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METHOD OF CONVERTING SECONDARY AMINES TO NITRAMINES

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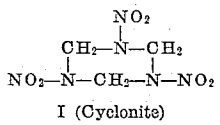
3 Claims. (Cl. 260—247)

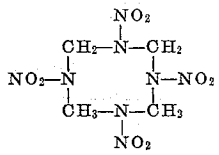
1

The present invention relates to nitramines and more particularly to a new and improved method of preparing the nitramines of secondary amines.

The nitramines comprise a group of organic compounds of considerable interest at the present time because of the great explosive strength and brisance of several members of the class; notably cyclonite (I), homocyclonite (II), Haleite (III) and DINA (IV).



I (Cyclonite)



II (Homocyclonite)

NO_2-NH-CH_2-CH_2-NH-NO_2

III (Haleite)

$(NO_2$-O-CH_2-$CH_2)_2$N-NO_2

IV (DINA)

All these indicated nitramines are considerably more powerful than TNT, with ballistic strengths ranging from about 1.3 to about 1.5 times that of TNT. The properties of these nitramines are more particularly described in the U. S. patents or patent applications:

(1) Bachmann application, Ser. No. 495,078, filed July 16, 1943 (Cyclonite);

(2) Wright et al. application, Ser. No. 560,704, filed October 27, 1944 (Homocyclonite);

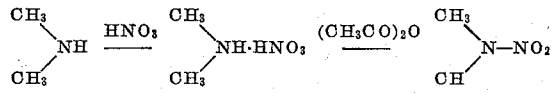
(3) Hale U. S. Patent No. 2,011,578 (Haleite); and

(4) Wright et al. application Ser. No. 570,813, filed of even date herewith (DINA).

Because of the increasing importance of this class of compounds as a whole, new methods of preparing various types of nitramines are of particular interest, and the provision of a greatly improved method of preparing one particular subclass of nitramines may be said to constitute one of the objects of the present invention.

2

A more particular object is the provision of a substantial improvement in, and extension of, a method originally described by Bamberger (Ber. 28, 399, 537 (1895) for the preparation of dimethylnitramine from dimethylamine nitrate by treating the latter with a lower fatty acid anhydride (acetic anhydride) according to the scheme:



The yields obtained by Bamberger in this preparation were not reported, but when his directions are repeated, yields of dimethylnitramine varying from zero to perhaps 6% are obtained. Moreover when an attempt is made to extend Bamberger's procedure to the preparation of related or homologous nitramines, either no product is obtained or very low yields are realized and the results are not reproducible. In short the method has heretofore been an isolated reaction that is entirely impractical as a preparative procedure, even on a laboratory scale. It is therefore an object of the present invention to provide a practical, reliable and general method of converting amines to the corresponding nitramine in consistently high yields.

Still another object of the present invention is to provide a catalyst that increases the yield, improves the reliability and greatly extends the applicability of the reaction by which a secondary amine nitrate is converted to the corresponding

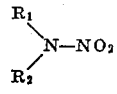
nitramine by treatment with a dehydrating acid anhydride.

Other objects and advantages will be apparent as the invention is hereinafter more particularly described.

The foregoing objects may be accomplished in accordance with the present invention by carrying out the amine nitrate-anhydride reaction in the presence of a small proportion of a chlorine-containing compound as a catalyst. In its most convenient form, the catalyst added to the reaction mixture consists of hydrogen chloride and/or any substance that is capable of forming or liberating hydrogen chloride. As a matter of convenience, such substances will hereinafter be referred to broadly as "chlorine-containing catalysts," or in their most convenient form, as "Chloride catalysts," these terms being understood to include hydrogen chloride itself.

The invention is based upon the discovery that if catalytic amounts of chlorine-containing materials such as the chlorides are added to the reaction mixture wherein a secondary amine nitrate is being treated with a lower fatty acid anhydride, greatly enhanced and consistently reliable yields of the corresponding nitramine are obtained.

Actually under the reaction conditions, when the preferred catalysts of the present invention (the chlorides) are added to the reaction mixture, they may be present therein in their original form, or as HCl, or as acids or compounds containing chlorine in a state of oxidation higher than Cl^-; for example, as hypo-chlorites, chlorates, or the like. Regardless of the form or the state of oxidation of the chlorine atom in the reaction mixture under reaction conditions, the addition of the catalysts of the present invention to the amine nitrate-anhydride reaction mixture results in a very significant improvement in the yield, vastly improves the reproducibility of the results, and converts what was formerly an impractical and isolated reaction into a reliable and general preparative method for producing nitramines, especially those of the type:



Inasmuch as HCl or any material capable of liberating HCl constitutes the preferred catalyzing agent of the present invention, it will be apparent that a wide variety of compounds may be selected as the catalyst. Among these, the following types may be mentioned purely by way of an example: metal and metalloid chlorides such as those of sodium, potassium, rubidium, caesium, barium, strontium, magnesium, zinc, boron, silicon, tin, lead, sulfur, phosphorous, aluminum, iron, nickel, cobalt, chromium, vanadium and the like, hydrochloride salts of basic nitrogen compounds such as ammonium chloride and amine hydrochlorides (including either the chloride of the secondary amine undergoing treatment or any other amine hydrochloride); fatty acid chlorides such as acetyl chloride; and a wide variety of obviously equivalent compounds, all of which will hereinafter be referred to generally as chlorides.

Although all of the foregoing types of compounds are effective as catalysts in accordance with the present invention, it has been found that certain chlorides are more efficient than others, either because of solubility or other factors, or because of inherent differences. Thus hydrochloric acid, fatty acid chlorides such as acetyl chloride, the salts of basic nitrogen compounds such as amine hydrochlorides, and the readily hydrolyzable metal chlorides such as those of zinc, ferric iron, aluminum and the like give especially good results. For these reasons the more efficient chloride catalysts enumerated above constitute the preferred catalysts for use in accordance with the present invention. It is apparent that these catalytic agents in the mass containing nitric acid form hypochlorous acid and with lower fatty acid anhydride also present form an ester of hypochlorous acid.

In some instances it is most convenient initially to prepare and isolate the secondary amine nitrate, and then subsequently to treat the isolated nitrate salt with a lower fatty acid anhydride and a small amount of the chloride catalyst. In other cases, however, it may be preferable to treat the secondary amine simultaneously with a nitrating agent such as concentrated nitric acid, a lower fatty acid anhydride and a small amount of the selected chloride catalyst. In this latter case in particular, it is conceivable that the chloride may be converted by the reaction mixture to a compound or compounds containing chlorine in a higher state of oxidation than Cl^-. Be that as it may, however, the conversion of the secondary amine nitrate to the corresponding nitramine takes place to a far greater extent and in much more reliable and reproducible manner if a chloride is added to the reaction mixture, regardless of whether the amine nitrate is (1) separately prepared and isolated before being treated with anhydride in the presence of the chloride or is (2) formed in situ by treatment with a nitrating agent in the presence of the anhydride and the added chloride catalyst.

As above indicated the catalyzed reaction of the present invention appears to be generally adaptable to the conversion of secondary amines or secondary amine nitrates to the corresponding nitramine. Indeed the wide scope of the reaction will be apparent from the number of specific examples which will be described hereinafter, these examples serving to illustrate the wide variety of nitramines obtainable by means of the present process. In some instances the nitramines described in the examples are old compounds, these particular examples providing an indication of the improvement in yield obtainable by means of the catalyst of the present invention. In other instances the nitramines given in the examples constitute new compounds which illustrate the broad scope and utility of the catalyzed process of the present invention.

In order more clearly to disclose the nature of the present invention a number of specific examples will now be described in particular detail. It should be clearly understood, however, that this is done solely by way of example and not for the purpose of restricting the ambit of the appended claims.

EXAMPLE 1

Preparation of dimethyl-, diethyl-, and di-n-butyl-nitramines

Two procedures were used in the preparation of dimethyl-, diethyl-, and di-n-butyl-nitramine.

In one case the nitrate salt of the appropriate amine was first prepared. This was done by exactly neutralizing the aqueous solution of the

amine with 70% nitric acid. Water was distilled from the amine nitrate under reduced pressure and the salt subsequently dried in a vacuum desiccator above sulfuric acid. The amine nitrate was then added to acetic anhydride containing 0.04 mole or zinc chloride or 0.06 to 0.08 mole of the hydrochloride of the same amine, and 0.05 to 0.10 mole of 98 to 100% nitric acid per mole of amine nitrate. Slightly more than 1 mole of acetic anhydride per mole of amine nitrite was used. The mixed reagents were allowed to stand at room temperature for 24 hours or they were heated at 40 to 50° C. for a shorter period. The reaction products were poured onto ice and water and the diluted products were neutralized with sodium carbonate and extracted with ether. The ether solution was dried over anhydrous sodium sulfate and then flash distilled, the liquid products being distilled either under atmospheric or reduced pressure.

The second preparation was a modification of the one described in the preceding paragraph. The proportions were in general those already given. The secondary amine and 98 to 100% nitric acid in slight excess over that required to neutralize the amine, were added at proportional rates to acetic anhydride containing a chloride catalyst. In a still further variation, used during preparations of di-n-butyl-nitramine, the amine was first neutralized and dissolved in 2 molar equivalents of glacial acetic acid. The solutions of amine acetate and nitric acid were then run into acetic anhydride at proportional rates. This latter modification was used when larger proportions of nitric acid were employed since charring and ignition occurred with these proportions when the amine and the concentrated nitric acid were added at the same rate. The products were worked up as already described. In preparing dimethylnitramine excellent results were obtained by passing gaseous dimethylamine into a premixed solution of acetic anhydride and nitric acid containing zinc chloride. The proportions of reagents, the conditions of the reaction and the yields are given in Table I which follows.

exactly neutralizing an aqueous solution of di-n-butylamine with 70% nitric acid. The neutral solution was evaporated under reduced pressure to give the amine nitrate which was dried in vacuum oven and then crystallized from benzene. The crystallized material melted at 164–166° C. To convert this compound to the corresponding nitramine, 28.8 g. (0.15 mole) of the nitrate was added to 16.3 g. (0.16 mole) of acetic anhydride along with 0.78 g. (0.006 mole) of zinc chloride and 0.20 cc. (0.0047 mole) of 99% nitric acid. The mixed reagents were protected against atmospheric moisture and left at room temperature. Undissolved nitrate remained after two hours for which reason the mixture was heated to 40° C. for one hour. The resulting solution was poured into 100 cc. of water producing two liquid layers. The upper liquid layer was separated, dissolved in ether and the lower or aqueous layer was extracted four times with a total of 100 cc. of ether. The combined ethereal solutions were shaken with aqueous sodium carbonate until neutral, washed with water and dried over anhydrous sodium sulfate. Flash distillation of the ethereal solution left 15.8 g. of a yellow liquid which was distilled at 120 to 127° C. at 7 to 8 mm. pressure. The distillate was then fractionally distilled three times from a modified Claisen flask having a 12" side arm containing indentations of the Vigreux type. A fraction 3.52 g. was obtained at 121° C. under 7 mm. pressure. This colorless liquid was decomposed on warming in concentrated sulfuric acid with the evolution of colorless gas and without charring.

In this preparation as well as in others, the crude product obtained in the reaction consisted of a mixture of the desired nitramine and the acetamide of the secondary amine used in the preparation. In the case of di-n-butylnitramine, the proportion of di-n-butylacetamide was determined by decomposing the nitramine with sulfuric acid. 1 g. of the crude nitramine was heated at reflux for three hours with 10 cc. of glacial acetic acid and 5 cc. of sulfuric acid. The product was diluted with 150 cc. of water,

[Quantities of reagents are given in moles of reagent per mole of amine. Chloride is given as atoms of chlorine per mole of amine. The symbols A, N, A-HOAc in the second column indicate respectively the use of amine, amine nitrate, or a solution of amine acetate in glacial acetic acid.]

Nitramine	Amine as—	HNO_3	Chloride	Ac_2O	HOAc	Time of Reaction, hrs.	Temp. of Reaction, ° C.	Yield Nitramine, percent	Yield Acetamide, percent	Amine Recovered, percent	Yield of products on unrecovered amine
Dimethyl	N	1.00	0.01	2.00	0	29	25	51			
	A	1.00	0.01	2.40	0	24	25	65			
Diethyl	N	1.05	0.08	2.50	0	2.5	50–55	52	4		
	A	1.08	0.06	1.10	0	1.5	40	0	35	45	64
	N	1.03	0.08	1.07	0	2	25	39	10		
						1	40				
	A	1.10	0.04	2.50	0	1	40	9	66		
	A-HOAc	3.0	0.20	1.40	2	0.25	50	13	24	38	60
Dibutyl	A-HOAc	3.0	0.20	1.30	2	1.25	25	18	2	54	43
						1.5	40–50				
	A-HOAc	3.0	0.12	1.30	2	4	50	12	3	67	45
	A-HOAc	3.0	0.20+HCl [1]	1.30	2	4	50	22	52	9	81
	A-HOAc	3.0	2.0	1.30	2	0.25	25	4	19	27	32
						0.25	40				
N-nitromorpholine	N	1.6	0.06	10.0	0	0.5	30	65			
						0.25	55				

[1] Slow and continuous addition of gaseous hydrochloric acid.

Since di-n-butylnitramine is a new compound its preparation will be described in greater detail. Di-n-butylnitramine nitrate was prepared by neutralized with 50% potassium hydroxide and extracted with water, evaporation of the dried ether solution leaving the di-n-butylacetamide.

The acetamide could be recovered in 97% yields from this treatment whereas the di-n-butylnitramine was completely destroyed. Using this procedure it was determined that the yield of di-n-butylnitramine in the foregoing preparation was 11.2 g. or 39% of the theoretical, while the yield of di-n-butylacetamide was 2.6 g. or 10%.

The elemental analysis of the fraction boiling at 121° C. at 7 mm. pressure corresponded to that for di-n-butylnitramine.

Anal. calcd. for $C_8H_{18}N_2O_2$:C, 55.1; H, 10.4; N, 16.1. Found: C, 55.3; H, 10.0; N. 16.3, 16.4.

EXAMPLE 2

Preparation of N-nitromorpholine

Morpholine nitrate was prepared by adding 67 cc. (0.77 mole) of morpholine to 34 cc. (0.77 mole) of 70% nitric acid. Vigorous stirring was employed and the temperature was held at 0 to 5° C. 17 cc. of water was added to secure mixing of the reagents. The nitrate was filtered off, washed with ether and dried to give a yield of 64 g. or 55% of the theoretical. Morpholine nitrate is very soluble in water and insoluble in cold ethanol. It melted at 138–138.5° C.

The preparation of nitromorpholine was carried out in a 1-l., 3-necked flask protected against moisture and provided with an efficient stirrer. 46.9 g. (0.46 mole) of acetic anhydride was placed in the flask. To the contents maintained at a temperature of 0 to 5° C., 9.9 cc. (0.25 mole) of 99% nitric acid was added dropwise. To the resulting solution was then added 64 g. (0.42 mole) of morpholine nitrate and 1.73 g. (0.013 mole) of anhydrous zinc chloride. The mixture was warmed to 30° C. for 30 minutes after which heat was applied and the temperature of the reaction mixture raised to 55° C. for 15 minutes. The reaction products were cooled and drowned in 1 l. of water, producing a clear solution which was extracted 12 times with 50 cc. portions of chloroform. The solvent in the extract was evaporated leaving a solid residue melting at 49–50° C. The crude product was purified by solution in hot ethanol (1.6 cc./g.), crystallization being induced by cooling to Dry Ice temperature. The purified product weighed 36.1 g., corresponding to a yield of 65% of the theoretical. Recrystallization from ethanol raised the melting point to 52.7–53.5° C.

The morpholine nitrate may be prepared in situ by addition of 1.07 mole of 99% nitric acid in 0.4 mole of acetic acid to 1 mole of morpholine in 1.68 mole of glacial acetic acid. This solution at 35° C. was added to 1.1 mole of acetic anhydride, containing 0.04 mole of zinc chloride, at 28–30° C. over a period of 30 minutes. The temperature was then raised to 55° C. for fifteen minutes. Acetic acid was then removed under 15 mm. vacuum and the residue steamed under reflux for fifteen minutes in a total of 550 cc. water and cooled to 7° C. A yield of 65% nitromorpholine was filtered off.

Nitromorpholine appears to be a new compound. It gives a positive Franchimont test provided water is added along with the reagents. The compound is stable at 97° C. It may be detonated by impact although with difficulty.

Anal. calcd, for $C_4H_8N_2O_3$:C, 36.3; H, 6.10; N. 21.2. Found: C, 36.2; H, 5.85; N, 21.4.

Alternatively one may nitrate chloromorpholine by adding with stirring to 17.6 cc. (0.4 mole) of 99% nitric acid at 10° C., 4.88 gms. (0.04 mole) of chloromorpholine B. P. 38–40° C. at 11 mm. After 12 minutes addition time at 10° C. the resulting solution was digested for 2 hours at 0° C. and then warmed to 40° C. over 35 minutes. After 20 minutes at temperature the whole was poured into 150 gms. of ice and water. After neutralization to pH 9 the product was separated by chloroform extraction. Upon evaporation of the chloroform the residue was fractionately distilled to give a 49% yield of nitromorpholine, B. P. 112° C. at 11 mm. and M. P. 50° C. A lower boiling fraction (33% by weight) boiled at 103 to 110° C. but was not identified. The chloromorpholine used herein was prepared by interaction of morpholine with hypochlorous acid.

EXAMPLE 3

Conversion of dinitroxydiethylamine nitrate to DINA

The contents of a mercury-sealed 5 l. flask containing 3780 g. (60 moles) of 99–100% nitric acid was stirred at 10 to 12° C. while 420 g. (4.0 moles) of diethanolamine, M. P. 26.5° C., was added over a 2½ hour period. Moisture was excluded. The reaction mixture was subsequently stirred for 1 hour at 40° C. and then poured on 6 kg. of ice. The white crystalline precipitate was filtered immediately at the lowest possible temperature, washed with 500 cc. of ice water, then with 300 cc. of ethanol and finally with 200 cc. of ether. After drying the resulting product to a constant weight in a current of air a yield of 846 g., corresponding to 82% of the theoretical, was obtained; M. P. 118°–119° C.

25.8 g. (0.10 mole) of dinitroxydiethylamine nitrate prepared as described in the preceding paragraph was added to a solution of 0.63 g. (0.01 mole) of 99–100% nitric acid and 0.54 g. (0.004 mole) of zinc chloride in 25.5 g. (0.25 mole) of acetic anhydride. The salt dissolved after the mixture was heated to 55° C. for five minutes. The solution was poured into 60 cc. of water and the water-insoluble portion cooled and stirred until it solidified. This solid was filtered off, washed with water until neutral to bromocresol green and dried to a constant weight. The crude DINA thus obtained weighed 22.1 g., corresponding to a yield of 92% of the theoretical. The crude product, melting at 49 to 51° C., was purified by repeated crystallizations from methanol, methanol-ether and benzene-petroleum ether (60–70° C.) The melting point of the purified product was 51–52° C.

DINA is more particularly described and claimed in our copending application, Ser. No. 570,313, filed of even date herewith, to which reference may be made for a detailed description of its properties.

The effectiveness of various materials as catalysts in the preparation of nitramines from secondary amines in accordance with the present invention is indicated in Table II. The data for each of the runs tabulated in this table was obtained by adding 5.16 g. (0.02 mole) of dinitroxydiethylamine nitrate to 6.12 g. (0.06 mole) of acetic anhydride along with the indicated proportion of other reagents. The mixture was heated in a bath at 55° C. until solution was complete. The duration of the heating is indicated in the table under the heading "reaction time." The reaction mixture was diluted with 2 volumes of water causing separation of the DINA, which was then filtered and dried.

TABLE II

Catalysis of the conversion of dinitroxydiethylamine nitrate to DINA

[The data for each of the runs tabulated below was obtained when 5.16 g. (0.02 mole) of dinitroxydiethylamine nitrate was added to 6.12 g. (0.06 mole) of acetic anhydride along with the listed proportion of other reagents. The mixtures were heated in a bath at 55° until solution was complete. The duration of the heating is the tabulated reaction time. Dilution with two volumes of water caused separation of the DINA which was filtered off and dried.]

Run	Moles HNO_3 / Moles Salt	Catalyst	Moles Catalyst / Moles Salt	Reaction Time, min.	Yield, Per cent
1				120	8.7
3	0.2			157	17.9
3		$ZnCl_2$	0.04	10	80.0
4	0.1	do	0.04	4	92.0
5	0.2	Al_2Cl_6	0.015	1	92.0
6	0.3	$FeCl_3$	0.03	3	79.0
7		NaCl	0.1	30	22.5
8		CH_3COCl	0.03	14	44
9		BF_3	0.05	15	0
10		$ZnBr_2$	0.03	20	6
11		ZnI_2	0.03	19	0
12		$ZnCl_2$ + NH_4Cl	0.04 + 0.10	22	77.5
13		$ZnCl_2$ + NH_4HOAc	0.04 + 0.10	16	55
14		$ZnCl_2$ + urea	0.04 + 0.10	19	8.9
15		$ZnCl_2$ + pyridine	0.04 + 0.10	13	24.9
16	0.15	$ZnCl_2$ + pyridine	0.04 + 0.10	4	81.3
17	0.15	$ZnCl_2$ + urea	0.04 + 0.10	12	58
18		$ZnCl_2$ + sulphamic acid	0.04 + 0.10	26	80.2
19		$ZnCl_2$ + dinitroxy-diethylamine	0.04 + 0.10	18	79.6

EXAMPLE 4

One-stage preparation of DINA

A 2 gal. stainless steel jacketed kettle fitted with thermometer and paddle stirrer rotating at 150 R. P. M. was equipped with 2 graduated dropping funnels. One of the funnels was filled with 823 g. (7.84 moles) of diethanolamine and the other with 1648 (25.6 moles) of 98% nitric acid (nitrous acid 0.11%). 2754 g. (27 moles) of acetic anhydride was placed in the kettle and cooled to 5° C. by means of tap water in the jacket of the kettle. 62 g. of nitric acid was then run into the kettle followed by 23 g. (0.16 mole) of diethanolamine hydrochloride. Then the diethanolamine and the remainder of the nitric acid was added at proportional rates during 45 minutes. Tap water at 5° C. sufficed to supply cooling which maintained the reaction temperature at 15–18° C. When the addition was complete the temperature was raised to 40° C. for 10 minutes. The products were then valved at 6480 cc. of water at 5° C. which was stirred during the ten minutes dilution period. The product was filtered at 22° C. and washed with 25–30 l. of water until neutral to bromocresol green. An aliquot of the damp crude material was dried in a vacuum pistol above refluxing ether. After deducting the moisture content it was computed that the crude yield was 1737 g. corresponding to 90.5% of the theoretical. The filtrate was cooled to 0° C. whereupon it deposited 25 g. of DINA thereby raising the yield to 1762 g. or 97.8%. The crude product melted at 49.5–51.5° C.

The preparation was equally successful when 95% nitric acid was used provided enough additional acetic anhydride was added to compensate for the water present in the 95% nitric acid.

In carrying out the method of the invention it is not necessary to have present a lower fatty acid anhydride. It is necessary to maintain the reaction conditions such that water released as the product is formed does not alter the active form of the reagents. In the following example the presence of a substantial amount of concentrated nitric acid and the hydrochloric acid insures such conditions.

EXAMPLE 5

Preparation of DINA from diethanolamine using nitric and hydrochloric acids

105 g. (1.0 mole) of diethanolamine was added dropwise to 954 g. (15 moles) of 99% nitric acid maintained at 20° C. The resulting solution was cooled to 0–5° C. and hydrochloric acid gas passed into the solution until the increase in weight was 36.5 g. (1.0 mole of hydrochloric acid). The reaction mixture was then heated to 55° C. for 20 minutes and poured onto 1900 g. of ice. The crude DINA was filtered off; it melted at 49–51° C. and weighed 100.8 g., corresponding to a yield of 42% of the theoretical.

Small yields of DINA were obtained when the hydrochloric acid was replaced by phosphorus pentachloride, phosphorus trichloride phosgene and chlorine while no yield was obtained with sulfuryl chloride or thionyl chloride.

EXAMPLE 6

Preparation of nitropiperidine

A 58% yield of the known N-nitropiperidine may be obtained from the corresponding nitrate by treatment with acetic anhydride in the presence of a chloride catalyst. If the same reaction is carried out without a chloride catalyst, a yield of only 4% of the product is obtained.

The details of the preparation of N-nitropiperidine are as follows:

Piperidine nitrate was prepared in 70% yield by neutralizing piperidine with an equivalent of 70% nitric acid at 25° C. and evaporating to dryness under 20 mm. with ether and then crystallized from hot absolute ethanol (4 g. 1 cc.) to melt at 155°–157° after ether-washing and vacuum drying.

To 5 g. (0.034 mole) of this piperidine nitrate (with or without 0.24 g. (0.0017 mole) of anhydrous zinc chloride, was added 10 g. (0.098 mole) of acetic anhydride. After ten to fifteen minutes stirring to complete solutions, the reaction mixture was heated to 60° for thirty minutes with slight evolution of nitrogen oxides. The solution was then cooled and neutralized with sodium hydroxide and finally with carbonate solutions to pH 7.6. After an hour the aqueous solution was extracted ten times with a total of 100 cc. ether, which solution after extraction with 10% sulfuric acid (to remove piperidine) was dried with calcium chloride and evaporated to dryness. The oil was saturated with hydrogen chloride in order to precipitate the nitrosopiperidine hydrochloride. The oil was filtered off as crude nitropiperidene which could be purified by vacuum distillation (110° under 15 mm. pressure).

A similar pair of catalyzed and uncatalyzed experiments were carried out wherein the reaction mixture was let stand twelve hours at 25° before final heating to 60° C.

The results are tabulated as follows:

	Percent yield after 45 min. reaction time		Percent yield after 765 minutes reaction time	
	nitramine	nitrosamine	nitramine	nitrosamine
catalyzed	58	2	57	10
uncatalyzed	4	trace	22	1.6

While acetic acid anhydride has been specified in specific examples, and are preferred under existing market conditions, it is to be understood that other lower fatty acid anhydrides, such as proprionic acid anhydride and butyric acid anhydride may be used. Furthermore, although symmetrical secondary amines have been used in the examples, it is to be understood that the method of the invention is equally applicable to unsymmetrical secondary amines.

It will be apparent to those skilled in the art

that many variations in proportions, conditions and reactants may be made in the foregoing preparations without departing from the spirit and scope of the invention. All such modifications are to be understood as included within the scope of the appended claims.

We claim:

1. In the preparation of a secondary nitramine of a compound of the group consisting of di-n-butylamine and morpholine, the method which comprises reacting the nitrate salt of one of said compounds with nitric acid and a lower fatty acid anhydride in the presence of a catalyst selected from a group consisting of hydrogen chloride and the chlorides of zinc, iron and aluminium.

2. A method as defined in claim 1 wherein the reaction mixture contains substantially 0.15 mole of di-n-butylamine nitrate, 0.0047 mole of 98% nitric acid, 0.16 mole of acetic anhydride and 0.006 mole of zinc chloride.

3. A method as defined in claim 1 wherein the reaction mixture contains substantially 0.42 mole of morpholine nitrate, 0.25 mole of 99% nitric acid, 0.46 mole of acetic anhydride and 0.013 mole of zinc chloride.

GEORGE F. WRIGHT.
WALTER JOHN CHUTE.

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The following references are of record in the file of this patent:

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Number	Name	Date
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