In accordance with this invention, isocyanates are prepared by the pyrolysis of aminimides. The preferred aminimides useful in this process are those of the formula

\[
R_1 \text{N} = \text{C} = \text{O}_n
\]

wherein \( R \), \( R_1 \) and \( R_2 \) are alkyl, aryl and radicals in which \( R_2 \) and \( R_3 \) are joined to form a heterocyclic ring, \( R \) is an aliphatic, cycloaliphatic or aromatic group and \( n \) is an integer of at least 1, usually 1 to 4.

\[ \text{NR}_1\text{R}_2\text{R}_3 \]

and tertiary amines of the formula

\[
R_1 \text{N} = \text{C} = \text{O}_n
\]

The process of this invention can be used to form mono-, di- and polyisocyanates, depending upon the particular aminimide employed. As just indicated, the aminimides used in the preparation of isocyanates have the formula:

\[ \text{NR}_1\text{R}_2\text{R}_3 \]

In this formula, \( R \) is any saturated or unsaturated aliphatic, cycloaliphatic, or aromatic group of valence 1. \( R \) can be alkyl, alkoxyl, polymethylene, or alkenylene. Preferably, \( R \) contains from 1-28 carbon atoms, and is substituted with \( n \) aminimide groups wherein \( n \) is an integer of at least 1. While \( n \) can be any integer, in practice it is preferred that \( n \) be an integer of from 1 to 4. On pyrolysis, each aminimide group yields an isocyanate substituent. As used in this specification and the appended claims, valence refers to the number of aminimides or isocyanate groups found on each R group. Nonlimiting examples of suitable R groups include methyl, ethyl, propyl, isopropyl, hazyl, cyclohexyl, cyclobexyl, dodecyl, octadecyl, phenyl, benzyl, naphthyl, thiophenyl, cyclohexenyl, butenyl, dodecenyln, linoleyl, erucyl, o-phenylene, m-phenylene, p-phenylene, methylene, dimethylene, trimethylene, and ethylene. The R group can contain functional substituents, but such substituents must not affect the aminimide structure of the molecule. Suitable functional substituents include halogens and alkyl groups. Additionally, ketone and aldehyde groups can be present as these do not affect the aminimide structure. Certain functional groups which have no effect on the aminimide but which react with the isocyanate product, such as hydroxyl, amine, and carboxyl, are to be avoided. Naturally, these functional groups can be present if they are protected by conversion to nonreactive derivatives.

Examples of aminimides which can be pyrolyzed to yield isocyanates include the following: trimethylamine benzimide, triethylamine benzimide, trimethylenamine benzimide, methylidimethylamine benzimide, phenylimidimethylamine benzimide, methylidismethylamine benzimide, methylidismethylamine benzimide, trimethylamine - 2 - methylbenzimide, N-methylpyrrolidone acetimide, N - ethylpyrrolidone acetimide, N - methyl-2-
The amimidine starting materials employed in the process of this invention are well known chemical compounds and can be prepared in accordance with the teachings of the prior art. In general, these amimidines are prepared by first forming an acyl hydrazine by the reaction of an acid anhydride or acid chloride with an unsymmetrical hydrazine. As this particular reaction is exothermic, it is preferred to cool the reaction mixture and to carry out the reaction in the presence of an inert, organic solvent capable of dissolving the reagents, such as ethers, ketones, esters, and the like.

The acyl hydrazine prepared in this manner can be converted to an amimidine by two routes. Firstly, the acyl hydrazine can be reacted with an alkyl halide in the presence of an alkali metal alkoxide to directly yield the amimidine. Secondly, the acyl hydrazine can be reacted with an alkyl halide, or an ester of a strong organic acid such as a sulfonic acid, to yield the hydrazonium salt. By diluting an aqueous solution of the hydrazonium salt with base, the amimidine is formed. Generally, the amimidine is isolated by extraction with a halogenated hydrocarbon such as chloroform. When the amimidine is to be substituted with one or more aryl groups, the aryl groups must be present in the original unsymmetrical hydrazine. The reason for this is that aryl halides cannot be used to alylate the acyl hydrazine. Generally, when the amimidines are made by the herein described sequence of reactions, at least one of B1, B2 and B4 will be alkyl.

The preparation of the amimidine starting material is illustrated by the following sequence of reactions:

\[
\begin{align*}
1. & \quad RCOO + HN-N \rightarrow R-CN-N \\
2. & \quad (RCO)O + HN-N \rightarrow R-CN-N + RCOH
\end{align*}
\]

In the above reaction scheme, X is halogen or an organic acid radical, and MeOR represents the alkali metal alkoxide.

By employing polybasic acid chlorides, such as the acid chlorides of phthalic acid, pyromellitic acid, malonic acid, succinic acid, adipic acid, and fumaric acid, in the above reaction scheme, polyamaminidines can be formed. These polyamaminimides are then pyrolyzed to produce polyisocyanates such as 1,2-diisocyanatobenzene, 1,4-diisocyanatobenzene, 1,3-diisocyanatobenzene, 1,2,4,5-tetraisocyanatobenzene, methylene diisocyanate, ethylene diisocyanate, propylene diisocyanate, and 1,2-diisocyanatooxyylene.

The following examples will point out, by way of illustration only, certain embodiments of this invention. Unless otherwise indicated, all parts are by weight.

**EXAMPLE 1**

Preparation of 1,1-dimethyl-2-benzoylhydrazine

140 grams (1.0 mole) benzoyl chloride in 300 milliliters absolute ether were added to an ice bath-cooled solution of 60 grams (1.0 mole) of unsymmetrical dimethyl hydrazine and 200 grams (1.37 moles) triethyamine in 1200 milliliters absolute ether, with stirring. The resulting mixture was stirred for 12 hours while warming to room temper-
at ure, followed by removal of the ether by distillation. 40 grams (1.0 mole) sodium hydroxide in 200 milliliters water was added to the remaining solid to form a 2-phase product. The phases were separated and the nonaqueous layer heated in vacuo to remove triethylamine. Benzene was added to the residue to recover product as the benzene azetrope. After the remaining benzene was removed in vacuo, 149 grams of a solid-off-white product, melting at 98° to 103° C., was recovered. The product was recrystallized from 100 milliliters acetone and 200 milliliters hex- ame, and purified 1,1-dimethyl-2-benzoylhydrazine melting at 104° to 106° C. was obtained. 105 grams of this material was recovered, resulting in a 64% yield.

EXAMPLE 2
Preparation of the hydrazinium salt of 1,1-dimethyl-2-benzoylhydrazine

The hydrazinium salt of 1,1-dimethyl-2-benzoylhydrazine was prepared by dissolving 114 grams (0.694 mole) 1,1-dimethyl-2-benzoylhydrazine and 130 grams (0.697 mole) methyl p-toluensulfonate in 100 ml benzene for 23 hours. Fine crystals separated during this refluxing period and were collected by filtration. After drying, 225 grams of crystalline product, melting at 180°-181.5° C., were recovered, giving a yield of 92.2%. After recrystallization from a mixture of chloroform and ethyl acetate, the hydrazinium salt weighed 224 grams and melted at 180.5° to 182° C. The product analyzed as follows:
Calculating C_{14}H_{14}N_{2}O_{5} (percent): C, 58.27; H, 6.33; N, 7.99. Found (percent): C, 58.18; H, 6.25; N, 7.79.

EXAMPLE 3
Preparation of the aminimide from the hydrazinium salt of 1,1-dimethyl-2-benzoylhydrazine

To 247 grams (0.705 mole) of the methyl-p-toluene-sulfonate derivative of 1,1-dimethyl-2-benzoylhydrazine in 200 ml water were added 28.2 grams sodium hydroxide. After the sodium hydroxide dissolved, the resulting solution was extracted from six 250 ml portions of chloroform and the chloroform extracts dried over sodium sulfate. The chloroform was removed by distillation with the last portion of chloroform being removed in vacuo. A residue of 91 grams remained. This residue was recrystallized from a chloroform-hexane mixture to give 56 grams of trimethylamine benzime melting at 166.5° to 168° C.

The aqueous layer from the chloroform extraction was evaporated to a crystalline paste on a steam bath, and the paste dried for four hours at 110° C. The residue was extracted with three 150 ml portions of chloroform. Upon removal of the chloroform by distillation, a residue of 38 grams was obtained. This residue was combined with the mother liquor residues from the original extraction product and the combined residue recrystallized from chloroform-hexane to give 25 grams of trimethylamine benzime melting at 166.5° to 168° C. The total yield of pure material was 81 grams, giving a yield of 64.5%.

EXAMPLE 4
Preparation of the trimer of phenyl isocyanate

Phenyl isocyanate was prepared by pyrolyzing trimethylamine benzime. In a distillation apparatus, 109 grams trimethylamine benzime were heated at 220°-230° C. A vigorous decomposition took place, producing a gaseous product (19.9 grams, 55% yield) which was collected in a cold trap at −78° C. and identified as trimethylamine and a liquid product which solidified in 20 minutes while hot. This solid weighed 44.2 grams and melted at 289°-290° C. when recrystallized from toluene. A 60.4% yield of this product was obtained. Infrared analysis confirmed that the solid product was the trimer of phenyl isocyanate.

EXAMPLE 5
Preparation of phenyl isocyanate

A mixture of 20.00 g. (0.112 mole) of trimethylamine benzime and 20.97 g. (0.225 mole) of anhydrous aniline was added to the aqueous solution of acetic acid where triethylamine decomposition ceased. The mixture was protected from moisture by means of a drying tube. Excess aniline was removed using reduced pressure and a white solid was obtained. This white solid product was recrystallized from methanol, filtered, and dried. The product yield was 21.30 g. corresponding to 0.100 moles or 89.7%. The melting point of the product was 240°-1° C. The structure was shown to be diphenylurea by its melting point, mixed melting point with the known compound (239.5-241° C.), NMR, and infrared spectrum. Equimolar portions of the diphenylurea product and hydrogen chloride were then reacted together using the procedure and apparatus set forth in U.S. Pat. No. 2,773,086 and phenyl isocyanate obtained thereby.

EXAMPLE 6
Preparation of phenyl isocyanate

Phenyl isocyanate was prepared by pyrolysing phenyltrimethylamine benzime (M.P. 156°-9°). In a distillation apparatus, 8.83 g. of phenyltrimethylamine benzime was heated at 170° C. and the volatile products (7.99 g.) were collected. Vapor phase chromatography analysis of the product indicated a mixture of 51.5% phenyl isocyanate and 48.5% dimethylamine. Distillation using an 8-plate column at reduced pressure (95 mm.) gave a 70% yield of phenyl isocyanate boiling at 94°-6° C. (95 mm.).

EXAMPLE 7
Preparation of 1-aceetamino-2-phenylpyrrolidine

To an ice bath-cooled, stirred solution of 75.0 grams (0.462 mole) 1-aceetamino-2-phenylpyrrolidine in 300 ml benzene was added dropwise a solution of 47.1 grams (0.461 mole) of acetic anhydride in 150 ml benzene, over a period of 2 hours. Stirring was continued for 30 minutes and the mixture allowed to stand overnight. Benzene solution was washed with a sodium carbonate solution and with water, followed by drying over sodium sulfate. The dried benzene solution was then distilled at atmospheric pressure to remove water, followed by distillation at reduced pressure to decrease its volume to 250 ml. To the resulting hot benzene solution were added 200 ml of hot cyclohexane, and the product allowed to crystallize slowly. 86.2 grams of white, needlelike product were collected by filtration, giving a yield of 91.2%. This product initially melted at 115°-117° C. and upon recrystallization from acetonitrile, the melting point was 116°-117.5° C. The product was identified as 1-aceetamino-2-phenylpyrrolidine.

Analytical: Calc'd for C_{14}H_{14}N_{2} (percent): C, 70.56; H, 7.90; N, 13.71. Found (percent): C, 70.41; H, 7.61; N, 13.60.

EXAMPLE 8
Preparation of the hydrazinium salt of 1-aceetamino-2-phenylpyrrolidine

A mixture of 77.0 grams (0.377 mole) of 1-aceetamino-2-phenylpyrrolidine and 100 grams (0.67 mole) methyl iodide in 200 ml dry ether and 100 ml acetonitrile was refuxed for 4 days. The heating was discontinued and the reaction mixture allowed to stand for one day. The mixture was then seeded and the product slowly crystallized. The reaction solvents were then decanted and 87.5 grams of white prisms melting at 137-139° C. were recovered. The reaction solvents were then refuxed for an additional two days, concentrated, and diluted with dry ether. An additional 11.6 grams of white prisms melting at 137-139° C. were recovered. The white prismatic material was identified as 1-aceetamino-2-phenylpyrrolidine. A 76% yield of this material was obtained.
EXAMPLE 9
Preparation of the aminimide, 1-methyl-2-phenylpyrrolidone acetamide

To 75.4 grams (0.218 mole) of 1-methyl-1-aminomethyl-2-phenylpyrrolidine iodide in 50 ml. water were added 9.0 grams of sodium hydroxide in 10 ml. water. An oil which separated from the aqueous reaction mixture was extracted with three 50-ml. portions of chloroform. The combined chloroform portions were dried over sodium sulfate, filtered, and concentrated to a colorless, viscous oil weighing 42.6 grams. This oil was identified as 1-methyl-2-phenylpyrrolidone acetamide. An 89.5% yield of this material was obtained.

Analyses—Calc’d for C_{10}H_{11}N_2O (percent): C, 71.53; H, 8.21; N, 12.83. Found (percent): C, 71.29; H, 8.49; N, 13.10.

EXAMPLE 10
Preparation of methyl isocyanate

49.4 grams (0.226 mole) 1-methyl-2-phenylpyrrolidine acetamide were distilled in vacuo at a pressure of 0.5 mm. at 180–230° C. 8.8 grams of methyl isocyanate were isolated in cold traps maintained at –78° C. A 67% yield of methyl isocyanate was obtained.

The foregoing examples have described in detail the preparation of phenyl isocyanate and methyl isocyanate. The methods and techniques described are wholly applicable to the preparation of corresponding isocyanates from any of the other previously mentioned aminimides. Thus, the process of this invention provides a novel route to the formation of valuable isocyanate compounds.

While the process of this invention has been described in detail as applied to the preferred embodiments, various modifications and changes in the process described will readily occur to those skilled in the art. Therefore, it is intended that the invention be limited only as indicated by the scope of the following claims.

What is claimed is:

1. The process for the preparation of an isocyanate having the formula R(N=CO)n wherein R is a member selected from the group consisting of aliphatic, cycloaliphatic, and aromatic groups which comprises: pyrolyzing an aminimide having the formula

   \[
   \begin{array}{c}
   \text{R} \\
   \text{O} - \text{N} - \text{N} - \text{R}_1 \\
   \text{R}_2
   \end{array}
   \]

   wherein R1, R2 and R3 are members selected from the group consisting of alkyl, aryl and radicals in which R3 and R3 are joined to form a heterocyclic ring, n is an integer of at least 1 and R is as defined above.

2. The process of claim 1 wherein at least one of R1, R2 and R3 is alkyl.

3. The process of claim 1 wherein said aminimide is a dialkylarylamide benzamide and said isocyanate is an untrimerized aryl isocyanate.

4. The process of claim 3 wherein said aminimide is phenyldimethylamine benzamide and said isocyanate is phenyl isocyanate.

5. The process of claim 4 wherein there is also formed during said pyrolysis, dimethylamine, and said phenyl isocyanate is separated therefrom in substantially pure form by simple distillation.

6. The process for the preparation of an isocyanate having the formula R(N=CO)n wherein R is a member selected from the group consisting of aliphatic and cyclo-

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