

PATENT SPECIFICATION

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(54) PROCESS FOR THE MANUFACTURE OF UREAS

(71) We, ATLANTIC RICHFIELD COMPANY, a corporation organised under the laws of the State of Pennsylvania, United States of America, of ARCO Plaza, 515 S. Flower Street, Los Angeles, State of California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the manufacture of ureas.

Urea and substituted ureas are important intermediates in the preparation of various products, particularly agricultural chemicals useful in soil treatment, as fungicides, insecticides and germicides, in weed control and other uses. For example 3 - (3,4 - dichlorophenyl) - 1,1 - dimethylurea is a preemergence weed control product; 1,1 - dimethyl-3 - phenylurea is an excellent herbicide; and 3 - (p - chlorophenyl) - 1,1 - dimethylurea is a non-selective weed control product. Thus any method which can be used to produce these and similar ureas is a valuable and useful process.

It is well known in the art to produce ureas by the reaction of an amine compound with an isocyanate or alternatively by the reaction of an amine with phosgene; the reaction chosen is dependent upon the nature of the desired urea. Such processes suffer from a number of disadvantages among which are the necessity for handling toxic and highly reactive compounds, the expense of the starting compounds and the necessity of working in expensive corrosion resistant apparatus resistant to by-product hydrogen chloride generated in the phosgene reaction. Other procedures are available; for example in U.S. Patent 2,877,268 there is described a process for preparing ureas by an apparently non-catalytic reaction of amines with carbonyl sulfide, while British Patent 1,275,702 describes a catalytic process for converting amines to ureas using selenium, carbon monoxide and oxygen. It should be noted

that in each of the processes it is an amine that is converted to a urea.

The instant invention provides a simple one-step process for the preparation of ureas which eliminates the need for an isocyanate or phosgene and makes it possible to start with cheaper and more readily available nitrogen-containing organic compounds.

In accordance with the invention at least one nitrogenous organic compound selected from organic nitro, nitroso, azo and azoxy compounds containing up to 24 carbon atoms is contacted with carbon monoxide and at least one compound selected from water, primary amines and secondary amines in a basic solution at an elevated temperature which is preferably in the range from 50°C to 250°C and an elevated pressure which is preferably in the range of from 10 atmospheres to 200 atmospheres gauge and in the presence of an active amount of a catalyst selected from selenium, compounds containing selenium and mixtures thereof, to produce a urea.

By means of the invention, the handling of toxic and reactive starting materials may be avoided, as may the co-production of corrosive hydrogen chloride.

The nitrogenous compound is preferably an organic nitro compound and most preferably a nitro aromatic or tertiary nitroaliphatic compound.

Nitro compounds for use in the process include mononitro compounds such as nitrobenzene, alkyl and alkoxy nitrobenzenes wherein the alkyl group contains up to 10 carbon atoms, aryl and aryloxynitrobenzenes, wherein the aryl group is phenyl, tolyl, xylyl, naphthyl, chlorophenyl, chlorotolyl, or chloronaphthyl, chloronitrobenzenes such as 4-chloronitrobenzene, 3,4 - dichloronitrobenzene, dinitrocompounds such as dinitrobenzene, alkyl and alkoxy dinitrobenzenes wherein the alkyl group contains up to 10 carbon atoms, aryl and aryloxy dinitrobenzenes wherein the aryl group is any of those mentioned above, chlorodinitrobenzenes, trinitrocompounds such as trinitrobenzene, alkyl and alkoxy-trinitrobenzenes, aryl and aryloxy-

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trinitrobenzenes with the substituents being any of those already mentioned and chloro-trinitrobenzenes as well as similarly substituted mono and polynitro derivatives of the naphthalene, diphenyl, diphenylmethane, anthracene and phenanthracene series as well as nitropyridines.

From this group of nitro compounds the aromatic nitrocompounds such as nitrobenzene-*p*-nitroanisole, *p*-nitrophenetole, *p*-nitrotoluene, 3,4 dichloronitrobenzene, *p*-chloronitrobenzene, *m*-chloronitrobenzene, dinitrobenzene, dinitrotoluene, and the tertiary aliphatic nitrocompounds such as 2-methyl-2-nitropropane and 2-methyl-1-nitrocyclohexane are preferred.

Examples of particularly suitable nitroso-compounds are the aromatic nitroso-compounds such as nitrosobenzene, nitrosotoluene and *p*-chloro-nitrosobenzene.

Preferably suitable azo compounds have the general formula



wherein R_1 and R_2 are either the same or different substituted or unsubstituted alkyl or aryl groups selected from among those already listed in the description of suitable nitrocompounds. Azobenzene, chloroazobenzenes and alkyl or aryl substituted azobenzenes are particularly preferred.

Particularly suitable azoxy compounds have the general formula



wherein R_3 and R_4 may be the same or different substituted or unsubstituted alkyl or aryl groups selected from among those already listed in the description of suitable nitrocompounds. Azoxybenzene, chloro-azoxybenzenes and alkyl and aryl substituted azobenzenes are particularly preferred.

The invention includes the use of any mixture of nitrocompounds, nitroso compounds, azo or azoxy compounds.

It is preferred to use nitrocompounds rather than nitroso, azo or azoxy compounds

When, in the practice of this invention, any of the above-mentioned nitrogen compounds; i.e., the nitro, nitroso, azo or azoxy compounds are used as the sole reacting nitrogen compound, the resulting ureas are the symmetrical 1,3-diarylureas, 1,3-dialkylureas, or substituted 1,3-diaryl or 1,3-dialkylureas. For example, when nitrobenzene is used as the only reacting nitrogen compound then carbanalide or 1,3-diphenylurea is the product. Likewise, *p*-methylnitrobenzene yields 1,3-di-*p*-tolylurea and 3,4-dichloronitrobenzene yields 1,3-bis(3,4-dichlorophenyl)urea.

The process of this invention, however, is not limited to the production of symmetrical 1,3-dialkyl and 1,3-diaryl ureas. Reaction of the nitrogenous organic compound with a primary or secondary amine in accordance with the invention can result in unsymmetrical 1,3-dialkyl-, 1,3-diaryl-, 1,1-diaryl-3-aryl-, 1,1-dialkyl-3-aryl-, 1-alkyl-3-aryl- and 1,1-dialkyl-3-alkyl ureas. Suitable primary and secondary amines are generally the primary and secondary aromatic, aliphatic, aralkyl and cycloalkyl amines.

Generally, the primary or secondary amine will conform with one or the other of the general formulae



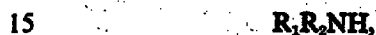
wherein R_1 and/or R_2 may be the same or two different optionally substituted aliphatic, cycloaliphatic or araliphatic groups, preferably containing from 1 to 20 carbon atoms, and R'_1 and/or R'_2 may be the same or two different aromatic groups containing one or more benzenoid rings and preferably not more than 3 rings which can be fused or joined by single valency bonds; directly or through bridging groups which may be, for example, oxygen, nitrogen or sulfur atoms or sulfoxide, sulfone, amine, amide, or carbonyl groups, or alkylene groups in which, if desired, the carbon chain may be interrupted by, for example, oxygen or sulfur atoms, sulfoxide, sulfone or carbonyl groups, for example, methylene, oxymethylene, dimethylene sulfone or dimethylene ketone groups.

The groups R_1 and R_2 may be alkyl, cycloalkyl, alkylene, cycloalkylene or aralkyl and the main carbon chain may, if desired, be interrupted, for example by oxygen, nitrogen or sulfur atoms, sulfoxide, sulfone, amine, amide, carbonyl or carboxylic ester groups. The main chain may bear as substituents, for example, alkyl, alkoxy, aryl or aryloxy groups normally containing less than 10 carbon atoms. Especially suitable compounds of the type R_1NH_2 and R_1R_2NH are those in which each of R_1 and R_2 is selected from methyl, ethyl, *n*- and iso-propyl, *n*-, iso-, sec- and tert-butyl, amyl, hexyl, lauryl, setyl, benzyl, chlorobenzyl, methoxybenzyl and cyclohexyl and in the case of the secondary amines R_1R_2NH R_1 and R_2 may be the same or any combination of the aforementioned groups.

Especially suitable compounds of the type

- 5 R'_1NH_2 and $R'_1R'_2NH$ are those in which each of R'_1 and R'_2 is a benzenoid ring which may carry substituents; for example, alkyl and alkoxy groups containing up to 10 carbon atoms and halogen atoms. Examples of R'_1 and R'_2 are phenyl, chlorophenyl, tolyl, xylyl, naphthyl, chloronaphthyl, pyridyl and chloropyridyl and in the case of secondary amines $R'_1R'_2NH$ R'_1 and R'_2 may be the same or any combination of the aforementioned groups.

10 Examples of particularly suitable amines fitting the general formulae



and



- 20 are methylamine, dimethylamine, ethylamine, diethylamine, propylamine, isopropylamine, dipropylamine, diisopropylamine, butylamine, dibutylamine, isobutylamine, diisobutylamine, amylamine, hexylamine, octylamine, cetylamine, cyclopropylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, cyclooctylamine, benzylamine, dibenzylamine, *p*-chlorobenzylamine, aniline, *p*-anisidine, *p*-toluidine, 3,4-dichloroaniline, *m*-chloroaniline, diphenylamine, 4,4''-dichlorodiphenylamine, N-methylethylamine, N-methylpropylamine, N-methylbutylamine, N-methylisobutylamine, N-ethylbutylamine, allylamine, N-methylcyclohexylamine, N-methylaniline, N-ethylaniline, N-allylaniline, N-methyl-4-chloroaniline and N-methyl-*p*-anisidine.

- Thus, for example, using the above described amine and nitro compounds under the conditions of our invention the following ureas can be prepared: 3-(3,4-dichlorophenyl)-1,1-dimethylurea by reaction of 3,4-dichloronitrobenzene with dimethylamine; 1,1-dimethyl-3-phenylurea by reaction of nitrobenzene with dimethylamine; 3-(*p*-chlorophenyl)-1,1-dimethylurea by reaction of *p*-chloronitrobenzene with dimethylamine; and 1,1'-(4-methyl-*m*-phenylene)bis[3-isopropylurea] by reaction of 2,4-dinitrotoluene with isopropylamine. Other combinations of amines and nitrocompounds can be used to obtain more or less readily the corresponding ureas. Such combinations are not limited to those amines and nitrocompounds described above and are apparent to one skilled in the art.

25 Catalysts for use in this invention are selenium, selenium compounds and mixtures

thereof. Selenium metal has been found to be as good as most selenium compounds and is conveniently handled in the powdered form. Other suitable selenium compounds are selenium dioxide, selenium trioxide, mixtures of these oxides, titanium diselenide, selenium disulfide, sodium selenite, zinc selenite, sodium selenide, potassium selenide, potassium hydrogen selenide, hydrogen selenide, carbonyl selenide, barium selenide and organic selenium compounds. These compounds are not all of equivalent activity.

The catalyst material, as indicated above, can be self-supported or can be deposited on an inert support or carrier for dispensing the catalyst to increase its effective surface. Alumina, silica, carbon, barium sulfate, calcium carbonate, organic ion exchange resins and analogous materials are useful as carriers for this purpose. A particular example of a supported catalyst is an ion exchange resin containing selenium as the cation an ad sulfonic or carboxylic acid function as the anionic part of the resin, such as a selenium containing sulfonated macroporous styrene divinylbenzene resin. Selenium containing molecular sieves can also be employed as well as complexes of selenium with a ligand.

Base and water are preferably added to the reaction unless the primary or secondary amine is used as the base. Organic bases suitable for the reaction include such amines as triethylamine, pyridine, quinoline, and N,N-dimethylaniline. Compounds normally considered as weak bases, such as the metal salts of carboxylic acids, sulfonic acids and phosphoric acid, are preferred bases. Examples of such compounds and salts of other weak acids are lithium acetate, sodium acetate, potassium acetate, palladium acetate, ruthenium acetate, the lithium salt of *p*-toluenesulfonic acid, the lithium salt of methyl sulfonic acid, lithium acid phosphate, the lithium salt of boric acid, calcium acetate, sodium formate, lithium formate and antimony triacetate. The acid salts can be added preformed or can be made in the reaction mixture by adding appropriate quantities of corresponding base and acid. There is no limit on the type of acid used or the corresponding metal oxide or hydroxide employed. Thus, aliphatic, cycloaliphatic and aromatic acids, such as propionic, octanoic, cyclohexane carboxylic, benzoic, oxalic, malonic and the like can be employed. However, oxides or hydroxides of transition metal compounds tend to be more expensive than the alkali and alkaline earth metal hydroxides.

In those cases where unsymmetrical ureas are prepared by reaction of a nitrocompound with a primary or secondary amine the amine itself is often suitable as a base and no other additional basic compound need be added. Even so, there are some instances

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where addition of a base other than the reacting amine can be advantageous and, in such instances, any of the above-described bases are suitable for this purpose.

While the process of the invention can typically be operated effectively in the absence of a solvent, a solvent can be employed. Aromatic solvents such as benzene, toluene, xylene; nitrile solvents such as acetonitrile and benzonitrile; amide type solvents such as N,N-dimethylformamide and N,N-dimethyl acetamide; aliphatic, alicyclic or aromatic sulfoxide and sulfone solvents, such as dimethyl sulfoxide; aliphatic halogenated hydrocarbons such as 1,1,2-trichloro-1,2,2-trifluoroethane; halogenated aromatic hydrocarbons such as monochlorobenzene, dichlorobenzene and trichlorobenzene; ketones; esters; and ether solvents such as tetrahydrofuran, 1,4-dioxane and 1,2-dimethoxyethane all can be employed as solvents. The ether compounds, for example can be aliphatic, aromatic or heterocyclic, and they can also be either mono or polyethers, or combinations of these compounds.

Also suitable are the organic amines such as pyridine, triethylamine and the reactant primary and secondary amines used when unsymmetrical ureas are prepared. Combinations of tertiary amines can be used as various combinations of tertiary amines with primary or secondary reactant amines.

The invention is carried out with at least molar amounts of reactants, e.g. nitrocompound, amine and carbon monoxide.

Preferably, however, a molar excess of the amine compound or the nitrogenous organic compound or both the present but, generally, in the case of preparing the unsymmetrical ureas, a molar excess of the amine is used.

The mole ratio of the nitrogenous organic compound to the catalyst can vary over a wide range, i.e. from 5:1 to 2000:1, however, a somewhat more preferred range of moles of nitrogenous organic compound to the catalyst is 5:1 to 1000:1. It will be understood that with reference to the moles of catalyst it is meant the element selenium and not the moles of the form in which the catalyst is charged.

Similarly, with respect to the amount of base employed the mole ratio (which for example is based on equivalent nitrogroups where the nitrogenous organic compound is a nitro compound) can vary from 50:1 to 1:10 of the nitrogenous organic compound to the base. When the desired products are unsymmetrical 1,3-ureas, in many cases the reacting amine can also serve as the base. When this is the case the mole ratio of nitrocompound to base may be well outside the limits described above without any detrimental effect on the reaction.

When symmetrical 1,3-ureas are produced by reaction of the nitrogenous organic com-

pound in the presence of water, the mole ratio of water to catalyst can range from as little as about 0.5:1 to as much as 1000:1 or more. Such water can be added separately or produced "in situ", for example, when a base such as potassium hydroxide and an acid such as acetic acid are employed in equivalent molar amounts to give the weakly basic compound potassium acetate and water in equi-molar amounts.

The order of mixing the reactants is not critical and can be varied within the limitations of the equipment employed. A simple procedure is to charge the nitrogenous compound (or compounds), catalyst, amine and/or water into the reaction vessel, introduce the required amount of carbon monoxide and then heat the mixture to obtain the desired reaction. A suitable pressure vessel, such as an autoclave, which is preferably provided with heating means and agitation means, such as a stirrer or an external rocking mechanism, is employed for the reaction.

Generally, the amount of carbon monoxide in the free space of the reactor is sufficient to maintain the desired pressure as well as to provide a reactant for the process. As the reaction progresses additional carbon monoxide can be fed to the reactor either intermittently or continuously. Although greater and lesser amounts of carbon monoxide can be employed if desired, generally the total amount of carbon monoxide added during the reaction is between about 3 and about 50 moles and preferably between about 8 and about 15 moles of carbon monoxide per non-cyclic group in which the nitrogen atom of the nitrogenous organic compound is directly attached to a single carbon atom and is also attached by a double bond to an oxygen or another nitrogen atom. The highest carbon monoxide requirements are generally utilized in a process in which carbon monoxide is added continuously, but suitable recycle of carbon monoxide containing gas streams greatly reduces the overall consumption of carbon monoxide.

The reaction temperature is preferably maintained in the range of about 50°C. to about 250°C. and more preferably within the range of from about 100 to about 200°C. These temperature ranges permit a convenient rate of reaction to be achieved while avoiding undesirable side reactions. It will be understood, however, that any elevated temperatures below that at which the starting materials or the products decompose can be used. The reaction is carried out, as indicated above, at a superatmospheric pressure which is preferably between about 10 and 200 atmospheres gauge, although higher or lower reaction pressures can be employed if other reaction conditions are suitably adjusted. Preferably, however, only moderate carbon monoxide pressures in the range of

about 10 to about 100 atmospheres gauge are employed and the reaction is conveniently run at a temperature of below about 200°C within this pressure range.

5 While the reaction of the present invention is normally carried out batchwise, if desired, the reaction can be carried out semi-continuously or even continuously. Ion exchange type catalysts, for example, are particularly suited for continuous reactions. 10 The reaction time is dependent upon the nature of the reactants, temperature, pressure and the type of catalyst employed, as well as the type of equipment which is used. Normally the reaction time is less than 180 minutes and generally the effectiveness of the catalysts of this invention permits the reaction to be completed within a time period between about ten minutes and about 120 minutes.

20 After the reaction has been completed, the temperature of the reaction mixture can be dropped to ambient temperature and the pressure vessel vented. The reaction product is then treated by conventional procedures, including filtration, distillation, or other suitable separation techniques, to effect separation of urea from unreacted starting material, solvent, by-product and catalyst.

30 The invention is further illustrated by, but not limited to, the following examples.

The reactions set forth in these examples were all run in 316 Stainless Steel shaking autoclaves. It will be understood, however, that less expensive forms of stainless steel can be used and that if desired equivalent reaction vessels, such as glass-lined vessels, can be employed. Conversions and yields reported in the examples were determined by gas chromatographic analysis and by isolation of the product. The ureas were purified by recrystallization and the infrared spectra and melting points obtained.

EXAMPLE I

45 Ten milliliters of nitrobenzene, 100 milliliters of tetrahydrofuran and two milliliters of water were charged into a 300 milliliter rocking autoclave along with 1.0 gram of selenium metal (grey powder) and 1.0 gram of sodium acetate. The autoclave was flushed with nitrogen and carbon monoxide and finally pressured to 800 psig with carbon monoxide. After heating to 150°C for one hour the autoclave was cooled, vented and the contents analyzed. A 66.3 per cent conversion of nitrobenzene resulted with a 33.8 per cent yield of purified carbanalide.

EXAMPLE II

60 Example I was repeated at 180°C using 0.5 gram water. A 48.9 per cent conversion resulted with a 57.7% yield of pure carbanalide.

EXAMPLE III

The autoclave was charged with 13.7

grams of 4-nitrotoluene, 100 milliliters of tetrahydrofuran, 1.0 gram of sodium acetate, 1.0 gram of selenium metal and 0.5 milliliters of water. After flushing with nitrogen and carbon monoxide it was pressured to 800 psig with carbon monoxide and heated to 180°C for one hour. After cooling and venting analysis indicated a 61.0 per cent conversion and a yield of pure 1,3-di-*p*-tolylurea of 45.9 per cent.

EXAMPLE IV

75 Similarly, 15.3 grams of 4-nitroanisole were reacted along with 100 milliliters of tetrahydrofuran, 1.0 gram selenium metal, 1.0 gram sodium acetate and 0.5 milliliter of H₂O at an initial carbon monoxide pressure of 800 psig. After one hour at 180°C a 68 per cent conversion was obtained giving a 44.1 per cent yield of pure 1,3-bis(4-methoxyphenyl) urea.

85 The following examples demonstrate the use of this invention to prepare unsymmetrical ureas by reaction of a nitro compound with an amine.

EXAMPLE V

90 Ten milliliters of nitrobenzene, 100 milliliters of tetrahydrofuran, 1.0 gram potassium acetate, 1.0 gram selenium metal and 9.0 grams of dimethylamine are charged to the autoclave. The autoclave is flushed and pressured to 800 psig with carbon monoxide and heated to 180°C for one hour. After reaction 1,1 - dimethyl - 3 - phenylurea is obtained.

EXAMPLE VI

100 Ten milliliters of nitrobenzene, 100 milliliters of tetrahydrofuran, 1.0 gram potassium acetate, 1.0 gram selenium and 21.4 grams of *p*-toluidine are charged to the autoclave which is then flushed and pressured to 800 psig with carbon monoxide. The temperature is raised to 180°C for one hour giving 1-*p*-tolyl-3-phenylurea as product.

WHAT WE CLAIM IS:—

1. A method for the production of ureas which comprises contacting at elevated temperature and elevated pressure in a basic solution at least one nitrogenous organic compound selected from organic nitro, nitroso, azo and azoxy compounds containing up to 24 carbon atoms, with carbon monoxide and at least one compound selected from water, primary amines and secondary amines, in the presence of an active amount of a catalyst selected from selenium, compounds containing selenium and mixtures thereof.

2. A method as claimed in claim 1 wherein said organic nitrogenous compound is a nitro aromatic compound.

3. A method as claimed in claim 2 where-



* C L M S *

about 10 to about 100 atmospheres gauge are employed and the reaction is conveniently run at a temperature of below about 200°C within this pressure range.

5 While the reaction of the present invention is normally carried out batchwise, if desired, the reaction can be carried out semi-continuously or even continuously. Ion exchange type catalysts, for example, are particularly suited for continuous reactions. 10 The reaction time is dependent upon the nature of the reactants, temperature, pressure and the type of catalyst employed, as well as the type of equipment which is used. Normally the reaction time is less than 180 minutes and generally the effectiveness of the catalysts of this invention permits the reaction to be completed within a time period between about ten minutes and about 120 minutes.

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WHAT WE CLAIM IS:—

1. A method for the production of ureas which comprises contacting at elevated temperature and elevated pressure in a basic solution at least one nitrogenous organic compound selected from organic nitro, nitroso, azo and azoxy compounds containing up to 24 carbon atoms, with carbon monoxide and at least one compound selected from water, primary amines and secondary amines, in the presence of an active amount of a catalyst selected from selenium, compounds containing selenium and mixtures thereof.

2. A method as claimed in claim 1 wherein said organic nitrogenous compound is a nitro aromatic compound.

3. A method as claimed in claim 2 where-



- in said nitro aromatic compound is nitrobenzene.
4. A method as claimed in claim 2 wherein said nitro aromatic compound is nitrotoluene.
5. A method as claimed in claim 2 wherein said nitro aromatic compound is 4-nitroanisole.
6. A method as claimed in claim 1 wherein said organic nitrogenous compound is a tertiary nitroaliphatic compound.
7. A method as claimed in any of claims 1 to 6 wherein the nitrogenous organic compound is reacted with carbon monoxide and water.
8. A method as claimed in claim 7 wherein said catalyst is selenium.
9. A method as claimed in claim 1 wherein the nitrogenous organic compound is reacted with carbon monoxide and at least one amine selected from primary and secondary amines.
10. A method as claimed in claim 9, wherein said amine is dimethylamine.
11. A method as claimed in claim 9 wherein said amine is *p*-toluidine.
12. A method as claimed in any one of claims 1 to 11 wherein said temperature is in the range of from 50°C to 250°C and said pressure is in the range of from 10 atmospheres to 200 atmospheres gauge.
13. A method as claimed in claim 1, substantially as hereinbefore described with particular reference to the Examples.
14. Any method which is substantially a method disclosed in the specification including the Examples as an embodiment of the method claimed in claim 1.
15. A urea obtained by the method of any one of the preceding claims.

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