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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for the Preparation of Isocyanates by the
Decomposition of N,N,N'-Trisubstituted Ureas

(72) Hackl, Kurt A. - Austria ;
Falk, Heinz - Austria ;

(71) Chemie Linz Gesellschaft m.b.H. - Austria ;

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Notice: This application is as filed and may therefore contain an
incomplete specification.

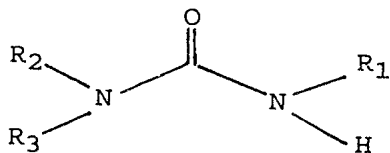
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Abstract

A process for the preparation of isocyanates which is characterized in that N,N,N'-trisubstituted ureas of the formula

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in which R₁, R₂ and R₃ are identical or different and are a linear, branched or cyclic (C₁-C₂₄)-alkyl radical which is unsubstituted or substituted by (C₁-C₆)-alkoxy, optionally substituted phenyl, halogen or other radicals which are inert under the reaction conditions used, or R₂ and R₃ together are a heterocyclic non- aromatic ring which can optionally contain further heteroatoms, are decomposed, in a diluent which is inert under the reaction conditions, at elevated temperature, to an isocyanate of high volatility of the formula R₁NCO and to a secondary amine of low volatility of the formula R₂R₃NH, whose boiling point is above that of the isocyanate and above the reaction temperature used, after which the isocyanate is drawn off at the top by means of a stream of carrier gas.

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Process for the preparation of isocyanates by the decomposition of N,N,N'-trisubstituted ureas

The invention relates to a process for the preparation of isocyanates by the decomposition of N,N,N'-trisubstituted ureas.

Isocyanates represent an economically important group of intermediates which are used inter alia in the plastics industry, in the production of lacquers and in the preparation of plant protection agents.

For this reason, there are also a large number of known processes for the preparation of isocyanates, although these have several disadvantages. Thus, for example, earlier processes use mainly phosgene or phosgene derivatives as starting materials, while more recent processes, which avoid the use of phosgene, only achieve poor yields of isocyanates.

Also, processes have already been described where the starting materials used are substituted ureas which are thermally decomposed.

In French patent 1,473,821, trisubstituted ureas are decomposed to isocyanic acid esters and amines at temperatures below 200°C in a solvent with a dielectric constant of less than 40. However, the isocyanates are only obtained in a yield of about 60%.

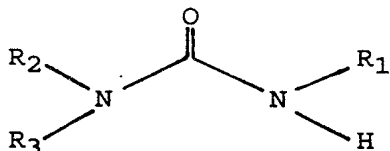
US patent 3,936,484 proposes a process for the thermal decomposition of disubstituted ureas, especially for the preparation of toluylene 2,4-diisocyanate. Preferably, the amine formed is removed from the reaction mixture by means of a stream of carrier gas, to which a further solvent can be added.

The disadvantages of this process, however, are that mainly only the amine formed can be drawn off at the top and the actual product remains at the bottom and then has to be isolated and purified, and that a good yield can only be achieved by the addition of a further solvent.

Surprisingly, a process for the preparation of isocyanates has now been found in which the starting

materials used are particular N,N,N'-trisubstituted ureas, which does not use phosgene and which provides the desired isocyanates in a simple manner and in high yield and purity.

5 The invention accordingly relates to a process for the preparation of isocyanates which is characterized in that N,N,N'-trisubstituted ureas of formula I:



in which R₁, R₂ and R₃ are identical or different and are a linear, branched or cyclic (C₁-C₂₄)-alkyl radical which is unsubstituted or substituted by (C₁-C₆)-alkoxy, optionally substituted phenyl, halogen or other radicals which are inert under the reaction conditions used, or R₂ and R₃ together are a heterocyclic non-aromatic ring which can optionally contain further heteroatoms, are decomposed, in a diluent which is inert under the reaction conditions, at elevated temperature, to an isocyanate of high volatility of the formula R₁NCO and to a secondary amine of low volatility of the formula R₂R₃NH, whose boiling point is above that of the isocyanate and above the reaction temperature used, after which the isocyanate is drawn off at the top by means of a stream of carrier gas.

In principle, suitable starting compounds are any N,N,N'-trisubstituted ureas which decompose under thermal stress to an isocyanate of high volatility and to a secondary amine of low volatility, whose boiling point is above that of the isocyanate and above the reaction temperature. Such compounds are those of formula I in which R₁, R₂ and R₃ are identical or different and are a linear, branched or cyclic (C₁-C₂₄)-alkyl radical which is unsubstituted or substituted by (C₁-C₆)-alkoxy, optionally substituted phenyl, halogen or other radicals which are inert under the reaction conditions used, such

as, for instance, a methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, tert-butyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, cyclohexyl or benzyl radical.

5 Examples of (C₁-C₆)-alkoxy radicals are methoxy, ethoxy, propoxy, butoxy and hexyloxy. For example, the phenyl radical can be substituted inter alia by (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, halogen, amino or nitro. R₂ and R₃ can also together form a heterocyclic non-aromatic ring
10 which can contain further heteroatoms, such as, for instance, pyrrolidine, piperidine, piperazine or morpholine.

 Preferred starting compounds are compounds of formula I in which R₁ is a linear, branched or cyclic (C₂-
15 C₁₀)-alkyl radical or a benzyl radical and R₂ and R₃ are a linear, branched or cyclic (C₁-C₂₀)-alkyl radical or a benzyl radical.

 Particularly preferred N,N,N'-trisubstituted ureas are therefore inter alia N,N-dioctyl-N'-ethylurea,
20 N,N-dioctyl-N'-propylurea, N,N-dicyclohexyl-N'-propylurea, N,N-dioctyl-N'-isopropylurea, N,N-dibenzyl-N'-butylurea, N,N-dioctyl-N'-butylurea, N,N-dioctyl-N'-benzylurea and N,N-dioctyl-N'-cyclohexylurea.

 The ureas can be prepared for example via the
25 N-alkylation of urea, as described in European Patent 0 471 983.

 The decomposition can take place in a diluent which is inert under the reaction conditions. Suitable inert diluents are higher-boiling aliphatic or aromatic
30 hydrocarbons such as, for instance, tetradecane, dodecane, hexadecane, octadecane, paraffin or mixtures thereof, although the amine formed by the decomposition of the urea can also be used as the diluent. The reaction temperature is between about 90 and 400°C, preferably
35 between 150 and 300°C and particularly preferably between 210 and 280°C, depending on the urea used. The isocyanates are isolated from the reaction mixture by means of a stream of inert gas, for instance by means of a stream of nitrogen or argon. The isocyanates are then

either condensed in a cold trap or absorbed in a solvent. Suitable solvents for the isocyanates are aliphatic or aromatic hydrocarbons which can optionally also be halogenated, such as, for instance, chloroform, methylene chloride, trichloroethylene and toluene, and ethers such as, for instance, tetrahydrofuran. The solvent, or part thereof, can already be incorporated as vapor with the stream of inert gas, or incorporated into the reaction mixture before decomposition begins.

10 If desired, the reaction can also be carried out under reduced or elevated pressure, the pressure being adjusted to the desired value according to the chosen starting materials and the end products formed.

15 The reaction time is between 15 and 120 minutes, depending on the reaction temperature, the reaction pressure and the starting compounds. The secondary amine, which remains at the bottom during the decomposition, can be isolated from the bottom for example by distillation under reduced pressure and used as the starting compound for a variety of reactions. The desired isocyanates are 20 obtained in high purity and in yields of up to 99.9%.

Example 1:

Ethyl isocyanate

25 In a suitable apparatus comprising, in addition to a temperature-regulated reaction vessel, a device for introducing and, ideally, distributing the stream of inert gas in the reaction mixture, and a column for facilitating product separation (e.g. a metal-coated 30 cm Vigreux column was used), 5 g of N,N-dioctyl-N'-ethylurea were heated at about 250°C for 30 minutes in 30 50 g of hexadecane and 2.5 g of CHCl₃.

During this time, the ethyl isocyanate formed was removed from the reaction mixture by means of a stream of nitrogen (ca. 2 l/h) and condensed as a CHCl₃ solution in 35 a cold trap cooled with liquid nitrogen.

Yield: 97% :

Example 2:**Propyl isocyanate**

In the apparatus described in Example 1, 5 g of N,N-dicyclohexyl-N'-propylurea were heated at about 250°C for 40 minutes in 50 g of hexadecane and the propyl isocyanate formed was removed from the reaction mixture by means of a stream of nitrogen and condensed in a cold trap cooled with liquid nitrogen.

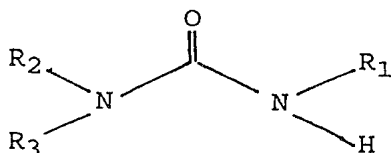
Yield: 99.9%

10 The following compounds were prepared analogously:

	Product	Educt	Solvent
	1 i-propyl isocyanate	N,N-dioctyl-N'-isopropylurea	hexadecane
15	2 butyl isocyanate	N,N-dioctyl-N'-butylurea	hexadecane
	3		paraffin octadecane
	4	N,N-dibenzyl-N'-butylurea	hexadecane
20	5 tert-butyl isocyanate	N,N-dioctyl-N'-tert-butylurea	hexadecane
	6 cyclohexyl isocyanate	N,N-dioctyl-N'-cyclohexylurea	hexadecane
25	7 benzyl isocyanate	N,N-dioctyl-N'-benzylurea	hexadecane

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the preparation of isocyanates, characterized in that N,N,N'-trisubstituted ureas of the formula



10 in which R_1 , R_2 and R_3 are identical or different and are a linear, branched or cyclic (C_1 - C_{24})-alkyl radical which is unsubstituted or substituted by (C_1 - C_6)-alkoxy, optionally substituted phenyl, halogen or other radicals which
15 are inert under the reaction conditions used, or R_2 and R_3 together are a heterocyclic non- aromatic ring which can optionally contain further heteroatoms, are decomposed, in a diluent which is inert under the reaction conditions, at elevated temperature, to an isocyanate of high volatility of the formula R_1NCO and to a secondary amine of low volatility of the formula R_2R_3NH , whose boiling point is above that of the isocyanate and above the reaction temperature used, after which the isocyanate is drawn off at the top by means of a stream of carrier gas.
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2. A process according to Claim 1, characterized in that, in the N,N,N'-trisubstituted ureas of formula I used, R_1 is a linear, branched or cyclic (C_2 - C_{10})- alkyl radical or a benzyl radical and R_2 and R_3 are a linear, branched or cyclic (C_4 - C_{20})-alkyl radical or a benzyl radical.
25

3. A process according to Claim 1, characterized in that the reaction temperature is about 150 - 300°C, preferably 220 - 280°C.

30 4. A process according to Claim 1, characterized in that the ureas are decomposed under a reduced pressure of about 0.01 to 100 mbar.

SUBSTITUTE
REPLACEMENT

SECTION is not Present
Cette Section est Absente