knowledge reported on this subject. References were obtained from Beilstein's "Handbuch der Organischen Chemie," "Chemical Abstracts," and from references found in turn from the primary sources.* For an excellent general review of hydrazine, "The Chemistry of Hydrazine," by L. F. Audrieth (1) should be consulted, and for a broader (but less recent) discussion of hydrazine derivatives, "Die Hydrazine," by H. Wieland (2) is still worth while.

C.   Compounds considered here have not been restricted to those possessing all the requirements of high-energy rocket fuels. This was found to be advantageous in that an overall picture of preparative methods is obtained, and a trend in physical properties can be noted. No single substituted group larger than propyl is included, however, and all the compounds are liquid at room temperature.

II.   NOMENCLATURE

A.   ALKYLHYDRAZINES

1.   Examples of all the possible alkylhydrazines have been prepared. The mono-derivatives are sometimes called hydrazino compounds (e.g., hydrazinomethane, CH_3NHNH_2), but more commonly by the alternative name, methylhydrazine, etc. The di-substituted derivatives are of two types; for example, unsym.-diethylhydrazine or 1,1-diethylhydrazine is

$$\begin{array}{c} Et \\ \diagdown \\ \quad N{-}N \\ \diagup \quad \diagdown \\ Et \qquad H \end{array} \begin{array}{c} H \\ \end{array}$$

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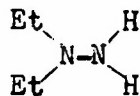
*A list of references is given at the end of this report, and numbers in parentheses refer to this list.

as distinguished from sym.-diethylhydrazine or 1,2-diethylhydrazine,

$$\underset{H}{\overset{Et}{\diagdown}}N\!-\!N\underset{H}{\overset{Et}{\diagup}}$$
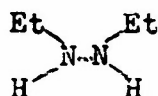
The latter is also called hydrazoethane.

    2.   Tri- and tetra-derivatives are named with consideration for the rules applying to the di-derivatives. 1,2-Dimethyl-1-isopropylhydrazine might also be called sym.-dimethyl-isopropylhydrazine or isopropyl-hydrazo-methane.

    B.   HYDRAZONES AND AZINES

    1.   Hydrazine and those of its organic derivatives with one nitrogen unsubstituted are capable of condensing with aldehydes and ketones. Hydrazones are formed by the reaction of one mole of aldehyde or ketone with one of a hydrazine:

$$RCHO + N_2H_4 \longrightarrow RCH\!=\!N\!-\!NH_2 + H_2O$$

$$\underset{R}{\overset{R}{\diagdown}}C\!=\!O + N_2H_4 \longrightarrow \underset{R}{\overset{R}{\diagdown}}C\!=\!N\!-\!NH_2 + H_2O$$
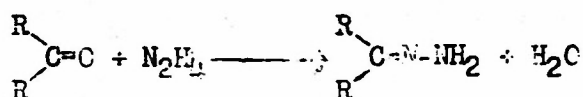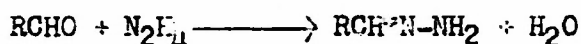
Hydrazine can condense with two moles of aldehyde or ketone, giving an azine:

$$2RCHO + N_2H_4 \longrightarrow RCH\!=\!N\!-\!N\!=\!CHR + 2H_2O$$

$$2\;\underset{R}{\overset{R}{\diagdown}}C\!=\!O + N_2H_4 \longrightarrow \underset{R}{\overset{R}{\diagdown}}C\!=\!N\!-\!N\!=\!C\underset{R}{\overset{R}{\diagup}} + 2H_2O$$
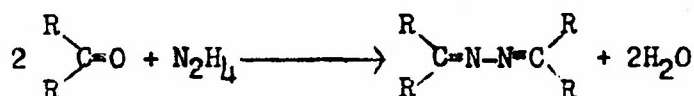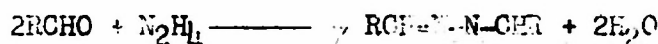
The reactions are reversible to the extent that

$$N_2H_4 + RCH\!=\!N\!-\!N\!=\!CHR \longrightarrow 2RCH\!=\!N\!-\!NH_2$$
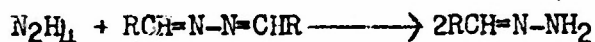
    2.   Examples of the typical nomenclature are: formalhydrazone, $CH_2\!=\!N\!-\!NH_2$; acetone isopropyl-hydrazone,

$$\underset{CH_3}{\overset{CH_3}{\diagdown}}C\!=\!N\!-\!N\underset{H}{\overset{IsoPr}{\diagup}}\quad;$$
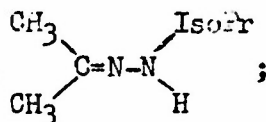
methyl ethyl ketone unsym.-dimethylhydrazone,

$$\underset{Et}{\overset{Me}{\diagdown}}C\!=\!N\!-\!N\underset{Me}{\overset{Me}{\diagup}}\quad;$$
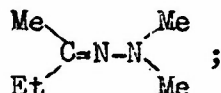
acetaldazine, $CH_3CH=N-N=CHCH_3$; and methylpropylketazine,

$$\underset{Pr}{\overset{Me}{\diagdown}}C=N-N=C\underset{Pr}{\overset{Me}{\diagup}}$$
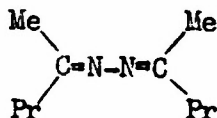
III. PROPERTIES OF ALKYLHYDRAZINES*

     A.   The mono- and di-alkylhydrazines are colorless, hygroscopic liquids of lower density than water. They fume in air and have an odor typical of ammonia and amines. Although the sym.-di-substituted derivatives are only weakly basic, the mono- and unsym.-di-substituted derivatives are more basic than hydrazine. Hydrazine is a strong reducing agent, the reducing power decreasing with increasing alkyl substitution. All of these compounds form solid salts with mineral acids, which affords an excellent method of isolating them. The free bases are known to attack cork and rubber, and they readily oxidize in an atmosphere of air. Most of them are miscible in water at room temperature and in organic solvents such as methanol, ethanol, ether, chloroform, and benzene. The methyl derivatives dissolve exothermally in water. Unlike hydrazine, there is no reported evidence of azeotrope formation with water.

     B.   Tri-alkyl and tetra-alkyl derivatives of hydrazine are also colorless, clear liquids. Their viscosity increases with increasing length of the substituent groups. They are even weaker bases than the sym.-di-substituted derivatives, and do not form solid salts with mineral acids. However, the tri-alkylhydrazines are capable of forming nitroso derivatives, a characteristic common to the mono- and sym.-di-alkyl members of the series. The higher alkyl compounds are insoluble in water and alkaline solutions, and slightly soluble in acids and methanol. Most organic solvents and lower alkylhydrazines are miscible with them.

IV. PREPARATION OF ALKYL DERIVATIVES

     A.   GENERAL

     1.   The investigations recently made by Westphal contributed greatly to the chemistry of the alkylhydrazines (3). In attempting the syntheses of these compounds by the direct alkylation of hydrazine, he found that the shorter the alkyl group, the more difficult it was to prepare the derivative. He reports the following yields from reactions conducted under similar conditions: tripropylhydrazine, 25%; triallylhydrazine, 12%; triethylhydrazine, 9.8%; and no yield of the methyl derivative. Primary alkyl chlorides produce trialkyl derivatives; secondary alkyl chlorides yield di-alkylhydrazines; and tertiary alkyl chlorides form only the mono-alkylhydrazine. An investigation of the effect of temperature was also made.

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*For a brief discussion of the properties of the alkylhydrazines, consult Beilstein System Nos. 386 and 387. Detailed physical properties of the individual compounds are listed in Table I.

2.   The direct, exhaustive methylation of hydrazine with methyl iodide initially produces methylhydrazine, then unsym.-dimethylhydrazine, and finally the salt trimethylhydrazonium iodide. Harries and Haga (4) found the ratio of hydrazine to methylation agent (R = moles N_2H_4/moles CH_3) to be quite significant: for R = 2, no hydrazonium salt formed; R = 1.5, slight salt formation; R = 0.25, hydrazonium salt is formed quantitatively. The ethylation of triethylhydrazine by ethyl chloride produced only a 10% yield of the tetraethylhydrazine, the main product being the hydrazonium salt. Westphal also observed the influence of halogen atoms by alkylation with butyl halides:

	% Yield Tri-alkyl derivatives	% Yield Hydrazonium salts
Butyl bromide	13	50
Butyl chloride	36	15

Judging from the results of the syntheses of tetra-alkyl hydrazines by Westphal and Eucken (5), it appears that the tendency toward azonium salt formation is greater, the smaller the substituent groups. This explanation may account for the difficulty in preparing trimethylhydrazine, and especially tetramethylhydrazine, by the direct route.

3.   Most of the syntheses involved drying the aqueous free bases over solid alkali (sodium or potassium hydroxide). In the majority of instances, potassium hydroxide was the drying agent employed (4, 6, 7, 8, 9, 10, 11). Sodium hydroxide is, however, reportedly a more powerful agent (1, p. 48). The final distillation of the free base was usually made from barium oxide (12, 13, 5).

a.   In some cases, the derivative decomposed in the presence of these drying agents. Brown reported explosions in his attempts to distill methylhydrazine from barium oxide (14), and the ethylhydrazine prepared by him decomposed while standing over either potassium hydroxide or barium oxide (15). Isopropyl derivatives proved extremely sensitive to drying agents and Lochte (8) found that aluminum amalgam or metallic sodium were the only suitable dehydrating agents. He comments that metallic sodium may be used as a rapid dehydrating agent, but it is difficult to remove the dried base from the sodium hydroxide formed without considerable loss of product. Either method gives results far superior to those obtained with barium oxide. Even more recently, Class and Aston (16) used calcium hydride to dry trimethylhydrazine. Attention is called to the fact that an explosive hydrazide is formed with sodium and hydrazine, and the method, if used at all, should be used with caution.

b.   The most significant technique for concentrating alkylhydrazines involves the separation into two liquid phases, which occurs when either sodium hydroxide or potassium hydroxide is added at room temperature to aqueous solutions of the mono- or di-alkyl derivatives. The method was first employed by Harries and Haga for the concentration of unsym.-dimethylhydrazine (4). Subsequently it was used to recover diisopropylhydrazine (7),

ethylhydrazine (15), trimethylhydrazine (16), and even methylethylketazine (10). This is the same phenomenon recently observed at temperatures above 60°C by Audrieth and Penneman for the system hydrazine-water-sodium hydroxide, although sodium hydroxide was the only successful compound of the many salting-out agents investigated by them for hydrazine hydrate (17).

B.   MONO-SUBSTITUTED DERIVATIVES

1.   Methylhydrazine

a.   Methylhydrazine, the simplest member of the alkyl-hydrazine series, is commonly prepared by methylation of benzalazine (the condensation product of hydrazine with benzaldehyde) by methyl sulfate in benzene. The reaction product is hydrolyzed to produce methylhydrazine sulfate, $CH_3NHNH_2 \cdot H_2SO_4$ (18, 19). The yield is 76 to 83% according to Thiele, but purification by the method in Reference 18 lowers the yield to 51 to 54%. This procedure has consistently met with success (20, 21, 15). Another recommended method involves the reduction of N-nitroso-N-methylurea with zinc dust in acetic acid, followed by isolation as the sulfate (12). In each case, the free base can be liberated from the acid salt by adding solid alkali, subsequently refluxing the mixture and distilling. The distillate contains appreciable quantities of water and must be dehydrated by prolonged drying over fused alkali and subsequent distillation from barium oxide. Aston (20) has reported purities as high as 99.75 mole%; this material had been concentrated by fractional melting (22) and was used to study the thermodynamic properties. Although the reactions probably have little preparative value, methylhydrazine was formed in the following instances:

(1)   by reduction of methylnitramine (23)

(2)   by shaking an aqueous solution of hydrazine hydrate with an excess of methyl iodide, forming also 1,1-dimethylhydrazine and 1,1,1-trimethyl-hydrazonium iodide (4)

(3)   by the reduction of diazomethane with sodium amalgam in alcohol (24)

(4)   by cleavage of azomethane with concentrated HCl (25)

(5)   by reduction of 4-amino-1,2,4-triazole with zinc dust and acetic acid (26)

(6)   by the thermal decomposition of the hydrochloride of hydrazine-carbonic acid methyl ester (6)

(7)   by refluxing nitrosomethylhydrazine-sulfonic acid with concentrated HCl (27)

(8)   by the action of chloroform on refluxing hydra-
zine in the presence of alcoholic KOH (28)

(9)   by the reduction of sodium methyl-isodiazotate
with aluminum in alkaline solution (19)

(10)   by the hydrolysis of equivalent quantities of
methylamine and hydroxylamine-o-sulfonic acid in
boiling water, or better in boiling dilute NaOH
(29)

(11)   by reduction of nitromethylurethane (30)

(12)   by direct alkylation with dimethyl sulfate (15, 19)

(13)   from methylurea by the Hofmann rearrangement (15)

(14)   by the reductive cleavage of 1,2-dimethyl-1-phenyl-
2-nitroso-hydrazine (31)

b.   Some of the methods are worthy of further consideration.
Thiele has suggested the substitution of dimethylketazine for benzalazine,
and thus far the relative merits have not been investigated. The use of methyl
chloride as the methylating agent for the azine has not been attempted.
Diazomethane, prepared by Staudinger's method (28), could be absorbed in
hydrazine methylating it at the expense of liberated nitrogen.

2.   Ethylhydrazine

Fischer prepared ethylhydrazine by the reduction of N-nitroso-
N,N'-diethyl urea with zinc dust in alcoholic solution (9). Prolonged digestion
of 2,4-diethyl-semicarbazide with HCl cleaves it, precipitating ethyl-hydrazine
as the hydrochloride. The free base may be recovered in the manner described
for methylhydrazine. A more recent method of preparation involves the direct
ethylation of anhydrous hydrazine with ethyl sulfate in an absolute alcohol
solution of KOH; the yield was 32% recovered as the hydrochloride, with 80%
recovery of the free base (15). Ethylhydrazine has also been prepared by
direct ethylation using ethyl chloride, although the predominant products were
the di- and tri-ethyl derivatives (3). The compound was reportedly identified
in the following reactions:

a.   The reduction of ethylnitramine with zinc and HCl
(and perhaps also by electrolytic reduction)   (23)

b.   as the sulfate, from the Grignard reaction between
C_2H_5MgI and diazo-ethylacetate, subsequently refluxed
with dilute sulfuric acid (32)

Thiele has suggested the reaction between ethyl bromide and dimethylketazine
for the preparation of ethylhydrazine.

3. Propylhydrazine

Propylhydrazine has been formed by the reaction between potassium propyl sulfate and hydrazine in boiling water, analogous to the methyl sulfate and ethyl sulfate alkylations (33, 34). The partial hydrogenation and subsequent hydrolysis of propionaldazine affords another method (35). Westphal found that direct alkylation with propyl chloride yields the compound, although conditions must be controlled to prevent further substitution (3).

4. Isopropylhydrazine

During a study of this derivative one of the most elegant methods of preparing alkyl derivatives was developed by Lochte and co-workers. As applied to the preparation of isopropylhydrazine, it involves mixing equimolar quantities of acetone and hydrazine hydrate in HCl, and subsequent hydrogenation in the presence of colloidal platinum (8). The same investigators prepared it in 60 to 70% yield by treating azo-isopropane with alcoholic HCl or with a solution of HCl in ether or benzene (36). Yields as high as 95% have been reported (37, 38). The compound is also formed in the following reactions:

a. the hydrolysis of acetone-isopropylhydrazone with water or dilute HCl (8)

b. the hydrolysis of 1-isopropyl-semicarbazide with 80% sulfuric acid (39)

Westphal directly alkylated hydrazine with isopropyl chloride, and reported that he obtained a moderate yield of di-substituted derivatives, but made no mention of the mono-compound (3).

5. Allylhydrazine

The hydrochloride of allylhydrazine has been prepared in 34% yield by heating an alcoholic solution of allyl chloride with hydrazine hydrate (40).

C. DI-SUBSTITUTED DERIVATIVES

1. unsym.-Dimethylhydrazine

unsym.-Dimethylhydrazine was the first alkyl derivative to be prepared (41). A highly efficient method for preparing the hydrochloride of this compound involves the reduction of the nitroso derivative of dimethylamine with zinc dust in acetic acid solution at room temperature. Crude yields are 77 to 83% of theoretical; purification reduces the yields to 69 to 73% (11, 42, 21). An improved method, recently reported, employs lithium aluminum hydride as the reducing agent for nitrosodimethylamine; 78% yields can be obtained (43). Additional methods of formation include the following:

a. methylation of hydrazine hydrate with methyl iodide, using a sufficient quantity of hydrazine to prevent formation of trimethylhydrazonium iodide (4)

b. reduction of dimethylnitramine with zinc dust and acetic acid (44)

c. dry distillation of trimethylhydrazonium hydroxide under reduced pressure (19% yield) (4)

d. electrolytic reduction of dimethylnitramine in 10% sulfuric acid on a tinned copper cathode (30)

e. prolonged refluxing of dimethylcarbamide acid azide in xylene and heating the insoluble portion with concentrated HCl in an autoclave (45)

f. the reaction between dimethylamine and amidoper-sulfuric acid (46)

Harries and Haga (4) methylated hydrazine with methyl iodide, producing methyl-hydrazine, 1,1-dimethylhydrazine, and the quaternary hydrazonium salt. Under controlled conditions, they obtained greater than 90% yields of the salt, but as recovery of the substituted hydrazine is an inefficient step from this material, the process is not practical.

2. 1,2-Dimethylhydrazine

The recommended method of preparing this compound involves the methylation of sym.-dibenzoylhydrazine (made in 66 to 75% yield) with dimethyl sulfate to form 1,2-dibenzoyl-1,2-dimethylhydrazine, followed by hydrolysis with HCl. The product is obtained in up to 93% yields of the crude dihydrochloride salt; purification of this salt results in a yield of pure product of 78% (47, 48, 49). A similar preparation involves the methylation of sym.-diformylhydrazine followed by HCl hydrolysis (25, 50). Both these preparations emphasize the need for both nitrogen atoms to be protected by substituents in order to form a symmetrically substituted alkyl derivative of hydrazine; steric hindrance prevents large acetyl groups from substituting unsymmetrically, which is the common tendency (4). Thiele has reported that azomethane can be reduced quantitatively to sym.-dimethylhydrazine with zinc dust in alkaline solution or with sodium amalgam (25). Reactions leading to the formation of varying quantities of sym.-dimethylhydrazine include:

a. basic hydrolysis of 1-methylpyrazoleiodomethylate (51)

b. the thermal decomposition of 1,2,3-trimethylpyrazolone with alcoholic KOH at 190°C (52)

c. the thermal decomposition of the reaction product of dimethylamine with azo-dicarboxylic acid diethylester (53)

d. the hydrolysis of N-nitroso-sym.-dimethylhydrazine
with HCl (19)

e. the hydrolysis of the addition compound of sodium
and azomethane (54)

3. 1,1-Diethylhydrazine

According to Fischer nitroso-diethylamine can be successfully
reduced with zinc dust in aqueous solution to unsym.-diethylhydrazine (9).
The direct ethylation of hydrazine with ethyl chloride should produce 1,1-di-
ethylhydrazine predominantly under controlled conditions (3), although West-
phal's reported yield is low (10%). 1,1-Diethylhydrazine was identified as a
reaction product after 1-hydroxy-3,3-diethylurea was thermally decomposed at
25 mm pressure (55).

4. 1,2-Diethylhydrazine

Hydrolysis of 1,2-diformyl-1,2-diethylhydrazine (prepared
in 40% yield) by refluxing with excess concentrated HCl affords a method of
preparing sym.-diethylhydrazine, in the manner identical with the preparation
of the dimethyl derivative (56). It is unlikely, however, that direct
ethylation of hydrazine with ethyl chloride would produce this compound in
appreciable yields under any conditions, because the unsym.-derivative would
predominate.

5. Dipropylhydrazine

This compound has only been prepared as a by-product in the
preparation of tripropylhydrazine by the action of propyl chloride on
hydrazine (3).

6. 1,1-Diisopropylhydrazine

Klages reduced diisopropylnitrosamine with zinc dust and
acetic acid to obtain a 40% yield of unsym.-diisopropylhydrazine (13).
Westphal also prepared mixed diisopropyl-derivatives in 49% yields by the
direct alkylation of hydrazine with isopropyl chloride (3). Klages performed
the same reaction using isopropyl bromide (13).

7. 1,2-Diisopropylhydrazine

Catalytic reduction of dimethylketazine, the condensation
product of 2 moles of acetone with 1 mole of hydrazine, produces sym.-diiso-
propylhydrazine in 90% yields (7, 57). Similarly, acetone isopropylhydrazone
can be reduced quantitatively in the presence of colloidal platinum (8).
Hydrogenation of diisopropyldiimide in the presence of colloidal platinum (58)
or reduction of that compound with sodium amalgam or sodium in alcohol,

effectively produce sym.-diisopropyl hydrazine (8). This particular derivative
of hydrazine is especially sensitive to oxidation. The usual procedure of
dehydrating hydrazines with barium oxide decomposed diisopropylhydrazine, and
only aluminum amalgam was effective in producing material of 99.5% purity (8).

8. 1,1-Diallylhydrazine

Diallylhydrazine was prepared by digesting 1,1-diallylhydrazine-
2-carbonic acid methyl ester with hydrazine under vigorous conditions (59).
Diallylhydrazine was also prepared by alkylating hydrazine with allyl chloride
(3).

9. 1-Methyl-2-isopropylhydrazine

Methylation of 1,2-dibenzoyl-1-isopropylhydrazine produced
a substituted hydrazine which was decomposed with HCl to 1-methyl-2-isopropyl-
hydrazine, the first mixed alkyl hydrazine to be prepared (60). Material of
99.8% purity was obtained in 50% yield by drying over aluminum amalgam.

D. TRI-SUBSTITUTED DERIVATIVES

1. Trimethylhydrazine

By the reduction of formaldehyde unsym.-dimethylhydrazone
(1,1-dimethyl-2-methylenehydrazine) with lithium aluminum hydride, the lowest
trialkyl derivative of hydrazine can be prepared in 49% yield (16). Tri-
methylhydrazine is also reportedly prepared in 20 to 25% yield by the action
of methyl iodide on the reaction product of 1,2-dimethylhydrazine and methyl
magnesium bromide (13).

2. Triethylhydrazine

This compound was prepared by Westphal and Eucken in 45%
yield by the action of the methyl Grignard reagent on formaldehyde unsym.-
diethylhydrazone (5). It occurs as a by-product (9.5% yield) in the direct
ethylation of hydrazine by ethyl chloride (3).

3. Tripropylhydrazine

Propyl chloride is capable of alkylating hydrazine to form
the tripropyl derivative in 25% yield (3). Some of the mono- and di-substituted
compounds are formed.

4. Triallylhydrazine

The yield of triallylhydrazine is only 12% from the reaction
between allyl chloride and hydrazine (3). In comparison allyl bromide and
allyl iodide gave no yield of this derivative.

5.   Triisopropylhydrazine

Triisopropylhydrazine has been prepared in 10% yield by the direct alkylation of hydrazine using isopropyl bromide (13).

6.   1,1-Dimethyl-2-ethylhydrazine

A yield of 65% is reported by Klages for this mixed tri-substituted alkylhydrazine. It was made by the reaction of methyl magnesium bromide with formaldehyde unsym.-dimethylhydrazone (13).

7.   1,2-Dimethyl-1-isopropylhydrazine

sym.-Dimethylhydrazine can be alkylated by isopropyl bromide to prepare sym.-dimethyl-isopropylhydrazine in 31% yield (13).

E.   TETRA-SUBSTITUTED DERIVATIVES

1.   Tetramethylhydrazine

The tetramethyl derivative of hydrazine has not yet been prepared.

2.   Tetraethylhydrazine

In the presence of magnesium hydroxide, triethylhydrazine is alkylated by ethyl chloride to produce tetraethylhydrazine in 10.2% yield (5).

3.   Tetrapropylhydrazine

Tetrapropylhydrazine is prepared in 40 to 50% yield from tripropylhydrazine and propyl bromide in the presence of magnesium hydroxide (3). A comparison of the yield of the tetrapropyl with that of the tetra-ethylhydrazine indicates the relative ease with which longer alkyl groups can be substituted.

4.   1,2-Dimethyl-1,2-diisopropylhydrazine

Klages observed that sym.-dimethylhydrazine and isopropyl bromide react to give predominantly 1,2-dimethyl-1,2-diisopropylhydrazine, although some of the mono-isopropyl derivative is also formed (13).

V.   CONDENSATION PRODUCTS OF HYDRAZINE AND SUBSTITUTED HYDRAZINES WITH ALIPHATIC CARBONYL COMPOUNDS

A.   A characteristic reaction of hydrazine and its mono- and unsym.-di-alkyl derivatives is condensation with carbonyl compounds. Reduction of these hydrazine derivatives affords a simple, indirect route to more highly

substituted alkylhydrazines. Many of these condensation products are known
for hydrazine, but few are reported for its derivatives. The compounds that
lie within the scope of this review of alkylhydrazines are briefly discussed
below.

1.   Formaldehyde Hydrazone, $CH_2 = NNH_2$

The simplest hydrazine-carbonyl condensation product is
formaldehyde hydrazone. It has been reported as a solid trimer (61).

2.   Acetone Hydrazone, $(CH_3)_2C=NNH_2$

The lowest member of the ketohydrazone series is acetone
hydrazone. Von Rothenburg prepared it by the reaction between acetoxime and
hydrazine hydrate (62).

3.   Formalazine, $CH_2 = NN = CH_2$

Pulvermacher was unsuccessful in attempting to reduce this
compound to sym.-dimethylhydrazine (63).

4.   Acetalazine, $CH_3CH = NN = CHCH_3$

Acetalazine was prepared only recently by Seibert during his
investigation of the Wolff-Kishner-Staudinger reaction (64).

5.   Dimethylketazine, $(CH_3)_2 C = NN = C(CH_3)_2$

Curtius found it necessary to cool the reaction vessel in
which he prepared dimethylketazine because the reaction was quite exothermic
(65). He produced the compound in 74% yield. Thiele, who unsuccessfully
attempted its reduction electrolytically, has suggested dimethylketazine as a
substitute for benzalazine, the hydrazine derivative which is alkylated in
the preparation of mono-alkylhydrazines. The Curtius method was also followed
by Lochte and his co-workers (10).

6.   Methylethylketazine, $(CH_3)(CH_3CH_2)C = NN = C (CH_2CH_3)CH_3$

Methylethylketazine was prepared by Curtius in 71% yield (65).
Barrick recommends using a 50% excess of methyl ethyl ketone to improve the
yield (10).

7.   Methylpropylketazine, $(CH_3)(CH_3CH_2CH_2)C = NN = C(CH_2CH_2CH_3)CH_3$

Curtius reports a yield of 57% of this compound (65). The
relative reactivity of methylpropylketone with hydrazine and the comparative
lower yield indicate that the smaller the alkyl groups on the carbonyl com-
pound, the greater the extent of condensation.

8.   Diethylketazine, $(CH_3CH_2)_2C = NN = C(CH_2CH_3)_2$

This compound was prepared in 16% yield by Curtius (65).

9.   <u>Formaldehyde 1,1-dimethylhydrazone</u>, $CH_2 = NN(CH_3)_2$

       Class and Aston had little apparent difficulty in preparing this derivative from a concentrated aqueous solution of <u>unsym.</u>-dimethylhydrazine and 40% formalin solution, although their yield was not reported (16). They used the anhydrous product in the preparation of trimethylhydrazine. Klages prepared this hydrazone in 90% yield and used it for the preparation of 1,1-dimethyl-2-ethylhydrazine by methylation, but he was unsuccessful in his attempt to reduce it because it formed a resin on the catalyst (13).

10.   <u>Formaldehyde 1,1-diethylhydrazone</u>, $CH_2 = NN(CH_2CH_3)_2$

       Westphal and Eucken prepared this compound in 48% yield, as a starting material for the preparation of triethylhydrazine (5).

11.   <u>Acetaldehyde 1,1-dimethylhydrazone</u>, $CH_3CH=NN(CH_3)_2$

       This hydrazone was prepared in 80% yield by Klages (13).

12.   <u>Acetone Isopropylhydrazone</u>, $(CH_3)_2C=NNHCH(CH_3)_2$

       Reddelien used zinc chloride as a catalyst for the preparation of this ketohydrazone (70% yield) (66). Lochte and co-workers found that a mole to mole ratio of reactants in an equal volume of absolute alcohol afforded a mixture from which acetone isopropylhydrazone could be distilled in 80% yield (8, 10). The hydrazone was used to prepare azo-isopropane.

      B.   The liquid hydrazones and azines have chemical and physical properties much like the hydrazines from which they are derived. In addition, these derivatives appeared to be quite resistant to reduction. Lochte (7) alludes to a statement by Wieland that purely aliphatic aldazines are not reducible and concludes that ketazines also fall within this category. Mailhe was successful in reducing ketazines, using the Sabatier-Senderens method of catalytic reduction over hot nickel (67). The dominant products, however, were amines. Lochte confirmed the fact that no neutral or alkaline reducing agents, e.g., aluminum amalgam, iron powder, sodium in ethanol, sodium amalgam in neutral or alkaline solution, were effective. After an extensive survey of the literature on reduction, Skita's (58) method of hydrogenation with palladium catalyst was singled out by Lochte and his co-workers for the preparation of the lower alkyl hydrazines.

VI.   QUANTITATIVE ANALYSIS OF HYDRAZINE COMPOUNDS

       While there are certain specific characteristics that all hydrazine compounds possess as a class, the analysis of these compounds by such properties is made difficult by the fact that often it is a mixture of similar compounds

that must be analyzed. In the case of hydrazine itself, the common impurities are water and ammonia, and the titration by potassium iodate of a hydrochloric acid solution of the sample to the iodine monochloride endpoint serves as an excellent method of analysis. Methylhydrazine has also been successfully analyzed by this method (15). A wide variety of hydrazine derivatives have been quantitatively analyzed by potentiometric titration (68), employing iodate as the oxidizer. In many cases, fractional electron changes were noted, but these changes were sufficiently reproducible so that the method can be used when a high degree of accuracy is not needed. The quantitative precipitation as an insoluble salt (e.g., the picrate) has been used for the determination of hydrazine compounds, but by far the greatest number of investigators have used standard carbon, hydrogen, and nitrogen analyses for the identification of the compounds under study.

REFERENCES

1. Audrieth, L. F., and Ogg, B. A., "The Chemistry of Hydrazine," John Wiley & Sons, Inc., N. Y. (1951).

2. Wieland, H., "Die Hydrazine," Ferdinand Enke, Stuttgart (1913).

3. Westphal, O., Ber., 74, 759 (1941).

4. Harries, C. D. and Haga, T., Ber., 31, 56 (1898).

5. Westphal, O. and Eucken, N., Ber., 76, 1137 (1943).

6. Diels, O., Ber., 47, 2183 (1914).

7. Lochte, H. L., Bailey, J. R., and Noyes, W. A., J. Am. Chem. Soc., 43, 2597 (1921).

8. Lochte, H. L., Noyes, W. A., and Bailey, J. R., J. Am. Chem. Soc., 44, 2556 (1922).

9. Fischer, E., Ann., 199, 281 (1879).

10. Barrick, L. D., Drake, G. W., and Lochte, H. L, J. Am. Chem. Soc., 58, 160 (1936).

11. Hatt, H. H., "Organic Synthesis," Coll. Vol. II, John Wiley & Sons, N. Y., 1943, p. 213.

12. von Bruning, G., Ann., 253, 5 (1889).

13. Klages, F., et al., Ann., 547, 1 (1941).

14. Brown, R. D., and Kearley, R. A., J. Am. Chem. Soc., 72, 2762 (1950).

15. Brown, R. D., et al, "Studies in the Preparation, Analysis, and Thermal Decomposition of Hydrazine, Methyl and Ethyl Hydrazine," Annual Progress Report, Project No. 349, (University of Alabama), 1 November 1948. (Unclassified).

16. Class, J. B. and Aston, J. G., J. Am. Chem. Soc., 73, 2359 (1951).

17. Penneman, R. A., and Audrieth, L. F., J. Am. Chem. Soc., 71, 1644 (1949).

18. Hatt, H. H., "Organic Synthesis," Coll. Vol. II, John Wiley & Sons, N. Y., 1943, p. 395.

19. Thiele, J., Ann., 376, 239 (1910).

REFERENCES (cont.)

20. Aston, J. G., et al., J. Am. Chem. Soc. 73, 1939 (1951).

21. Aston, J. G., et al., J. Am. Chem. Soc. 74, 2484 (1952).

22. Aston, J. G. and Mastrangelo, S. V. R., Anal. Chem. 22, 636 (1950).

23. Thiele, J., and Meyer, C., Ber. 29, 963 (1896).

24. von Peckmann, H., Ber. 28, 855 (1895).

25. Thiele, J., Ber., 42, 2575 (1909). Y-19.

26. Hantzsch, A., and Silberrad, O., Ber., 33, 58 (1900).

27. Traube, W., and Brehmer, E., Ber., 52, 1284 (1919).

28. Staudinger, H., and Kupfer, O., Ber. 45, 501 (1912).

29. Sommer, F., Schulz, O. F., and Nassau, M., Z. anorg. Chem. 147, 142-55 (1925).

30. Backer, H. J., Rec. trav. chim., 31, 150 (1912).

31. Harries, C. D., Ber. 27, 696 (1894).

32. Zerner, E., Monatsh 34, 1628 (1913).

33. Stolle, R., J. prakt. Chem. 66, 332 (1902).

34. Stolle, R., and Benrath, A., J. prakt. Chem. 70, 263 (1904).

35. Taipale, K. A., and Smirnoff, S. A., Ber. 56, 1794 (1923).

36. Lochte, H. L., and Bailey, J. R., Ber. 56, 1799 (1923).

37. Taipale, K. A., J. Russ. Phys.-Chem. Soc. Chem Part 54, 638, (1922-3).

38. Taipale, K. A., J. Russ. Phys.-Chem. Soc. Chem Part 56, 81 (1925).

39. Neighbors, DeW., et al, J. Am. Chem. Soc., 44, 1557 (1922).

40. Gabriel, S., Ber. 47, 3028 (1914).

41. Fischer, E., Ber. 8, 1587 (1875).

42. Renouf, E., Ber. 13, 2171 (1880).

REFERENCES (cont.)

43. Schueler, F. W., and Hanna, C., J. Am. Chem. Soc. 73, 4996 (1951).

44. Franchimont, A.P.N., Rec. trav. chim. 3, 427 (1884).

45. Stolle, R., Nieland, H., and Merkle, M., J. prakt. Chem. 117, 185 (1927).

46. Sommer, F., and Schulz, O. F., Ger. Pat. 338,609, 1921.

47. Hatt, H. H., "Organic Synthesis," Coll. Vol. II, John Wiley & Sons, N. Y., 1943, p. 208.

48. Aston, J. G., et al., J. Am. Chem. Soc. 73, 1943 (1951).

49. Folpmers, T., Rec. trav. chim. 34, 34 (1915).

50. Harries, C. D., and Klamt, E., Ber. 28, 503 (1895).

51. Knorr, L., and Kohler, A., Ber. 39, 3257 (1906).

52. Knorr, L., Ber. 39, 3267 (1906).

53. Diels, O., and Paquin, M., Ber. 46, 2000 (1913).

54. Schlenk, W., and Bergmann, E., Ann. 463, 315 (1928).

55. Hurd, C. D., and Spence, L. V., J. Am. Chem. Soc. 49, 266 (1927).

56. Harries, C. D., Ber. 27, 2279 (1894).

57. Taipale, K. A., Ber. 56, 955 (1923).

58. Skita, A., and Meyer, W. A., Ber. 45, 3579, 3589 (1912).

59. Diels, O., Ber. 56, 1933 (1923).

60. Ramsperger, H. C., J. Am. Chem. Soc. 51, 918 (1929).

61. Stolle, R., Ber. 40, 1505 (1907).

62. von Rothenburg, R., Ber. 26, 865, 2060 (1893).

63. Pulvermacher, G., Ber. 26, 2360 (1893).

64. Seibert, W., Ber. 80, 494 (1947).

REFERENCES (cont.)

65.   Curtius, T. and Thun, K., J. prakt. Chem. (2) 44, 161 (1891).

66.   Reddelien, G., Ann. 388, 170 (1912).

67.   Mailhe, A., Compt. rend. 170. 1265 (1920).

68.   McBride, W. R., Henry, R. A., and Skolnik, S., "Potentiometric
      Analytical Methods for Hydrazine Compounds Part 2. Org. Derivatives
      of Hydrazine," U.S. Naval Ordnance Test Station, NAVORD Report 1279
      Part 2, 21 August 1951 (Unclassified).

69.   Bruhl, J. W., Ber. 30, 160 (1897); Z. physik. Chem. 22, 388 (1897).

TABLE I

PHYSICAL PROPERTIES OF ALKYLHYDRAZINES*

Compound	mp, °C	bp, °C[†]	Density	Index of Refraction	Heat of Combustion Kcal/mole
Methylhydrazine	-52.37 (20)	87_{45} (12)[‡]			311.711 (21)
Ethylhydrazine		99.5_{709} (9)			
Allylhydrazine		$122\text{-}4_{757}$ (40)			
Propylhydrazine		119 (33,34)			
i-Propylhydrazine		$106\text{-}7_{750}$ (8)			
1,1-Dimethylhydrazine		$62.2\text{-}63.9_{752}$ (69)	$0.7914_{4}^{22.3}$ (69)	$1.40753_{D}^{22.3}$ (69)	472.648 (21)
1,2-Dimethylhydrazine	-8.88 (48)	81_{747} (51)[§]	0.8274_{4}^{20} (51)	1.4209_{D}^{20} (51)	473.454 (21)
1,1-Diethylhydrazine		$96\text{-}9$ (9)			
1,2-Diethylhydrazine		$84\text{-}6$ (56)			
1,1-Diallylhydrazine		145_{752} (59)			
Dipropylhydrazine[⁋]		49_{11} (3)			
1,1-Diisopropylhydrazine		$128\text{-}9_{720}$ (13)			
1,2-Diisopropylhydrazine		124_{740} (7)	0.7712_{4}^{31} (7)	1.41211_{D}^{25} (10)	

* Numbers in parenthesis indicate references.
† The subscript gives the pressure in mm corresponding to the boiling point quoted.
‡ $\text{Log}_{10}\ P_{mm} = -7.83\ \log T - 3146/T + 31.746$ (20).
§ $\text{Log}_{10}\ P_{mm} = -10.54\ \log T - 3407/T + 39.352$ (48).
⁋ The exact constitution was not ascertained.

Table I
Sheet 1 of 3

TABLE I (cont.)

Compound	mp, °C	bp, °C	Density	Index of Refraction	Heat of Combustion Kcal/mole
1,2-Diisopropylhydrazine		$124.5\text{-}5.0_{750}$ (10)	0.7844^{27}_{4} (8)		
1-Methyl-2-isopropylhydrazine		100.2_{760} (60)	0.7851^{25}_{4} (10) 0.7956^{20}_{4} (60)		
Trimethylhydrazine		59_{740} (16)	0.8144^{18}_{4} (16)	1.4064^{18}_{D} (16)	
Triethylhydrazine		46_{42} (5)		1.420^{20}_{D} (3)	
Triallylhydrazine		$62\text{-}3_{12}$ (3)		1.464^{23}_{D} (3)	
Tripropylhydrazine		$59\text{-}61_{11}$ (3)		1.428^{20}_{D} (3)	
Triisopropylhydrazine		155-60 (13)			
1,1-Dimethyl-2-ethylhydrazine		$76\text{-}7_{720}$ (13)	0.751^{20} (13)		
1,2-Dimethyl-2-isopropylhydrazine		95-7 (13)			
1-Methyl-1,2-diisopropylhydrazine		130-5 (13)			
Tetraethylhydrazine		151_{760} (5) $52\text{-}3_{42}$ (5)			
Tetrapropylhydrazine		226_{760} (5)	$0.8103^{19.8}$ (3)	$1.439^{19.8}_{D}$ (3)	
1,2-Dimethyl-1,2-diisopropylhydrazine		$88.6\text{-}9.9_{11}$ (3) 143-6 (13)			

Table I
Sheet 2 of 3

TABLE I (cont.)

Compound	mp, °C	bp, °C	Density	Index of Refraction	Heat of Combustion Kcal/mole
Dimethylketazine	-12.5 (10)	132-3$_{760}$ (10)	0.3380$^{25}_{4}$ (10)	1.45067$^{25}_{D}$ (10)	
Methylethylketazine		131$_{760}$ (65) 168-72$_{750}$ (65) 75$_{12}$ (65)	0.8365$^{21.5}$ (65) 0.8335^{24} (65)	1.45127$^{25}_{D}$ (10)	
Methylpropylketazine		168-70$_{750}$ (10) 195-200$_{760}$ (65) 95$_{12}$ (65)	0.8441$^{25}_{4}$ (10) 0.8330 (55)		
Diethylketazine		190-5$_{760}$ (65) 92$_{12}$ (65)	0.836^{24} (65)		
Formaldehyde-1,1-di-methylhydrazone		70-1 (16, 13)			
Formaldehyde-1,1-di-ethylhydrazone		114-5$_{760}$ (5)			
Acetaldehyde-1,1-di-methylhydrazone		89-94 (13)			
Acetone isopropyl-hydrazone		132-4$_{750}$ (8)	0.8225$^{26.5}_{4}$ (10) 0.8184$^{25}_{4}$ (10)	1.43722$^{25}_{D}$ (10)	

Table I
Sheet 3 of 3