

The present invention relates to N-sulfomethyl glycinate compounds, a process for the preparation of these compounds and the use of these compounds for the preparation of herbicides of the glyphosate type.

5 Technical context

Glyphosate (N-phosphonomethylglycine) and its salts are wide-spectrum herbicides which are well known in the art. These herbicides and the processes for obtaining them are described, for example, in the following patents: US 3,799,758; US 3,835,000; US 3,868,407; 10 US 3,950,402; US 4,083,893; US 4,147,719 and EP-A-0,019,384. Furthermore, the compound N-sulfomethylglycine is known from US Patent 4,069,048.

Subject of the invention

15 The subject of the invention is to suggest a way of arriving at the glyphosate-type herbicides which has numerous advantages: economy, restricted number of stages, excellent yields and ease of development to the industrial scale.

20 The invention

Firstly the invention relates to a N-sulfomethyl glycinate of formula:



in which formula:

25 COOR_1 is a hydrolysable carboxylic ester group.

Hydrolysable groups are well known in the art. Within the scope of the present invention, a hydrolysable COOR_1 group is understood to mean all the groups which can be lysed in the presence of water, optionally in an acid 30 or basic medium, to give the corresponding $-\text{COOH}$ acid and R_1OH alcohol.

A hydrolysable COOR_1 group is understood to mean a group in which the R_1 radical is in particular chosen from the following radicals:

- 35 linear or branched C_1-C_{18} alkyl, preferably C_1-C_{12}
linear or branched C_2-C_{18} alkenyl, preferably C_2-C_{12}
linear or branched C_2-C_{18} alkynyl, preferably C_2-C_{12}
linear or branched C_3-C_{18} cycloalkyl, preferably C_3-C_{12}

C₆-C₁₄ aryl, preferably C₆-C₁₀
linear or branched C₇-C₁₅ aralkyl, preferably C₇-C₁₁,
these radicals being optionally substituted with one or
more halogen atoms or C₁-C₆ alkoxy or alkylthio radicals,
5 the aryl or aralkyl radicals being capable, in addition,
of comprising 1 to 4 hetero atoms chosen from the atoms
of oxygen, sulfur and nitrogen (for example furyl,
thiophenyl or pyridyl).

Even more preferably, R₁ is chosen from the C₁-C₆
10 alkyl or C₆-C₁₀ aryl (phenyl) or C₇-C₁₁ aralkyl (benzyl,
phenethyl) groups, the said radicals being optionally
substituted with one or more halogen atoms or C₁-C₆ alkoxy
radicals.

In the present specification the chemical
15 compounds are designated by their French nomenclature,
but the numbering of the position of the substituents is
placed before the name of the substituents according to
English nomenclature, and not after according to French
nomenclature.

20 [Translator's note: The immediately preceding paragraph
is redundant in the contest of the present English
translation.]

In the present specification the formulae of
chemical compounds are represented in the nonionic form.
25 It is nevertheless clear to those versed in the technique
that in the case of the amino acids, such as, for example
the compound of formula (I) these can exist in the
zwitterionic form.

Preparation process

30 One preparation process consists in putting
formaldehyde, sulfur dioxide and a glycinate of formula:
H₂N - CH₂ - COOR₁ in contact.

The reaction is preferably carried out with the
following molar proportions:

35	glycinate	1 mole
	sulfur dioxide	0.95 mole to saturation
	formaldehyde	0.95 to 3 moles

The reaction is preferably carried out with the following molar proportions:

- 5 glycine 1 mole
sulfur dioxide 0.95 mole to saturation
formaldehyde 0.95 to 3 moles
but preferably in a proportion greater than that of
the glycinate (1.5 to 2.5 moles).
- 10 R_1OH greater than 0.95 mole
but preferably in a proportion greater than that of
the glycine (greater than 1.2 moles), advantageously
greater than 1.5 moles, and very advantageously
greater than 1.8 moles.

15 According to an advantageous form of the invention the R_1OH alcohol will be used as solvent, the other aprotic solvents mentioned above being capable of being used, optionally, as cosolvents. Preferably, ethanol will be chosen as solvent.

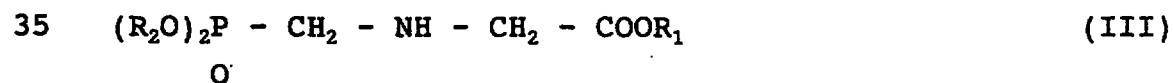
20 The reaction is, otherwise, carried out in the
same conditions as above.

This last process is particularly preferred, and moreover absolutely unexpected, since it leads to the N-sulfomethylglycinate with a practically quantitative yield.

The subject of the invention is also the use of compounds of formula (I) in the preparation of known herbicides of the glyphosate type, the use consisting in putting the compound of formula (I) in contact with a phosphite of formula:



(R₂O)₂P(=O)- being a hydrolysable phosphonic ester group in order to arrive at the compound of formula:



These hydrolysable groups are well known to those versed in the technique. A hydrolysable $(R_2O)_2P(=O)$ -group

is understood to mean a group which, under the action of water, optionally in an acid or basic medium, is lysed to an alcohol R_2OH and an acid $(O=)P(OH)_2$.

A hydrolysable $(R_2O)_2P(=O)-$ group is understood to mean a group the R_2 radical of which is in particular

- chosen from the following radicals:
- linear or branched C_1-C_{18} alkyl, preferably C_1-C_{12}
 - linear or branched C_2-C_{18} alkenyl, preferably C_2-C_{12}
 - linear or branched C_2-C_{18} alkynyl, preferably C_2-C_{12}
 - 10 linear or branched C_3-C_{18} cycloalkyl, preferably C_3-C_{12}
 - linear or branched C_6-C_{14} aryl, preferably C_6-C_{10}
 - linear or branched C_7-C_{15} aralkyl, preferably C_7-C_{11} ,
- these radicals being optionally substituted with one or more halogen atoms or C_1-C_6 alkoxy or alkylthio radicals,
- 15 the aryl or aralkyl radicals being capable, in addition, of comprising 1 to 4 hetero atoms chosen from the atoms of oxygen, sulfur and nitrogen (for example furyl, pyridyl and thiophenyl).

Even more preferably, R_2 is chosen from the C_1-C_6 alkyl or C_6-C_{10} aryl or C_7-C_{11} aralkyl groups, the said radicals being optionally substituted with one or more

halogen atoms or C_1-C_6 alkoxy radicals.

The reaction is carried out in the bulk phase or in an inert solvent.

25 Among the aprotic solvents, saturated aliphatic hydrocarbons such as n-pentane, isopentane, 2-methylhexane and 2,2,5-trimethylhexane, aromatic hydrocarbons such as benzene, toluene, xylene and ethylbenzene, saturated aliphatic ethers such as tetrahydrofuran

30 and isopentyl ether, aromatic ethers such as benzylethyl ether, saturated aliphatic or aromatic ketones such as methyl ethyl ketone, methyl isobutyl ketone and acetophenone, saturated aliphatic or aromatic halogenated hydrocarbons such as fluorobenzene, 1-chloro-2-methylpropane and isobutyl chloride, and saturated aliphatic or

35 aromatic esters such as isobutyl isobutyrate, ethyl acetate and methyl benzoate may be mentioned. All these solvents may be present alone or as a mixture.

Among the protic solvents the saturated aliphatic or aromatic alcohols such as methanol, isopropanol and phenol and the saturated aliphatic or aromatic acids such as acetic acid and benzoic acid may be mentioned.

5 The reaction temperature is between 50°C and 250°C or the boiling point of the solvent, and preferably 100 to 200°C.

 Although a large excess (3/1 to 1/3 in molar ratios) of one of the reactants with respect to the other
10 is possible, it is more advantageous in practice not to diverge from the stoichiometry by more than 20%.

 The compound of formula (III) is a product which is known from the document EP 0,135,454. It may be hydrolysed in a known manner to arrive at the N-phos-
15 phonomethylglycine or glyphosate herbicide.

 The following examples illustrate the invention:
 Glycine (7.5 g; 100 millimoles), 95% ethanol (120 cc) and a 31.5% aqueous solution of formaldehyde (19 g; 200 millimoles) are introduced successively into
20 a two-necked flask provided with an alcohol thermometer. The suspension obtained is saturated with SO₂ until it has completely dissolved (increase of the temperature to 45°C). After 1 h 30 min stirring at ambient temperature a precipitate starts to appear. Stirring is maintained
25 for a further 3 h and the precipitate is filtered and washed with ethanol (30 cc) and then ether (30 cc). After drying ethyl sulfomethylglycinate (18.8 g) is obtained in a purity greater than 95% (determined by NMR at 360 MHz): this is a 95.5% yield with respect to the starting
30 glycine.

 m.p. (Kofler) = 154°C.

 Ethyl sulfomethylglycinate (2.46 g; 12.5 millimoles), xylene (20 cc) and diisopropyl phosphite (2.07 g; 12.5 mmol) are introduced successively into a two-necked
35 flask provided with a thermometer and a means of cooling. The suspension is heated for 1 h at 105°C, and after evaporation of the solvent under a vacuum provided by a water-jet pump an orange oil (3.81 g) is recovered, which

is shown by titration to contain 40% protected glyphosate (isopropyl N-phosphonomethylglycinate).



CLAIMS

1. N-sulfomethylglycinate of formula:
 $\text{HO}_3\text{S} - \text{CH}_2 - \text{NH} - \text{CH}_2 - \text{COOR}_1$ (I)
COOR₁ being a hydrolysable carboxylic ester group.
2. N-sulfomethylglycinate according to claim 1, in which the COOR₁ group is such that R₁ is chosen from the following radicals:
linear or branched C₁-C₁₈ alkyl, preferably C₁-C₁₂
linear or branched C₂-C₁₈ alkenyl, preferably C₂-C₁₂
linear or branched C₂-C₁₈ alkynyl, preferably C₂-C₁₂
linear or branched C₃-C₁₈ cycloalkyl, preferably C₃-C₁₂
linear or branched C₆-C₁₄ aryl, preferably C₆-C₁₀
linear or branched C₇-C₁₅ aralkyl, preferably C₇-C₁₁,
these radicals being optionally substituted with one or more halogen atoms or C₁-C₆ alkoxy or alkylthio radicals, the aryl or aralkyl radicals being capable, in addition, of comprising 1 to 4 hetero atoms chosen from the oxygen, sulfur and nitrogen atoms.
3. N-sulfomethylglycinate according to claim 2, in which the COOR₁ group is such that R₁ is chosen from the C₁-C₆ alkyl or C₆-C₁₀ phenyl or C₇-C₁₁ aralkyl radicals, the said radicals being optionally substituted with one or more halogen atoms or C₁-C₆ alkoxy or C₁-C₆ alkylthio radicals.
4. Process for the preparation of N-sulfomethylglycinate according to one of claims 1 to 3, in which formaldehyde, sulfur dioxide and a glycinate of formula:
 $\text{H}_2\text{N} - \text{CH}_2 - \text{COOR}_1$
are put in contact, COOR₁ having the same meaning as in claim 1.
5. Process for the preparation of N-sulfomethylglycinate according to claim 4, in which the compounds are put in contact in the following molar proportions:
- | | |
|----------------|-----------------------------|
| glycinate | 1 mole |
| sulfur dioxide | 0.95 [lacuna] to saturation |
| formaldehyde | 0.95 to 3 moles |
6. Process for the preparation of N-sulfomethylglycinate according to one of claims 1 to 3, in which



formaldehyde, sulfur dioxide, an alcohol of formula R_1OH and glycine are put in contact.

7. Process for the preparation of N-sulfomethylglycinate according to claim 6, in which the compounds are put in contact in the following molar proportions:

glycine	1 mole
sulfur dioxide	0.95 [lacuna] to saturation
formaldehyde	0.95 to 3 moles
R_1OH	greater than 0.95 mole

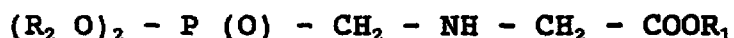
8. Process for the preparation of N-sulfomethylglycinate according to claim 7, in which the molar proportion of R_1OH is greater than 1.2 moles, and advantageously R_1OH is used as solvent.

9. Process for the preparation of N-sulfomethylglycinate according to claim 4 or 6, in which the reaction is carried out between 0 and 100°C, optionally in an inert solvent (or cosolvent).

10. Use of the N-sulfomethylglycinate of formula (I) according to one of claims 1 to 3, for the preparation of herbicides of the glyphosate type, in which the N-sulfomethylglycinate of formula (I) is put in contact with a phosphonate or a phosphite of formula:



- (R_2O)₂P(=O)- being a hydrolysable phosphonic ester group, in order to arrive at the compound of formula (III)



this compound being capable of then being optionally hydrolysed in a known manner.

11. Use according to claim 10, in which the R_2 group is chosen from the following groups:

- linear or branched C_1-C_{18} alkyl, preferably C_1-C_{12}
 - linear or branched C_2-C_{18} alkenyl, preferably C_2-C_{12}
 - linear or branched C_2-C_{18} alkynyl, preferably C_2-C_{12}
 - linear or branched C_3-C_{18} cycloalkyl, preferably C_3-C_{12}
 - linear or branched C_6-C_{14} aryl, preferably C_6-C_{10}
 - linear or branched C_7-C_{15} aralkyl, preferably C_7-C_{11} ,
- these radicals being optionally substituted with one or more halogen atoms or C_1-C_6 alkoxy or alkylthio radicals,



the aryl or aralkyl radicals being capable, in addition, of comprising 1 to 4 hetero atoms chosen from the oxygen, sulfur and nitrogen atoms.

12. Use according to claim 10, in which a molar ratio
5 (I):(II) of between 1/3 and 3, and advantageously between 0.8 and 1.2, is used.