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(54) **Process for the preparation of N-substituted methacrylamides and acrylamides**

(57) A process for preparing N-alkylamides of acrylic acid or methacrylic acid, wherein acrylonitrile or methacrylonitrile is reacted with a compound having an optionally substituted alkyl group with 3 to 40 carbon atoms, capable of forming an alkyl carbonium ion under the effect of sulphuric acid, is characterized in that the nitrile together with the alkyl group containing compound is added to a quantity of concentrated sulphuric acid, in a mole ratio of sulphuric acid to added nitrile of from about 1:1 to 2:1, which is at reaction temperature, and then the mixture is left to react at a reaction temperature of from 10 to 100°C and after dilution, e.g. with water, the unsaturated N-alkylamides are isolated, if required, by extraction with an inert extracting agent which is immiscible with the dilute sulphuric acid.

GB 2 103 216 A

SPECIFICATION

**Process for the preparation of N-substituted methacrylamides and acrylamides**

The invention relates to a process for the preparation of N-substituted methacrylamides and acrylamides.

Various methods have been proposed for preparing the technically useful amides of acrylic and methacrylic acid. Of the various possible starting compounds, acrylonitrile and methacrylonitrile are for example, particularly suitable, partly because these nitriles are comparatively easily obtained on an industrial scale. The unsubstituted amides can be obtained most simply by partial hydrolysis of acrylonitrile or methacrylonitrile.

Another method uses the so-called Ritter reaction, wherein—in mechanistic terms—carbonium ions of adequate stability react with nitriles ultimately to form N-substituted amides. In practice, the nitriles are generally reacted with alkenes or alcohols in the presence of sulphuric acid. The Ritter reaction may also be used on unsaturated nitriles (see H. Plant and J. J. Ritter, J. Am. Chem. Soc. *73*, 4076, (1951)). Generally, the following rules apply: in the case of alcohols and olefins which form secondary carbonium ions, the Ritter reaction proceeds with considerably more difficulty than in the case where tertiary carbonium ions are formed. If primary alcohols are reacted, extremely drastic reaction conditions are required (vide K. Hamamoto and M. Yoshioka, Nippon Kagaku Zasshi *80*, Chem. Abstr. *55*, 4349 (1961).

U.S. Patent No. 2 448 991 describes a process for the preparation of N-isopropyl-methacrylamide which involves mixing isopropyl alcohol with methacrylonitrile at elevated temperature in the presence of an acidic catalyst.

According to French Patent No. 1 436 391, 1:1 mixtures of acrylonitrile and isopropanol may be reacted together with 3 moles of sulphuric acid in a reactor. After neutralisation with ammonia, the reaction mixture is worked up, for example, by extracting with xylene.

U.S. Patent No. 3,161,679 also teaches the reaction of unsaturated nitriles and olefins with 10 to 40 carbon atoms, in which an excess of from 30 to 250% of sulphuric acid is added to the mixture of nitrile and olefin. The reaction mixture is worked up by pouring it on to ice and then neutralising it.

According to published European Patent Application No. 0 004 362A, acrylamides and methacrylamides with an $\alpha$-methyl-substituted alkyl group with 5 to 10 carbon atoms or a multiply branched alkyl group with about 6 to 8 carbon atoms at the nitrogen can be prepared using the Ritter reaction.

According to Canadian Patent No. 996128, N-3-aminoacrylamides may be obtained, by applying the Ritter reaction to the corresponding aminoalkenes.

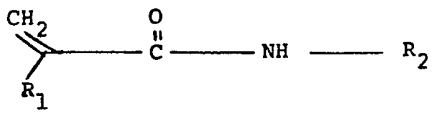
The methods proposed have not proved fully satisfactory. Further research has therefore been devoted to the synthesis of N-substituted amides of $\alpha,\beta$-unsaturated carboxylic acids from the unsaturated nitriles, using other specific catalysts.

Thus, in published Japanese Patent Application 75/135018, silicic, phosphoric or tungsten-molybdic acids are recommended as catalysts for the preparation of N-substituted acrylamides. From U.S. Patent No. 3,948,989, it is known to use $PdCl_2$ as a catalyst for the preparation of N-tert-butylacrylamides from acrylonitrile and tert.butanol or isobutylene.

However, these proposed embodiments of the Ritter reaction have not proved completely satisfactory and there remained a need to provide a process whereby N-substituted acrylamides and methyacrylamides could be prepared in good yields, as simply as possible, from acrylonitrile or methacrylonitrile and the widest possible variety of carbonium ion—forming starting compounds.

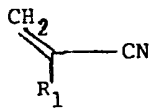
We have now found that N-substituted methacrylamides and acrylamides may be prepared satisfactorily by reaction of methacrylonitrile or acrylonitrile with carbonium ions in sulphuric acid under certain conditions.

According to the present invention there is provided a process for the preparation of compounds of formula I



(I)

(wherein $R_1$ represents a hydrogen atom or a methyl group, and $R_2$ represents an optionally substituted, optionally cyclic, alkyl group with at least 3 and up to 40 carbon atoms) which comprises reacting a nitrile of formula (II)



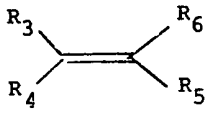
(II)

(wherein $R_1$ is as hereinbefore defined) with a compound containing an optionally substituted, optionally cyclic alkyl group with at least 3 and up to 40 carbon atoms (a compound of formula III),

which compound is capable of forming a carbonium ion of formula $R_2^{\oplus}$ (wherein $R_2$ is as hereinbefore defined) under the effect of sulphuric acid, the said reaction being effected by adding the nitrile of formula (II) and from a slight molar deficiency up to a slight molar excess of the compound of formula (III) to a quantity of concentrated sulphuric acid, in a mole ratio of sulphuric acid to added nitrile of from about 1:1 to 2:1, allowing the mixture to react at 10 to 100°C, and then diluting the reaction mixture so as to obtain a compound of formula (I), preferably without neutralisation of the sulphuric acid, and suitably with water. The reaction mixture may then be worked up by separating off the compounds of formula (I) precipitated and/or by extraction with an inert extracting agent which is substantially immiscible with the dilute sulphuric acid.

In general, the nitrile of formula (II) is reacted with the compound capable of forming carbonium ions in a mole ratio of from 1:0.9 to 1:1.1. It has proved advantageous to keep the concentration of water in the reaction mixture as low as possible, e.g. in the catalytic range, based on the nitrile of formula (II) of the alkyl compound of formula (III), until the working-up stage.

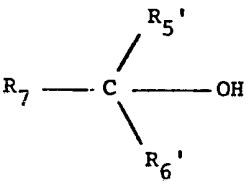
Of the above-mentioned alkyl group-containing compounds of formula (III) capable of forming carbonium ions under the effect of sulphuric acid (i.e. under the conditions of the Ritter reaction), particular mention should be made of optionally substituted alkyl group containing compounds which can be used in the Ritter reaction, and particularly the compounds of formula (IIIA)



(IIIA)

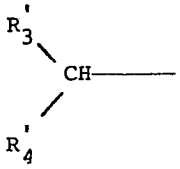
(wherein $R_3$, $R_4$ and $R_5$, which may be the same or different, each represents a hydrogen atom, an optionally substituted $C_{1-21}$ alkyl group, or an aryl group and $R_6$ represents an optionally substituted $C_{1-21}$ alkyl group or an optionally substituted aryl group; or two of the groups $R_3$, $R_4$, $R_5$ and $R_6$ together form a carboxylic or heterocyclic ring; with the proviso that no more than two of the groups $R_3$, $R_4$, $R_5$ and $R_6$ represent aryl groups), and

the alcohols of formula (IIIB)



(IIIB)

(wherein $R_7$ represents an aryl group or a group of formula



;

$R_3'$, $R_4'$ and $R_5'$, which may be the same or different each represents a hydrogen atom, an optionally substituted $C_{1-21}$ alkyl group, or an aryl group; have the same meanings as $R_3$, and $R_6'$ represents a hydrogen atom, an optionally substituted alkyl group, or an aryl group; or two of the groups $R_3'$, $R_4'$, $R_5'$, and $R_6'$ together form a carboxylic or heterocyclic ring, with the proviso that no more than two of the groups $R_3'$, $R_4'$, $R_5'$ to $R_6'$ and $R_7$ represent aryl groups).

By the term "optionally substituted alkyl groups" is meant alkyl groups having substituents which survive the conditions of the Ritter reaction without any harmful secondary reactions, e.g. phenyl groups, acid amide groups, alkyl- and aryl-ketone groups. "Aryl group" within the scope of this invention refers to a phenyl or naphthyl group which may in turn be substituted with such inert substituents.

When the reaction is carried out with the starting compounds of formula (III) (e.g. the olefins of formula (IIIA) or the alcohols of formula (IIIB)), a reaction temperature of from 10 to 40°C is generally sufficient, if, according to current opinion, tertiary carbonium ions are formed from the starting compounds under the reaction conditions. If the reaction proceeds with the formation of secondary carbonium ions, higher temperatures, for example from 60 to 100°C, are appropriate, as a rule. The reaction is generally carried out without any application of pressure.

As a rule, the reaction with acrylonitrile (formula (II), $R_1$=hydrogen) can be carried out at a reaction temperature which is 10 to 30°C below the temperature of the reaction with methacrylonitrile (formula (II), $R_1$=methyl).

Particular mention should be made of the reaction with the olefins or alcohols of formula (III) with a lower carbon number, for example the reaction with olefins with 3 to 5 carbon atoms. The reaction with propylene, isobutylene, pent-1-ene and n-butene, *inter alia*, should be mentioned.

It is also useful to carry out the reaction with alcohols with 3 to 5 carbon atoms, for example to effect the reaction with tert.butanol, tert.amyl alcohol, propan-2-ol or butan-2-ol.

Another useful process is the reaction with olefins unsaturated in the end position, e.g. from pent-1-ene to heneicos-1-ene, such as hex-1-ene, oct-1-ene, dec-1ene, tetradec-1ene and octadec-1-ene, and the reaction with cyclic compounds, such as cyclopentene, cyclohexene and norbornene.

Moreover, the reaction according to the invention provides a simple method of preparing the corresponding amides of formula (I) from more complex cyclic alcohols or olefins, such as, for example, from isoprene derivatives such as bicyclene, borneol and norbornene or from tricyclic systems, such as adamantol, and it is also advantageous to carry out the reaction with substituted compounds of formula (III) such as phenyl-substituted compounds, e.g. styrene, $\alpha$-methylstyrene, benzyl alcohol, etc.

Mention should also be made of the use of higher $\alpha$-olefin mixtures, e.g. the so-called SHOP olefins (SHOP represents Shell Higher Olefin Process).

Reactions which are of special technical interest are the reactions with isopropanol or with tert.butanol to form N-isopropyl methacrylamide or N-tert.-butyl methacrylamide and the corresponding N-acrylamides.

The process according to the invention is distinguished, *inter alia*, by the fact that the neutralisation of the sulphuric acid, which is an expensive and laborious step, particularly under industrial conditions, can be dispensed with. Particularly in the case of products of formula (I) with higher alkyl substituents (carbon number 4) the product is frequently precipitated as the second phase, either in crystalline form or as an oil. After separation of the second phase formed, extraction may be carried out with a suitable inert extracting agent which is substantially immiscible with the aqueous sulphuric acid. Suitable extracting agents include, for example, optionally halogenated hydrocarbons, such as toluene, methylene chloride or ethers, such as diethyl ether and the like.

One procedure which has proved particularly advantageous involves adding the two components of formula (II) and (III) together to the sulphuric acid, which is preferably already substantially at the reaction temperature. The concentrated sulphuric acid used according to the invention is usually a 95 to 100% acid, preferably a 96 to 98% acid. The duration of the reaction is, as a rule, from 0.5 to 4 hours, in the process according to the invention. Thus, the process advantageously differs from certain processes of the prior art which require substantially longer reaction times. Moreover, the method of addition (the addition of the components of formula (II) and (III) in admixture to the sulphuric acid which is already at reaction temperature) has proved highly advantageous, with respect to the technical procedure used (continuous or discontinuous method, control of the process), whereas the processes of the prior art leave much to be desired in this respect.

In general, the reaction mixture is worked up by diluting it with, as a rule, 10 to 40 moles of water per mole of nitrile of formula (II) used, corresponding to a dilution of the sulphuric acid down to a concentration of about 20 to 50%. A further advantage of the process according to the invention is the fact that the crude product can generally be isolated without neutralisation, by filtration, phase separation and/or extraction. Advantageously, the sulphuric acid obtained can be regenerated, for example using the methods conventionally used in the art.

In some cases, a neutralisation step may help to increase the yield and/or purity of the product. In these cases, the neutralisation step is appropriately carried out after isolation of the crude product (unsaturated N-alkylamide of formula (I)). The neutralisation is preferably effected with ammonia in gaseous or aqueous form.

Unlike the comparable processes of the prior art, the process according to this invention is suitable for use on an industrial scale. A particularly valuable aspect is that the process according to the invention is suitable for continuous operation. In view of the relatively high concentrations of the reaction partners and reaction media and the short retention times, relatively small apparatus may be used even at an industrial level. Owing to the mild conditions of the reaction (normal pressure, maximum temperature 100°C) reaction vessels made from readily available materials, such as glass, enamel-coated materials, V4-A steel and the like, may be used.

The following Examples are provided to illustrate the process of the invention without serving to limit the scope of protection sought therefor. Percentages are by weight unless otherwise indicated.

**Examples**

**Examples 1 to 12**

96% sulphuric acid is taken and heated to reaction temperature. A mixture of methacrylonitrile and olefin or alcohol is added dropwise at the reaction temperature, within 45 to 90 minutes, with stirring and cooling, and then the mixture is stirred at the reaction temperature. The methacrylonitrile has previously been stabilised with 50 ppm of hydroquinone monomethylether and 15 ppm of 4-methyl-2,6-di-tert.butyl-phenol.

The reaction mixture is poured into ice-cold water (minimum 10 to 15 mol of $H_2O$ per mole of nitrile used), the resulting mixture is stirred for 30 minutes and the crude product is obtained by filtration, phase separation or extraction. If necessary, further purification may be effected by fractional vacuum distillation or recrystallisation.

| Example No. | Quantities used [mole] methacrylonitrile | olefin or alcohol | | Reaction conditions $H_2SO_4$ | Temperature [°C] | Duration [h] | Yield % of theory | Product |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.5 | cyclohexene | 2.5 | 5 | 45 | 4 | 97 | N-cyclohexyl-methacryl-amide |
| 2 | 2.5 | isopropanol | 2.6 | 5 | 5 | 80 | 76 | N-isopropyl-methacryl-amide |
| 3 | 1.25 | tert.butanol | 1.5 | 2.5 | 15 | 3 | 86 | N-tert.butyl-methacryl-amide |
| 4 | 1.25 | tert.butanol | 1.5 | 2.5 | 40 | 3 | 55 | N-tert.butyl-methacryl-amide |
| 5 | 2.5 | isobutylene | 2.6 | 3.75 | 10 | 3 | 92 | N-tert.butyl-methacryl-amide |
| 6 | 1 | acetone | 2.4 | 2.4 | 60 | 4 | 80 | 4-(N-methacrylamido)-4-methyl-pentan-2-one |
| 7 | 1 | mesityl oxide | 1.2 | 2.4 | 60 | 4 | 76 | 4-(N-methacrylamido)-4-methyl-pentan-2-one |
| 8 | 0.5 | norbornene-2 | 0.5 | 1 | 65 | 3 | 82 | N-norbornyl-methacryl-amide |
| 9 | 0.33 | adamantanol-1[a.] | 0.33 | 1.3 | 50—70 | 3.5 | 96 | N-adamantyl-methacryl-amide |
| 10 | 0.5 | d 1-borneol-[b.] | 0.5 | 1 | 70 | 4 | 87 | N-borneyl-methacryl-amide |
| 11 | 1 | dec-1-ene | 1 | 2 | 50 | 3.5 | 88 | N-decyl-methacrylamide |
| 12 | 0.16 | dec-2-ol | 0.16 | 0.32 | 65 | 3 | 96 | N-decyl-methacrylamide |

[a.] dissolved in 350 ml of glacial acetic acid
[b.] dissolved in 150 ml of glacial acetic acid

**Example 13**

Reaction mixture:

250 mol (25.6 kg) of 96% $H_2SO_4$
150 mol (11.2 kg) of tert.butanol
125 mol (8.4 kg) of methacrylonitrile
1 g of di-tert.butyl-p-cresol

Apparatus:

120 litre vessel, stirrer, condenser, inspection inlet, cooling brine

Procedure:

25.6 kg of 96% $H_2SO_4$ were placed in a 120 litre vessel and cooled to 10°C with cooling brine. A mixture of 1 g of di-tert.butyl-p-cresol, 8.4 kg of methacrylo-nitrile and 11.2 kg of tert.butanol was added dropwise within $2\frac{1}{2}$ hours with stirring and cooling (cooling brine) at a reaction temperature of from 10—18°C. Then the mixture was stirred for a further $3\frac{1}{2}$ hours at 16 to 21°C. At 9 to 22°C, 35 litres of distilled $H_2O$ were added, whereupon a white crystalline precipitate was formed. The reaction mixture was adjusted to pH 7—8, with cooling, with 29.7 kg of 25% ammonia solution, and the temperature rose to a maximum of 26°C. The reaction mixture was stirred overnight at ambient temperature. The next morning, 20 litres of distilled $H_2O$ were added to reaction mixture, the product was removed by suction filtering and washed with 10 litres of distilled $H_2O$. The white crystals separated by sution filtering were dried overnight in a drying oven at 30°C.

The total yield is 15.36 kg, i.e. 87.0% of theory.
Purity according to GC: 98.5%.
Molecular weight: 141.2
Melting point: 60°C.

**Example 14**

Reaction mixture:

250 mol (25.6 kg) of 96% $H_2SO_4$
125 mol (8.4 kg) of methacrylonitrile
150 mol (9.02 kg) of isopropanol
1 g of di-tert.butyl-p-cresol

Apparatus:

120 litre vessel, stirrer, cooling means, steam heating (low pressure steam).

Procedure:

25.6 kg of 96% $H_2SO_4$ were placed in a 120 litre vessel and brought to a temperature of 90°C with low pressure steam. A mixture of 1 g of di-tert.butyl-p-cresol, 8.4 g of methacrylonitrile and 9.02 kg of isopropanol was added dropwise within 45 minutes at a reaction temperature of 90—130°C, with stirring and cooling (water). Then the mixture was stirred for a further $2\frac{1}{4}$ hours at 91—106°C. At 30 to 50°C, 34 litres of distilled $H_2O$ were added. The reaction mixture was adjusted to pH 5, with cooling, with 25% ammonia solution and the temperature rose to a maximum of 56°C. The reaction mixture was stirred overnight at ambient temperature; the product crystallised out during this time. The next morning, the reaction mixture was suction filtered and washed with about 35 litres of ice-cold water. The light-yellow crystals removed by suction filtering were dried in a drying oven at 30°C over the week-end (8.5 kg of crude product). The mother liquor and filtrate were stirred with 10 litres of methylene chloride. The organic phase was separated off, dried with $Na_2SO_4$, filtered and concentrated by evaporation in the rotary evaporator (3.2 kg of crude product). The total crude yield was 11.7 kg, i.e. 73.5% of theory.

**Example 15**

1 mole of 96% of sulphuric acid was taken and heated to 40°C and a mixture of 0.5 mole of acrylonitrile, 70 g of $C_8$—$C_{12}$ olefin (SHELL) and 5 mg of di-tert.butyl-p-cresol was added within 35 minutes, with stirring and cooling. (The reaction temperature rose to a maximum of 45°C).

The mixture was stirred for a further 3 hours at 40°C, then the reaction mixture was added to 400 ml of ice-cold water. After 15 minutes, the aqueous mixture was extracted twice with methylene chloride, the organic phases were combined and the methylene chloride was drawn off. The desired mixture of product was obtained in a crude yield of 99%.

**Example 16**

The process of Example 15 was repeated using instead a reaction temperature of 20 to 24°C and giving a yield of 96% of theory.

**Examples 17—25**

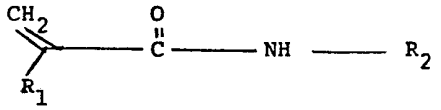
**Preparation of N-decyl-arylamide**

An equimolar mixture of dec-1-ene and acrylonitrile is added dropwise at reaction temperature to sulphuric acid (96%) and then stirred; the reaction mixture is added to ice-cold water and the product is obtained by extraction and removal of the extracting agent.

| *Example No.* | *$H_2SO_4$ [mol/mol nitrile]* | *Temperature [°C]* | *Duration [h]* | *Quantity of $H_2O$ [mol/mol nitrile]* | *Yield % of theory* |
|---|---|---|---|---|---|
| 17 | 2 | 30 | 1 | 20 | 72 |
| 18 | 2 | 30 | 4 | 20 | 87 |
| 19 | 2 | 30 | 3.5 | 4 | 60 |
| 20 | 2 | 30 | 3.5 | 8 | 67 |
| 21 | 2 | 30 | 3.5 | 16 | 85 |
| 22 | 2 | 30 | 3.5 | 40 | 83 |
| 23 | 1.4 | 30 | 4 | 20 | 70 |
| 24 | 3 | 30 | 4 | 20 | 94 |
| 25 | 2 | 60 | 0.5 | 20 | 86 |

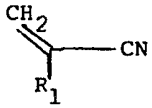
**Claims**

1. A process for the preparation of compounds of formula (I)



(I)

(wherein $R_1$ represents a hydrogen atom or a methyl group, and $R_2$ represents an optionally substituted, optionally cyclic, alkyl group with at least 3 and up to 40 carbon atoms) which comprises reacting a nitrile of formula (II)



(II)

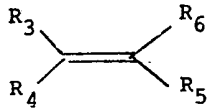
(wherein $R_1$ is as hereinbefore defined) with a compound containing an optionally substituted, optionally cyclic, alkyl group with at least 3 and up to 40 carbon atoms (a compound of formula III) which compound is capable of forming a carbonium ion of formula $R_2^{\oplus}$ (wherein $R_2$ is as hereinbefore defined) under the effect of sulphuric acid; the said reaction being effected by adding the nitrile of formula (II) together with from a slight molar deficiency up to a slight molar excess of the compound of formula (III) to a quantity of concentrated sulphuric acid, in a mole ratio of sulphuric acid to added nitrile of from about 1:1 to 2:1, allowing the mixture to react at 10 to 100°C, and then diluting the reaction mixture so as to obtain a compound of formula (I).

2. A process as claimed in claim 1 wherein the said dilution of the reaction mixture is effected with water.

3. A process as claimed in either of claims 1 and 2 wherein, following dilution of the reaction mixture, the compound of formula (I) is isolated by extraction with an inert extracting agent which is not miscible with the diluted sulphuric acid.

4. A process as claimed in either of claims 1 and 2 wherein, following dilution of the reaction mixture the compound of formula (I), if precipitated is isolated by filtration.

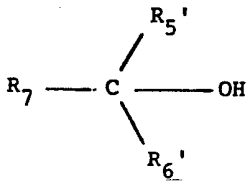
5. A process as claimed in any one of claims 1 to 4 wherein the said compound of formula (III) is an olefin of formula (IIIA)



(IIIA)

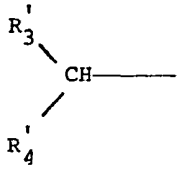
(wherein $R_3$, $R_4$ and $R_5$, which may be the same or different, each represents a hydrogen atom, an optionally substituted $C_{1-21}$ alkyl group, or an aryl group and $R_6$ represents an optionally substituted $C_{1-21}$ alkyl group or an optionally substituted aryl group or two of the groups $R_3$, $R_4$, $R_5$ and $R_6$ together form a carbocyclic or heterocyclic ring; with the proviso that no more than two of the groups $R_3$, $R_4$, $R_5$ and $R_6$ represent aryl groups).

6. A process as claimed in any one of claims 1 to 4 wherein the said compound of formula (III) is an alcohol of formula (IIIB)



(IIIB)

(wherein $R_7$ represents an aryl group or a group of formula



;

$R_3'$, $R_4'$ and $R_5'$, which may be the same or different, each represents a hydrogen atom, on optionally substituted $C_{1-21}$ alkyl group, or an aryl group; and $R_6$ represents a hydrogen atom, an optionally substituted $C_{1-21}$ alkyl group, or an aryl group or two of the groups $R_3'$, $R_4'$, $R_5'$ and $R_6'$ together form a carbocyclic or heterocyclic ring, with the proviso that no more than two of the groups $R_3'$, $R_4'$, $R_5'$, $R_6'$ and $R_7$ represent aryl groups).

7. A process as claimed in any one of claims 1 to 6 wherein the nitrile of formula (II) and the compound of formula (III) are reacted in a molar ratio of from 1:0.9 to 1:1.1.

8. A process as claimed in any one of claims 1 to 7, wherein the reaction between the compounds of formula (II) and (III) is allowed to proceed for from 5 minutes to 4.5 hours.

9. A process as claimed in any one of claims 1 to 8, characterised in that it is carried out continuously.

10. A process as claimed in any one of claims 1 to 9, wherein the concentration of water in the reaction mixture is maintained in the catalytic range up to the stage where the reaction mixture is diluted.

11. A process as claimed in claim 5, wherein, in the compound of formula (IIIA) $R_4$, $R_5$ and $R_6$ each represent hydrogen atoms and $R_3$ represents an optionally substituted $C_{1-12}$ alkyl group.

12. A process as claimed in claim 1 wherein the compound of formula (III) is selected from isopropanol, tert.butanol, cyclohexanol, benzyl alcohol, isobutylene and cyclohexene.

13. A process for the preparation of N-substituted methacrylamides or acrylamides substantially as herein disclosed in any one of the Examples.

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