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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: MANUFACTURING METHOD FOR 4-NITROSOANILINE FROM UREA AND NITROBENZENE

(57) Abstract: Disclosed herein is a method for preparing 4-nitrosoaniline, comprising reacting urea and nitrobenzene in a polar organic solvent in the presence of a base at a temperature of room temperature to 150 °C. The method uses a relatively cheap urea and nitrobenzene as the raw materials, and also a relatively cheap base, thereby decreasing the manufacturing cost. Urea used as an amine donor is excellent in a reactivity to nitrobenzene, and a reaction intermediate is unstable as compared with 4-(4-nitrophenyl)benzamide to easily decompose into 4-nitroaniline and 4-nitrosoaniline. This allows a reaction time and a process time to be shortened. Moreover, the method is advantageous in that waste hazardous to the environment is not produced as a byproduct.

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MANUFACTURING METHOD FOR 4-NITROSOANILINE FROM UREA
AND NITROBENZENE

Technical Field

The present invention relates to methods for
5 preparing 4-nitrosoaniline and, more particularly, relates
to a method of selectively preparing 4-nitrosoaniline
wherein urea is reacted with nitrobenzene in a polar
organic solvent in the presence of a base.

Background Art

10 4-Nitrosoaniline is used in some applications, such
as an intermediate for the preparation of dyestuffs or for
the preparation of a hair dye, and a light stabilizer.
However, it had not been greatly studied in its
applications, due to a difficulty in its preparation.

15 It is known to prepare 4-nitrosoaniline by
synthesizing N-nitrosoaniline from aniline and sodium
nitrite (NaNO_2) and subsequent Fischer-Hepp rearrangement
(Tetrahedron, 1975, 31, 1343-9, and US Patent No.
3,338,966). This method is disadvantageous in that a
20 denitrososation occurs during the Fischer-Hepp
rearrangement, and waste containing a nitroso (NO)
compounds harmful to the environment can be generated in
great quantities.

It is also known to prepare 4-nitrosoaniline by
25 reaction of p-nitrosophenol and ammonia or ammonium
chloride (J. Chem. Soc., 1955, 2049). This method is
disadvantageous in that the yield of 4-nitrosoaniline is
too low.

Recently, it is found that 4-nitrodiphenylamine (4-
30 NDPA), a precursor of 4-aminodiphenylamine which is

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utilized for the preparation for antiozonants for rubber, is produced by reacting aniline and nitrobenzene in the presence of a base via a nucleophilic aromatic substitution for hydrogen (NASH). Compared with other
5 methods for preparing 4-NDPA, the NASH process provides dramatic reductions (90% or more) in generated chemical waste and wastewater, eliminates the use of an environmentally unfavorable chemical (chlorine), and improves process safety. In addition, this method is
10 advantageous in that a process for separating 4-chloronitrobenzene from an isomer mixture is not required, and also the purity of a final product is extremely high.

Among reactions of using the NASH, it is well-known to prepare 4-NDPA and 4-nitrosodiphenylamine (4-NODPA) by
15 a direct reaction of aniline with nitrobenzene in the presence of tetramethylammonium hydroxide (TMA(OH)). See, J. Am. Chem. Soc., 1992, 114(23), 9237-8; US Patent No. 5,117,063; US Patent No. 5,253,737; US Patent No. 5,331,099; US Patent No. 5,453,541; US Patent No.
20 5,552,531; and US Patent No 5,633,407.

It is reported that the ratio of 4-NDPA and 4-NODPA produced in the reaction can be controlled by the molar ratio of aniline to nitrobenzene. For example, where a molar ratio of aniline to nitrobenzene is about 1, yield
25 of 4-NODPA and 4-NDPA are shown to be 15 mole% and 80 mole%, respectively. On the other hand, where a molar ratio of aniline to nitrobenzene is about 50, 4-NODPA and 4-NDPA are obtained in yields of 86 mole% and 9 mole%. The selectivity to final products is known to be dependent
30 on whether a hydride ion (H^-) of an intermediate adduct formed from aniline and nitrobenzene is leaving via an intramolecular reaction or an intermolecular reaction.

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It is also known to prepare 4-nitroaniline from nitrobenzene and benzamide in the NASH reaction. This is carried out by a two step reaction consisting of synthesizing N-(4-nitrophenyl)benzamide as a stable
5 intermediate, and then adding water(or ammonia) to decompose the adduct into 4-nitroaniline and benzoic acid (or benzamide). See, J. Am. Chem. Soc., 1992, 114(23); J. Org. Chem., 1993, 58, 6883-6888; US Patent No. 5,436,371; US Patent No. 5,380,946; and PCT publication WO 93/24447.
10 In the reaction, the yield of N-(4-nitrophenyl)benzamide is about 98% when moisture was completely removed, whereas the yield of N-(4-nitrophenyl)benzamide is only about 20% when prepared under an oxygen atmosphere without removal of moisture. From these results, it was shown that making
15 a moisture-free reaction condition was particularly important. Moreover, this reaction was reported to produce 4-nitroaniline without referring to the production of 4-nitrosoaniline.

Meanwhile, 4-nitrosoaniline is subjected to a
20 hydrogenation process to produce p-phenylenediamine (PPD). PPD is broadly used as a raw material for cosmetics and antioxidants, and additives to fuel, and also has a great utility in a dye application due to its property of being capable of being easily oxidized to form a colorant.
25 Also, PPD has the greatest utility for manufacturing aramid as a functional fiber that has high chemical resistance, high thermal resistance and high strength, as well as for producing phenylene diisocyanate that is a raw material for polyurethane.

30 Disclosure of the Invention

We have made diligent efforts to find an improved

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method for preparing 4-nitrosoaniline, as compared with the prior methods problematic in that a nitroso compound hazardous to the environment is produced as a byproduct after the reaction, a reaction is very difficult to produce, and also the yield of 4-nitrosoaniline is low. As a result, we have found that a direct reaction of urea with nitrobenzene in the presence of a base could produce 4-nitrosoaniline, and also have found that, when using an alkali metal or an alkaline earth metal as the base and appropriately controlling the amount of urea and nitrobenzene used, 4-nitrosoaniline could be produced in a high yield and selectivity, whereby the present invention was achieved.

The present invention is advantageous in that 4-nitrosoaniline can be produced in high yield with little or no ortho compounds, such as 2-nitroaniline and 2-nitrosoaniline, and hydrogenated to PPD with high purity. Moreover, the present invention is useful in that a reaction is not influenced by moisture content to a great degree, and it is not necessary to make a reaction condition moisture-free state. Additionally, the method has an advantage in that a two step reaction, in which an intermediate is formed and then decomposed, is not performed, such that the reaction can be achieved in one reactor in a short period of time.

Best Mode for Carrying Out the Invention

The foregoing and other objects, features and advantages of the invention will be apparent to those skilled in the art to which the present invention relates from reading the following specification.

The present invention relates to a method of

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preparing 4-nitrosoaniline from urea and nitrobenzene in a polar organic solvent in the presence of a general base.

The present invention applies the NASH reaction to producing selectively 4-nitrosoaniline under mild
5 conditions as compared with those of the prior method, by reacting urea with nitrobenzene in the presence of a cheap alkali metal base.

Urea that can easily lose a proton in the presence of a base, is excellent in a reactivity with nitrobenzene,
10 and is not substantially influenced by moisture content. Moreover, an adduct of urea and nitrobenzene is unstable, such that it is easily decomposed into 4-nitroaniline and 4-nitrosoaniline by moisture generated during a reaction. This thus allows the reaction time and the process time
15 to be shortened.

In accordance with the present invention, an appropriate control of a molar ratio of nitrobenzene/urea used can play a critical role in a selectivity to a final product. Where a molar ratio of nitrobenzene/urea is in
20 excess of 1, produced are mainly 4-nitroaniline and 4,4'-dinitrodiphenylamine (hereinafter, called "DNDPA"). However, where a molar ratio of nitrobenzene/urea is less than 1, a main product is 4-nitrosoaniline.

A variety of polar organic solvents can be used in
25 the practice of the present invention. Among these solvents, examples of the polar organic solvents preferred in view of a miscibility with the base include, but are not limited to, dimethylsulfoxide (hereinafter, called "DMSO"), N,N-dimethylformamide (hereinafter, called
30 "DMF"), and N-methyl-2-pyrrolidinone (hereinafter, called "NMP"). A reaction in DMSO results in the highest reactivity and yield. The weight ratio of the solvent to

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urea used is in the range of about 50:1 to about 1:1, with the preferred ratio being in the range of about 30:1 to about 1:1.

Examples of the base used in accordance with the present invention include, but are not limited to, alkali metal and alkaline earth metal bases, such as sodium hydroxide(NaOH), potassium hydroxide(KOH), potassium t-butoxide(t-BuOK), and sodium hydride(NaH), and TMA(OH). The molar ratio of the base to urea used is in the range of about 1:1 to about 10:1, with the preferred ratio being in the range of about 1:1 to about 4:1.

The amount of nitrobenzene used in accordance with the present invention has a great effect on a selectivity to the final product. A molar ratio of nitrobenzene to urea used in excess of 1 increases a selectivity to 4-nitroaniline and accelerates a production of DNDPA. On the other hand, a molar ratio of nitrobenzene to urea less than 1 results in an excellent selectivity to 4-nitrosoaniline.

To remove moisture produced upon the beginning of or during the reaction from the reaction solution, a vacuum distillation is performed, or a drying agent is used. Materials useful as the drying agent, for example, include anhydrous calcium carbonate, anhydrous sodium sulfate, anhydrous magnesium sulfate, sodium hydroxide, potassium hydroxide, sodium hydride, molecular sieve, and the like. However, as the method of the present invention is not influenced by the amount of moisture to a great degree during the reaction, the use of the drying agent or a continuous distillation to remove moisture from the reaction solution results in a little increase in yield. The reaction can be carried out under a nitrogen or oxygen

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atmosphere or in the air. Additionally, a molar ratio of the moisture to the base in excess of 3 results in a decrease in a reaction rate.

The reaction in accordance with the present invention is carried out under an atmosphere through which oxygen or nitrogen is passed. Under the nitrogen atmosphere, there is produced a byproduct, such as azobenzene, azoxybenzene and the like. However, in the case that a molar ratio of nitrobenzene/urea is less than 1, the reaction is not influenced by the atmosphere, and produces azoxybenzene in the amount of 1% even under the nitrogen atmosphere.

Examples

The following examples are for illustration purposes only and in no way limit the scope of this invention.

In the following examples, products were analyzed by the Nuclear Magnetic Resonance(NMR) spectrum and the Gas Chromatography/Mass Selective Detector to identify them. Also, the products were analyzed by gas chromatography and high performance liquid chromatography to determine their quantitative analysis values. In this quantitative analysis, all the materials except for DNDPA were analyzed by gas chromatography, and analysis conditions were as follows:

Capillary column:	ULTRA 2(Crosslinked 5% Ph Me Silicon) 50m X 0.2mm X 0.33 μ m.
Carrier gas:	nitrogen
Head pressure:	20 psig
Oven:	150°C(2min.) to 280°C, β =10°C/min.
Detector and temperature:	FID(280°C).
Split ratio:	30:1
Make up gas flow rate:	38ml.

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As DNDPA is a material unsuitable to be analyzed by gas chromatography due to its high boiling point, it was quantitatively analyzed using high performance liquid chromatography. Such a high performance liquid chromatography was carried out using a product manufactured by Hitachi Co. in Japan and consisting of L-6200 intelligent pump and L-4200 UV-VIS detector. In high performance liquid chromatography, all quantitative values were measured at a wavelength of 254 nm, and elution rate was 1 ml/minute. Furthermore, in high performance liquid chromatography, a Cosmosil 5C18-AR (4.6 x150 mm) packed column was used. An elution gradient of high performance liquid chromatography is shown in Table 1 below.

Table 1: Elution gradient of HPLC

Elution gradient		
	Solvent A	Solvent B
Time (minute)	% Distilled water	% Acetonitrile
0	65	35
25	0	100
33	65	35

20

For the quantitative analysis of each product, pyrene was used as an internal standard. An area ratio for a concentration of each material was calculated relative to an area of pyrene and standard-calibrated. A molar concentration of a product was calculated from the calibration curve, and a yield was based on nitrobenzene.

25

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Example 1

Into a 100ml three-neck reactor equipped with a condenser and a thermometer were charged 3.60 g (60mmol) of urea, 1.50 g of potassium carbonate, 3.96 g (60 mmol) of potassium hydroxide, 0.3034 g of pyrene, and 25 g of DMSO. Then, the resulting mixture was heated to 90 °C while stirring under an oxygen atmosphere. Once the reaction temperature reached 90 °C, a mixed solution of 2.48 g(20 mmol) of nitrobenzene and 5g of DMSO was slowly added dropwise over a period of time of 5 to 10 minutes via a syringe. Then, a temperature was cautioned to keep 90 $\pm$ 4°C while adding a nitrobenzene solution. For a quantitative analysis, a sample was taken out and dissolved in 2.5 ml of ethyl acetate containing a small amount of water, and moisture was then removed from the resulting solution with magnesium sulfate (MgSO₄). The quantitative analysis have shown that 4-nitrosoaniline and 4-nitroaniline were obtained in yields of 87 mole% and 12 mole%, respectively, based on nitrobenzene.

Comparative Example 1

Into a 100 ml three-neck reactor equipped with a condenser and a thermometer were charged 7.32 g (60 mmol) of benzamide, 1.50 g of potassium carbonate, 3.96 g (60 mmol) of potassium hydroxide, 0.3034 g of pyrene, and 25 g of DMSO. Next, the resulting mixture was stirred under oxygen, and then heated to 90 °C. Once the reaction temperature reached 90 °C, a mixed solution of 2.48 g(20 mmol) of nitrobenzene and 5g of DMSO was slowly added dropwise over a period of time of 5 to 10 minutes via a syringe. After reacting for 2 hours, a sample was taken out, and dissolved in 2.5 ml of ethyl acetate. Then,

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moisture of the resulting solution was removed with magnesium sulfate (H_2SO_4). A quantitative analysis of the product by GC has indicated that 4-nitrosoaniline and 4-nitroaniline were obtained in yields of 14 mole% and 1 mole%, respectively, based on nitrobenzene, and an intermediate N-(4-nitrophenyl)benzamide was also obtained. For the identification of a production of N-(4-nitrophenyl)benzamide, the reaction solution was treated with hexane, added with 5 g of water and 30 g of DMSO, and then left to react at a temperature of 80 to 90 °C for 8 hours. After that, a sample was taken out, and dissolved in 2.5 ml of ethyl acetate. Then, moisture in the resulting solution was removed with magnesium sulfate (H_2SO_4). A quantitative analysis of the resulting material has shown that 4-nitroaniline was obtained in an yield of 26 mole% basd on nitrobenzene.

Example 2

Reactions were carried out under the same conditions as those in Example 1 except that a reaction temperature for each reaction was changed. Results are shown in Table 2 below.

Table 2

Reaction temperature (°C)	Conversion (mole%)	Yield (mole%)		
		Nitrobenzene	4-Nitrosoaniline	4-Nitroaniline
50	65	28	18	-
70	97	75	12	9

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90	100	87	12	-
130	35	4	2	-

*Yield obtained by liquid chromatography.

Example 3

- 5 Reactions were carried out under the same conditions as those in Example 1 except that a molar ratio of nitrobenzene to urea for each reaction was changed. Results are shown in Table 3 below.

Table 3

10	Nitrobenzene/ Urea	Conversion (mole%)	Yield (mole %)	
			4 -	4 -
			Nitrosoaniline	Nitroaniline
	1/5	100	87(18) *	12(2)
	1/4	100	86(22)	13(3)
	1/3	100	87(27)	12(5)
15	1/2	98	59(29)	13(6)
	1	64	18(18)	8(8)

*Yield based on urea

Example 4

- 20 Reactions were carried out under the same conditions as those in Example 1 except that a kind of base for each reaction was changed. Results are shown in Table 4 below.

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Table 4

	Base	Conversion (mole%)	Yield (mole%)		
			Nitrobenzene	4- Nitrosoaniline	4- Nitroaniline
					DNDPA
	Sodium hydroxide	100	62	14	5
5	Potassium hydroxide	100	87	12	-
	tBuOK	100	35	16	-
	TMA (OH)	100	94	6	-

Example 5

10 A 100 ml three-neck reactor equipped with a condenser and a thermometer was charged with 1.20 g (20 mmol) of urea, 2 g of potassium carbonate, 0.1011 g of pyrene, 25 g of DMSO, and KOH of a molar ratio varying to urea shown in Table 5. Then, the resulting mixture was allowed to

15 stir while heating to a temperature of 90 °C. Once the reaction temperature reached 90 °C, a mixed solution of 0.83 g (6.7 mmol) and 5 g of DMSO was slowly added dropwise over a period of time of 5 to 10 minutes via a

20 syringe. The resulting mixture was left to react for 2 hours while a temperature inside of the reactor did not exceed 90 ± 4°C. Then, a quantitative analysis of the product was carried out. Results are shown in Table 5 below.

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Table 5

KOH/Urea	Conversion(mole%)	Yield (mole%)	
		Nitrobenzene	4-Nitrosoaniline 4-Nitroaniline
1	94	44	13
2	100	76	14
5 4	100	70	17
6	100	73	16

Example 6

Reactions were carried out under the same conditions as those in Example 1 except that a kind of solvent for each reaction used was changed. Results are shown in Table 6 below.

Table 6

Solvent	Conversion (mole%)	Yield (mole%)	
		Nitrobenzene	4-Nitrosoaniline 4-Nitroaniline
DMSO	100	87	12
15 NMP	90	5	2
DMF	0	0	0
Xylene*	60	19	4
Dioxane*	71	32	8

*Xylene and dioxane were mixed with DMSO, respectively, in the weight ratio of 1:1.

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Example 7

Reactions were carried out under the same conditions as those in Example 1 except for amounts of solvents used were changed. Results are shown in Table 7 below.

5

Table 7

DMSO (g)	Conversion (mole%)	Yield(mole%)		
		Nitrobenzene	4-Nitrosoaniline	4-Nitroaniline
5	100		73	10
10	100		87	12
20	100		86	14
30	88		49	9

10

Example 8

Reactions were carried out under the same conditions as those in Example 1 except that moisture content in a reaction system for each reaction was changed. Results are shown in Table 8 below.

15

Table 8

Moisture content and drying agent	Conversion (mole%)	Yield (mole%)			
		Nitrobenzene	4-Nitrosoaniline	4-Nitroaniline	DNDPA
Drying agent was not used ^A	100		72	11	-

20

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K ₂ CO ₃ ^B	100	87	12	-
Vacuum ^C	100	75	11	5
Water (1 mole) ^D	100	77	13	5
Water (3 mole) ^E	82	60	8	2

5 A: Commercially available solvent was used without the purification.

B: Drying agent was used to remove moisture in a reaction system.

C: A reaction was carried out while removing moisture under a vacuum condition.

D and F: The used amount of water based on KOH.

10 Example 9

Reaction were carried out under the same conditions as those in Example 1 except that an atmosphere for each reaction was oxygen, nitrogen, and air, respectively. Results are shown in Table 9 below.

15 Table 9

Atmosphere	Conversion (mole%)	Yield (mole%)		
		Nitrobenzene	4-Nitrosoaniline	4-Nitroaniline
				DNDPA
Oxygen	100	87	12	-
Nitrogen	100	77	10	-
Air	100	75	10	-

20 Industrial Applicability

As apparent from the above description, the present invention provides the method for preparing 4-

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nitrosoaniline in which a relatively cheap urea and nitrobenzene are used as the raw materials, and also a relatively cheap base is used, thereby decreasing a manufacturing cost. In the method in accordance with the present invention, urea used as an amine donor is excellent in a reactivity to nitrobenzene, 4-nitrosoaniline is produced in high yield with little or no ortho compounds, and a reaction intermediate is unstable as compared with 4-(4-nitrophenyl)benzamide to easily decompose into 4-nitroaniline and 4-nitrosoaniline. This allows a reaction time and a process time to be shortened. Moreover, the method of the present invention is advantageous in that waste hazardous to the environment is not produced as a byproduct.

Although the preferred embodiments of the invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

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Claims

1. A method for preparing 4-nitrosoaniline, comprising reacting urea and nitrobenzene in a polar organic solvent in the presence of a base at a temperature
5 of room temperature to 150 °C.
2. The method of claim 1, wherein a molar ratio of the nitrobenzene to urea is less than 1.
3. The method of claim 1, wherein the polar organic solvent is selected from the group consisting of
10 dimethylsulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP), xylene mixed with dimethylsulfoxide, and dioxane mixed with dimethylsulfoxide.
- 15 4. The method of claim 1, wherein the base is selected from the group consisting of sodium hydroxide, sodium hydride, potassium hydroxide, potassium t-butoxide, and tetramethylammonium hydroxide.
- 20 5. The method of claim 1, wherein a molar ratio of the base to the urea is in the range of 1 to 10.
6. The method of claim 1, wherein the reaction is carried out in a nitrogen, oxygen, or air atmosphere.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/00205

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C07C 211/52, C07C 209/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patents and applications for invention since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS On line

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5 331 099 (Stern et al) 19 July 1994 see abstract	1 - 6
A	JP, A, 53-77026 (Hiroshige et al) 08 July 1978 see example 1-12	1 - 6
A	US, A, 3 338 966 (Snyder et al) 29 August 1967 see the whole document	1 - 6

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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