AUSTRALIA

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PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

I/We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] Applicant: HOECHST AKTIENGESELLSCHAFT

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[70] Nominated Person: HOECHST AKTIENGESELLSCHAFT

Address: D-6230 Frankfurt/Main 30, Federal Republic of Germany

[54] Invention Title: PROCESS FOR THE PREPARATION OF SULFONYLUREAS

[72] Name(s) of actual inventor(s): LOTHAR WILLMS, STEPHEN LACHHEIN, GUNTER SCHLEGEL and HEINZ KEHNE

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BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
P41 07 326.6	Germany	DE	7th March 1991

Drawing number recommended to accompany the abstract .....

By my/our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.....
D. B. Mischlewski

.....5th.March.1992.....
(Date)

Registered Patent Attorney

FO32227 06/03/92

653386

P/00/008b 12.11 91
Section 29 (1)
Regulation 3.1 (2)

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NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, HOECHST AKTIENGESELLSCHAFT, of D-6230 Frankfurt am Main 80, Germany, being the applicant in respect of Application No. 11464/92 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors by virtue of an employment contract.

The person nominated for the grant of the patent is the applicant of the basic application listed on the patent request form.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.....

Darryl B. Mischlewski
Registered Patent Attorney

DATED this 29th day of July, 1994

AU9211464

12) PATENT ABRIDGMENT (11) Document No. AU-B-11464/92
19) AUSTRALIAN PATENT OFFICE (10) Acceptance No 653386

54) Title
PROCESS FOR THE PREPARATION OF SULFONYLUREAS

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C07D 239/52 C07D 251/16 C07D 251/22 C07D 251/46

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74) Attorney or Agent
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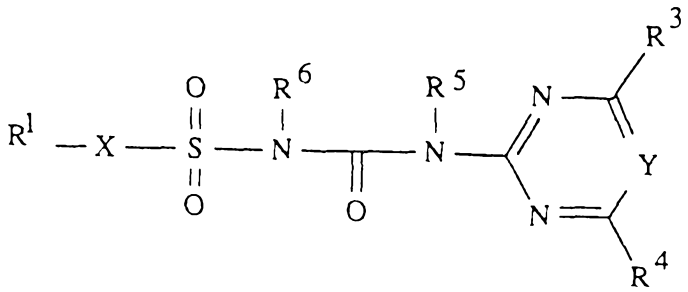
56) Prior Art Documents
AU 11178/92 C07C

57) Claim

1. A process for the preparation of a compound of the formula (I) or a salt thereof,



(I)

in which

X is oxygen, $-O-NR^2-$ or $-SO_2-NR^2-$, the O or SO_2 of the two last-mentioned divalent groups being directly bound to R^1,

Y is nitrogen or CH,

R^1 is (C_1-C_6)-alkyl, (C_2-C_6)-alkenyl or (C_2-C_6)-alkynyl, each of said 3 radicals being unsubstituted or mono- or polysubstituted by radicals selected from the group comprising halogen, (C_1-C_4)-alkoxy and (C_1-C_4)-alkoxycarbonyl, or, where X = oxygen, is alternatively phenyl which is unsubstituted or substituted by one or more radicals selected from the group compris-

ing halogen, nitro, (C_1-C_4)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-alkoxy, (C_1-C_4)-haloalkoxy or (C_1-C_4)-alkoxycarbonyl,

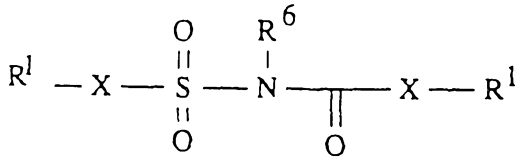
R^2 is hydrogen, (C_1-C_6)-alkyl, (C_2-C_6)-alkenyl, (C_2-C_6)-alkynyl or (C_3-C_6)-cycloalkyl,

R^3, R^4 are, independently of each other, hydrogen, (C_1-C_4)-alkyl or (C_1-C_4)-alkoxy, each of the last-mentioned two radicals being unsubstituted or mono or polysubstituted by radicals selected from the group comprising halogen, alkoxy and alkylthio, or halogen, (C_1-C_4)-alkylthio, (C_1-C_4)-alkylamino or di-[(C_1-C_4)-alkyl]amino and

R^5, R^6 are, independently of each other, hydrogen or (C_1-C_4)-alkyl,

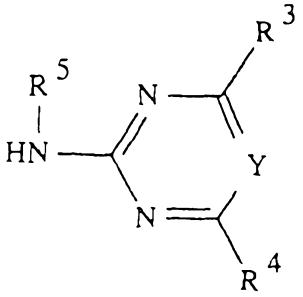
or their physiologically tolerated salts with acids, or, where at least one of the R^5 and R^6 radicals is hydrogen, with bases,

which comprises reacting compounds of the formula II,



(II)

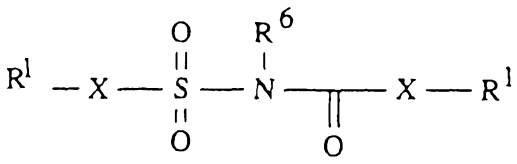
in which R^1, R^6 and X are defined as in formula I, with compounds of the formula III,



(III)

in which R^3, R^4, R^5 and Y are defined as in formula I.

9. A compound of the formula II,



(II)

in which R^1, R^6 and X are defined as in formula I.

P/00/011 28/5/91
Regulation 3.2(2)

AUSTRALIA

Patents Act 1990

653386

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:

Lodged:

Invention Title: PROCESS FOR THE PREPARATION OF SULFONYLUREAS

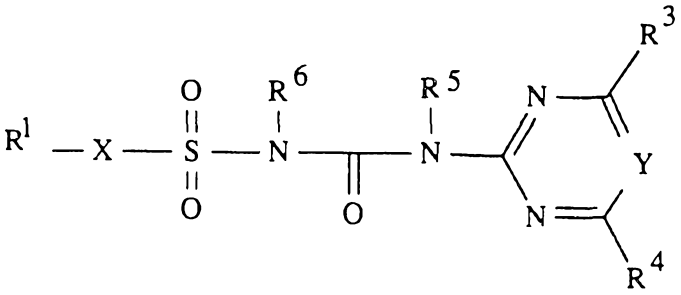
The following statement is a full description of this invention, including the best method of performing it known to :- us

HOECHST AKTIENGESELLSCHAFT HOE 91/F 071 Dr.WE/je

Description

Process for the preparation of sulfonylureas

The invention relates to processes for the preparation of herbicides selected from the group comprising the heterocyclically substituted sulfonylureas, especially the compounds of formula I



(I)

in which

X is oxygen, $-O-NR^2-$ or $-SO_2-NR^2-$, the O or SO_2 of the two last-mentioned divalent groups being directly bound to R^1,

Y is nitrogen or CH,

R^1 is (C_1-C_6)-alkyl, (C_2-C_6)-alkenyl or (C_2-C_6)-alkynyl, each of said 3 radicals being unsubstituted or mono- or polysubstituted by radicals selected from the group comprising halogen, (C_1-C_4)-alkoxy and (C_1-C_4)-alkoxycarbonyl,
or, where X = oxygen, is alternatively phenyl which is unsubstituted or substituted by one or more radicals selected from the group comprising halogen, nitro, (C_1-C_4)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-alkoxy, (C_1-C_4)-haloalkoxy or (C_1-C_4)-alkoxycarbonyl,

R^2 is hydrogen, (C_1-C_6)-alkyl, (C_2-C_6)-alkenyl, (C_2-C_6)-alkynyl or (C_3-C_6)-cycloalkyl,

R^3, R^4 are, independently of each other, hydrogen, (C_1-C_4)-alkyl or (C_1-C_4)-alkoxy, each of the last-mentioned two radicals being unsubstituted or

mono- or polysubstituted by radicals selected from the group comprising halogen, alkoxy and alkylthio, or halogen, (C_1-C_4)-alkylthio, (C_1-C_4)-alkylamino or di[(C_1-C_4)-alkyl]amino and

R^5, R^6 are, independently of each other, hydrogen or (C_1-C_4)-alkyl,

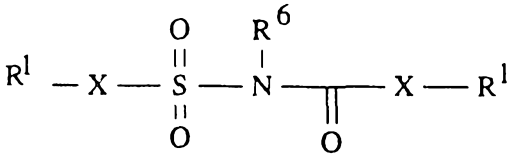
and their physiologically tolerated salts with acids, or, where at least one of the R^5 and R^6 radicals is hydrogen, with bases.

Compounds of the formula I are known and are used as crop protection agents having herbicidal activity; see EP-A-0131258 (US-A-4,601,747), EP-A-0342569 (ZA-A-89/3643) and EP-A-4163 (US-A-4,191,553). Some processes are also cited or described therein, according to which compounds of the formula I can be prepared.

The known processes have the disadvantage of relatively low yields of at most about 65-70%. As a result, comparatively large amounts of impurities and by-products are produced, which, for application on a commercial scale, represent waste which must be expensively disposed of, for example by means of incineration. The known processes are therefore unfavorable from the ecological and also the economic point of view for carrying out on an industrial, commercial scale. Moreover, at such a low yield, a drastic loss of the starting materials used occurs, which reduces the economic efficiency of the processes.

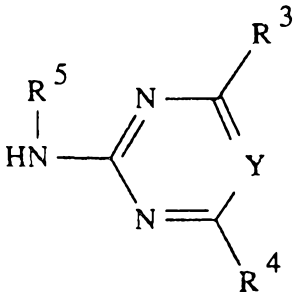
A new process has now been found by which the compounds of the formula I can be prepared in surprisingly high yield and purity, and which is suitable for carrying out on a large industrial scale.

The present invention relates to a process for the preparation of said compounds of the formula I or their salts, which comprises reacting compounds of the formula II,



(II)

in which R^1, R^6 and X are defined as in formula I, with compounds of the formula III,



(III)

in which R^3, R^4, R^5 and Y are defined as in formula I.

In the formulae mentioned, alkyl is straight-chain or branched alkyl; this applies correspondingly to the hydrocarbon moiety in the other radicals, such as alkoxy, haloalkyl, haloalkoxy, alkylcarbonyl, alkylamino, alkenyl, alkynyl, alkylsulfonyl etc. Halogen is fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine. Haloalkyl is alkyl which has been substituted by one or more halogen atoms; this applies correspondingly to haloalkoxy.

Among the processes according to the invention for the preparation of compounds of the formula I, those in which R^1X is N-(C_1-C_6)-alkylsulfonyl-N-(C_1-C_3)-alkylamino or (C_1-C_4)-alkoxyphenoxy, R^3 and R^4 are, independently of each other, (C_1-C_2)-alkyl or (C_1-C_2)-alkoxy, R^5 is hydrogen and R^6 is hydrogen or methyl are of particular interest. Preferably in this case R^1X is N-[(C_1-C_3)-alkylsulfonyl]-N-[(C_1-C_2)-alkyl]amino, in particular N-(methylsulfonyl)-N-(methyl)amino, N-(methylsulfonyl)-N-(ethyl)amino, N-(ethylsulfonyl)-N-(methyl)amino or N-(ethylsulfonyl)-N-(ethyl)amino, or (C_1-C_3)-alkoxyphenoxy, in particular 2-methoxyphenoxy, 2-ethoxyphenoxy, 2-n-propoxyphenoxy or 2-isopropoxyphenoxy, and R^3 and R^4 are, independently of each other, (C_1-C_2)-alkyl or (C_1-C_2)-alkoxy, in particular

methyl or methoxy, and R^5 and R^6 are each hydrogen or methyl.

The yields from the process according to the invention are comparatively high, for example 95% of theory and above, the purities of the resulting sulfonylureas of the formula I often being greater than 95% by weight.

The process according to the invention is generally carried out in the presence of inorganic or organic solvents which are inert under the reaction conditions, or mixtures thereof. Inert organic solvents are suitable solvents, but so are water and aqueous organic solvents.

Examples of suitable solvents are aliphatic or aromatic, halogenated or nonhalogenated hydrocarbons, aprotic polar organic solvents, such as dialkylalkanoylamides, dialkyl sulfoxides, polyalkylene glycol dialkyl ethers, N-alkylated cyclic amides and nitriles and also mixtures of said solvents.

Preference is given to solvents such as for example toluene, xylene, chlorobenzene, 1,2-dichloroethane, dimethylformamide, dimethyl sulfoxide, di-, tri- or tetraethylene glycol dialkyl ethers, in particular the dimethyl or diethyl ethers, N-methylpyrrolidone, acetonitrile or alternatively mixtures of two or more of said solvents.

However, the process according to the invention can also be carried out in an aqueous medium, for example a purely aqueous medium.

It is generally advantageous to use the compound of the formula II in an equimolar ratio to the compound of the formula III, or in a slight excess. Preference is given to a molar ratio for II:III of 1:1 to 1.2:1, in particular 1:1 to 1.1:1.

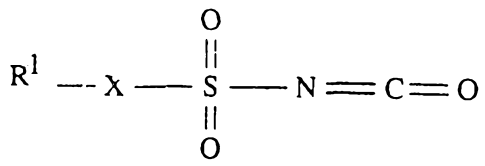
The reaction temperatures are preferably from 0°C to the boiling point of the solvent used, in particular from room temperature (for example 20°C) to 110°C.

An advantage of the process according to the invention is that the compound of the formula IV, eliminated from compounds of the formula II,

$$R^1\text{-}X\text{-}H \qquad (IV)$$

in which R^1 and X are defined as above, can be quantitatively recycled in the course of carrying out the process according to the invention and, with subsequent syntheses to give the compounds of the formula II, can be directly reused. If required, prior to recycling, the compounds of the formula IV can be purified, for example in a simple manner by distillation.

A further advantage of this process is the avoidance of the use of compounds of the formula V,



(V)

which are used in conventional processes for the preparation of compounds of the formula I and which are formed as intermediates in these cases at the conventional reaction temperatures of above 110°C. However, under these conventional conditions, the isocyanates of the formula V can be highly thermally labile and partially decompose, which is reflected in low yields (see EP-A-0131258 (US-A-4,601,747), DE-A-2257240 (US-A-3,931,277), G. Lohaus, Chem. Ber. 105, 2791-2799 (1972)).

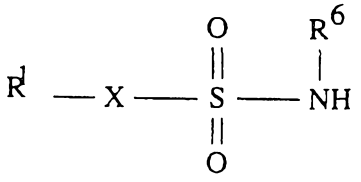
An additional advantage of the process according to the invention is that the solvents can be recycled in almost quantitative yield, as the products of the formula I

precipitate as sparingly soluble compounds from the reaction medium in high purity and yield. The solvents can subsequently be purified, for example by distillation, and then reintroduced into the process.

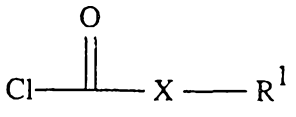
Some of the starting compounds of the formulae II and III, required for the preparation of the compounds of the formula I by the process according to the invention, may be prepared by methods known from the literature.

Thus the heterocyclic compounds of the formula III are either commercially available or may be easily prepared by suitable laboratory methods; see for example US-A-4,310,470; EP-A-0027200; US-A-4,299,960; M.J. Langermann, C.K. Banks, J. Am. Chem. Soc. 73,3011 (1951).

The compounds of the formula II are novel and can be obtained by analogy with conventional methods (see for example Tietze and Eicher in "Reaktionen und Synthesen" [Reactions and Syntheses], p. 92, Thieme Verlag, Stuttgart 1981) by reaction of the corresponding sulfonamides VI with the corresponding acid chlorides VII,



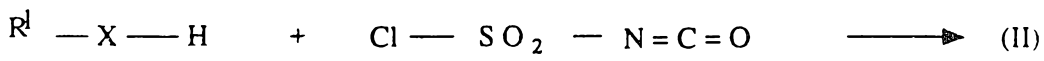
(VI)



(VII)

which can themselves be synthesized by conventional laboratory methods by reaction of the compound of the formula R^1-X-H (said formula IV) and the corresponding amidosulfonyl chlorides of the formula Cl-SO_2-NHR^6 (giving the product of the formula VI) or phosgene or chloroformate (giving the product of the formula VII) (see for example "Organikum" [Practical Organic Chemistry], 7th edition, p. 539, VEB Deutscher Verlag der Wissenschaften, Berlin 1967).

Furthermore, the compounds of the formula II can be prepared in excellent yield by a new process, which is likewise a subject-matter of the invention. The process comprises reacting compounds of the formula IV with about half the amount of chlorosulfonyl isocyanate:



(IV) (II)

In this case the compounds of the formula IV can be used either as free alcohols, hydroxylamines or amides (depending on the definition of R^1 and X), in the presence or absence of an organic or inorganic base, or as a mixture of the free compound IV and a corresponding salt of the compound IV. In the last-mentioned case, preference is given to a mixture of free compound IV with an alkali metal salt of the compound IV, such as the sodium salt or potassium salt, in a molar ratio of about 1:1.

The compound of the formula IV is generally used in a molar ratio to the chlorosulfonyl isocyanate of 1.0:0.5 to 2.0:0.5, preferably 1.0:0.5 to 1.5:0.5.

It is usually appropriate to carry out the reaction in the presence of an inert solvent, the inert organic solvents and types of solvents mentioned in the above-mentioned reaction of the compounds of the formulae II and III also being suitable in this case.

The novel process for the production of the compounds II can be carried out in such a manner that the compounds of the formula IV are converted into a 1:1 mixture, based on molar amounts, of the free compound IV and its alkali metal salt using 0.5 mole equivalent of an inorganic base, for example an alkali metal hydroxide or an alkali metal alcoholate, and the mixture is subsequently reacted with 0.5 mole equivalent of chlorosulfonyl isocyanate. Alternatively the free compound IV can be reacted with

.5 mole equivalent of chlorosulfonyl isocyanate and a base then added, for example an organic base (for example a tertiary amine such as triethylamine) and the reaction continued until consumption of the compound IV. It is also possible in some instances to achieve complete conversion without a base by reaction of the free compound IV with 0.5 mole equivalent of chlorosulfonyl isocyanate with heating of the reaction mixture to the boiling point of the solvent and, if required, distilling off the resulting HCl.

The reaction temperatures for producing the compounds of the formula II depend on the specific compounds of the formula IV and the process variant, and are generally 0°C to 140°C, preferably 20°C to 130°C.

The reaction is preferably carried out using a 1:1 mixture of the free compound of the formula IV and an alkali metal salt of the compound of the formula IV. This last process variant results in high yields and, surprisingly, proceeds successfully even at low temperatures suitable for chlorosulfonyl isocyanate of less than 100°C, preferably 50 to 90°C.

In a particularly advantageous development of the invention, the entire reaction sequence for the preparation of a compound of the formula I can be carried out directly, without isolation of the intermediate of the formula II, from the starting compounds of the formula IV and chlorosulfonyl isocyanate, preferably in a one-pot reaction.

The invention therefore also relates to the combination of the part processes mentioned, which comprises

a) reacting the compound of the formula IV and chlorosulfonyl isocyanate in the molar ratio mentioned to give the compound of the formula II and, preferably without isolating the intermediate of the formula II,

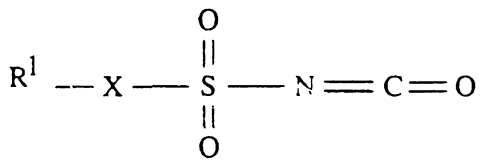
b) subsequently reacting the compounds of the formulae II and III to give the compound of the formula I.

The problem-free course of the process according to the invention and the high yield are considered surprising, since the starting product of the formula II contains a plurality of activated, electrophilic and nucleophilic centers. In particular, all of the electrophilic centers can in principle react with the nucleophilic substances of the formula III and thus produce a multiplicity of by-products by fragmentation reactions; cf. Beyer, Lehrbuch der org. Chemie [Textbook of Organic Chemistry], 19th edition, p. 128, Hirzel Verlag Stuttgart, according to which sulfonyl groups and phenoxy groups are very good leaving groups.

The process according to the invention is particularly surprising in the case of compounds of the formula II in which X = $-SO_2NR^2-$ or $-ONR^2-$, since in this case a transamidation occurs in process step b), which leads virtually quantitatively to the desired product; however, a mixture of the compounds of the formulae II and I in a ratio of about 1:1 was rather to be expected. However, surprisingly, the side reactions and the expected mixture hardly occur at all in the process according to the invention; rather, yields of over 95% of theory and purities of over 95% are generally obtained. Therefore the process according to the invention is a novel, simple, highly reproducible even on a relatively large industrial scale and highly selective process for the production of the compounds of the formula I in virtually quantitative yields. The process can be carried out continuously or discontinuously.

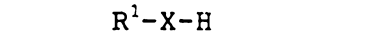
As already briefly mentioned above, it has surprisingly been found that the salts of the compound of the formula IV react at low temperatures in high yields with chlorosulfonyl isocyanate. In a further development of this process variant, a gentle process for the preparation of

isocyanates of said formula V has been additionally found, which shows significant advantages in comparison to the conventional process for the preparation of this intermediate for the preparation of the compounds of the formula I. The invention therefore also relates to a process for the preparation of a compound of the formula V



(V)

which comprises reacting a salt, preferably an alkali metal salt, of a compound of the formula IV



(IV)

with chlorosulfonyl isocyanate in a molar ratio of at most 1:1, preferably 1:1 to 0.9:1.

The reaction is advantageously carried out in inert organic solvents, for example those already mentioned above for the other process variants. The reaction temperature is generally less than 100°C, preferably 50 to 90°C. In comparison to conventional processes (see for example DE-A-2257240), the yield of compound of the formula V in the last-mentioned process is improved and thermal decomposition of the isocyanate is avoided. Improvement in the yield of intermediate is simultaneously accompanied by an increase in the economic efficiency of the total process for the preparation of herbicides of the formula (I).

The reaction of IV and chlorosulfonyl isocyanate proceeds with high selectivity at the Cl-S bond and hardly at all at the isocyanate group. This was particularly unexpected since the isocyanate group in chlorosulfonyl isocyanate is normally considered to be more reactive than the C-S bond (see for example DE-A-2257240 and Lohaus, Chem. Ber.

105, 2791-2799 (1972)).

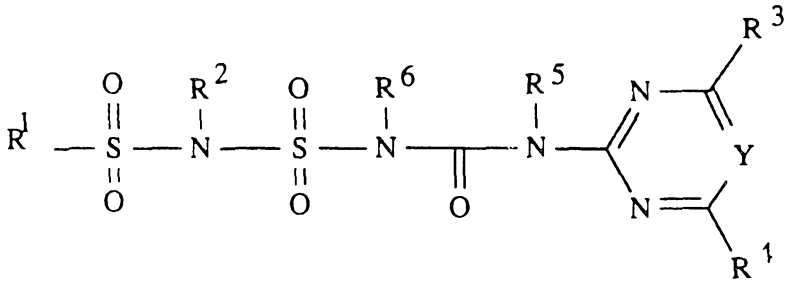
EXAMPLE 1 1-[(N-Methylsulfonyl-N-methyl-amino)-sulfonyl]-3-(4,6-dimethoxy-2-pyrimidyl)urea

32.3 g of 1-[(N-methylsulfonyl-N-methylamino)-sulfonyl]-3-(N-methylsulfonyl-N-methylamino)urea are slurried in 500 ml of chlorobenzene, 15.5 g of 2-amino-4,6-di-methoxypyrimidine are added at 80°C with stirring, and the mixture is heated for 3 hours at 80°C. After cooling to 20°C, the precipitate is filtered off and washed with 100 ml of chlorobenzene. 36.4 g of the desired product are obtained with a purity of 98.1%, corresponding to a yield of 96.8% of theory. The melting point for the product is 183-185°C. 5.1 g of N-methylmethanesulfonamide are recovered from the filtrate by distillation, corresponding to a yield of 92.7% of theory.

EXAMPLE 2 1-(2-Ethoxyphenoxysulfonyl)-3-(4,6-dimethoxy-2-pyrimidyl)urea

38.1 g of 2-ethoxyphenyl N-(2-ethoxyphenoxysulfonyl)carbamate are dissolved in 500 ml of toluene, 15.5 g of 2-amino-4,6-dimethoxypyrimidine are added at room temperature, and the mixture is heated for 2 hours at 100°C. After cooling to 30°C, the precipitate is filtered off and washed with 100 ml of toluene. 38.8 g of the desired product are obtained with a purity of 98.8%, corresponding to a yield of 96.4% of theory. The melting point for the product is 147-149°C. 6.5 g of 2-ethoxyphenol are recovered from the mother liquor by distillation.

The compounds of the formula Ia listed in Table 1 below can be synthesized by analogy with Examples 1 and 2.



(Ia)

Table 1: Compounds of the formula (Ia)

Ex.	R^1	R^2	R^3	R^4	R^5	R^6	Y	m.p.[°C]
3	CH_3	C_3H_7	CH_3	CH_3	H	H	CH	156-157
4	CH_3	$CH(CH_3)_2$	CH_3	CH_3	H	H	CH	122-123
5	C_2H_5	C_2H_5	CH_3	CH_3	H	H	CH	
6	CH_3	CH_3	CH_3	CH_3	H	H	CH	
7	CH_3	CH_3	CH_3	CH_3	H	CH_3	CH	
8	C_4H_9	CH_3	CH_3	CH_3	H	H	CH	
9	CH_3	c-C_6H_{11}	CH_3	CH_3	H	H	CH	
10	C_2H_5	C_2H_5	OCH_3	OCH_3	H	H	CH	148
11	C_2H_5	CH_3	OCH_3	OCH_3	H	H	CH	
12	C_2H_5	CH_3	Cl	CH_3	H	H	CH	110-112
13	CH_2Cl	CH_3	OCH_3	CH_3	H	H	CH	
14	CH_3	CH_3	CH_3	OCH_3	CH_3	H	N	
15	CH_3	C_3H_7	CH_3	OCH_3	H	H	N	
16	CH_3	$CH(CH_3)_2$	CH_3	CH_3	H	H	N	
17	C_2H_5	C_2H_5	CH_3	CH_3	H	H	N	
18	C_2H_5	CH_3	OCH_3	OCH_3	H	H	N	
19	C_2H_5	C_2H_5	OCH_3	OCH_3	H	H	N	
20	C_9H_4	CH_3	CH_3	CH_3	H	H	N	

EXAMPLE 21 (Preparation of compounds of the formula II)

1-[(N-Methylsulfonyl-N-methylamino)-sulfonyl]-3-(N-methylsulfonyl-N-methylamino)urea

109 g of N-methylmethanesulfonamide are dissolved in 1000 ml of chlorobenzene, 20 g of sodium hydroxide are added, and the resulting water of reaction (9 ml) is removed from circulation. 70.0 g of chlorosulfonyl isocyanate are subsequently added dropwise to the reaction solution at 80°C, and the mixture is then heated for 3 hours at 90°C. During the period of the reaction the resulting sodium chloride is precipitated. The reaction mixture is filtered at room temperature and the filter residue is washed free of sodium chloride.

157 g of a product having a purity of 97.2% are obtained, corresponding to a yield of 94.5% of theory. The melting point is 128-129°C and is identical to that of a product prepared by an alternative synthesis route.

EXAMPLE 22 (One-pot process)

1-(2-Ethoxyphenoxysulfonyl)-3-(4,6-dimethoxy-2-pyrimidyl)urea

138 g of 2-ethoxyphenol are dissolved in 1000 ml of chlorobenzene, 20 g of sodium hydroxide are added, and the resulting water of reaction (9 ml) is distilled off. 70.5 g of chlorosulfonyl isocyanate are then added dropwise at 50°C and the mixture is heated for 3 hours at 100°C. During the period of the reaction the resulting sodium chloride is precipitated. The reaction temperature is reduced to 80°C; 77.5 g of 2-amino-4,6-dimethoxypyrimidine are then added. After stirring for 4 hours at 80°C, the mixture is cooled to room temperature and filtered. The common salt still present is washed from the filtrate with water. There remain 186.5 g of the

title sulfonylurea of a purity of 97.8%, corresponding to a yield of 91.6% of theory. The melting point of the product is 146-148°C. 63.2 g of 2-ethoxyphenol are recovered from the mother liquor by distillation.

EXAMPLE 23 (Preparation of compounds of the formula V)

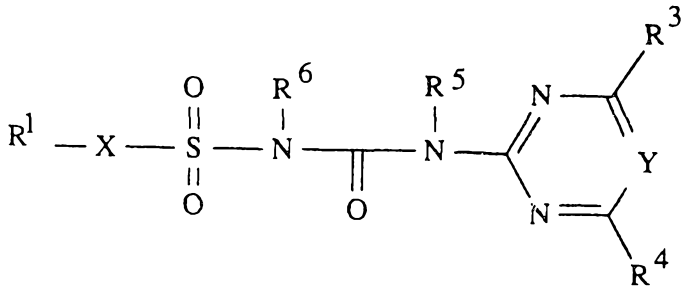
N-Methanesulfonyl-N-methylaminosulfonyl isocyanate

109 g of N-methylmethanesulfonamide are dissolved in 1000 ml of chlorobenzene, and 180 g of 30% strength sodium methylate solution are added. The mixture is then heated to reflux temperature and the methanol is distilled off. The mixture is subsequently cooled to 50°C and 141.5 g of chlorosulfonyl isocyanate are slowly added. After addition is completed, the mixture is stirred for 2 h at 80 to 90°C and the sodium chloride is subsequently filtered off by suction. The crude product solution is freed from the solvent by distillation under reduced pressure. 212 g of crude sulfonyl isocyanate of a purity of 94.3% by weight remain, corresponding to a yield of 93.4% of theory. The refractive index is $n_D^{25} = 1.4768$. The ^{1}H-NMR spectrum corresponds to that of a comparison sample prepared by a known synthesis route.

Patent Claims

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the preparation of a compound of the formula (I) or a salt thereof,



(I)

in which

X is oxygen, $-O-NR^2-$ or $-SO_2-NR^2-$, the O or SO_2 of the two last-mentioned divalent groups being directly bound to R^1,

Y is nitrogen or CH,

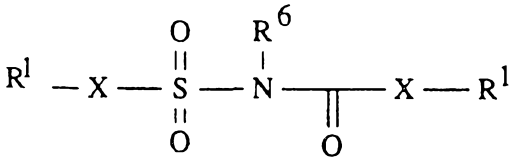
R^1 is (C_1-C_6)-alkyl, (C_2-C_6)-alkenyl or (C_2-C_6)-alkynyl, each of said 3 radicals being unsubstituted or mono- or polysubstituted by radicals selected from the group comprising halogen, (C_1-C_4)-alkoxy and (C_1-C_4)-alkoxycarbonyl, or, where X = oxygen, is alternatively phenyl which is unsubstituted or substituted by one or more radicals selected from the group comprising halogen, nitro, (C_1-C_4)-alkyl, (C_1-C_4)-haloalkyl, (C_1-C_4)-alkoxy, (C_1-C_4)-haloalkoxy or (C_1-C_4)-alkoxycarbonyl,

R^2 is hydrogen, (C_1-C_6)-alkyl, (C_2-C_6)-alkenyl, (C_2-C_6)-alkynyl or (C_3-C_6)-cycloalkyl,

R^3, R^4 are, independently of each other, hydrogen, (C_1-C_4)-alkyl or (C_1-C_4)-alkoxy, each of the last-mentioned two radicals being unsubstituted or mono- or polysubstituted by radicals selected from the group comprising halogen, alkoxy and alkylthio, or halogen, (C_1-C_4)-alkylthio, (C_1-C_4)-alkylamino or di-[(C_1-C_4)-alkyl]amino and

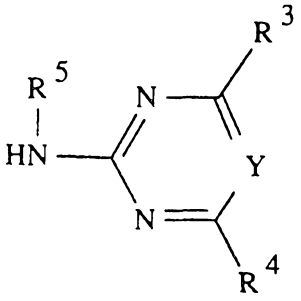
R^5, R^6 are, independently of each other, hydrogen or (C_1-C_4)-alkyl,

or their physiologically tolerated salts with acids, or, where at least one of the R^5 and R^6 radicals is hydrogen, with bases,
which comprises reacting compounds of the formula II,



(II)

in which R^1, R^6 and X are defined as in formula I, with compounds of the formula III,



(III)

in which R^3, R^4, R^5 and Y are defined as in formula I.

2. The process as claimed in claim 1, wherein R^1X is N-(C_1-C_6)-alkylsulfonyl-N-(C_1-C_3)-alkylamino or (C_1-C_4)alkoxyphenoxy, R^3 and R^4 are, independently of each other, (C_1-C_2)-alkyl or (C_1-C_2)-alkoxy and R^5 and R^6 are each hydrogen or methyl.

3. The process as claimed in claim 1 or 2, wherein R^1X is N-[(C_1-C_3)-alkylsulfonyl]-N-[(C_1-C_2)-alkyl]amino or (C_1-C_3)-alkoxyphenoxy and R^3 and R^4 are, independently of each other, (C_1-C_2)-alkyl or (C_1-C_2)-alkoxy and R^5 and R^6 are each hydrogen or methyl.

4. The process as claimed in one or more of claims 1 to 3, wherein the process is carried out in the presence of an inorganic or organic solvent which is inert under the reaction conditions, or mixtures of

a plurality of corresponding solvents.

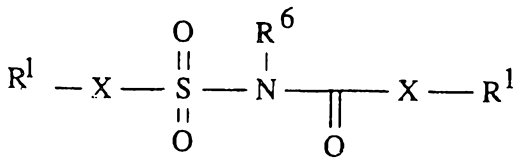
5. The process as claimed in one or more of claims 1 to 4, wherein the process is carried out in the presence of an inert organic solvent.

6. The process as claimed in one or more of claims 1 to 5, wherein the compound of the formula II is used in an equimolar ratio to the compound of the formula III or in a slight excess.

7. The process as claimed in claim 6, wherein the molar ratio II:III is in the range from 1:1 to 1.2:1.

8. The process as claimed in one or more of claims 1 to 7, wherein the reaction temperatures are in the range from 0°C to the boiling point of the solvent used.

9. A compound of the formula II,



(II)

in which R^1, R^6 and X are defined as in formula I.

10. A process for the preparation of a compound of the formula II as claimed in claim 9, which comprises reacting a compound of the formula IV,

$$R^1\text{-}X\text{-}H \qquad (IV)$$

in which R^1 is defined as in formula II, with about half the molar amount of chlorosulfonyl isocyanate.

11. The process as claimed in claim 10, wherein the compound of the formula IV is used as the free (neutral) compound.

12. The process as claimed in claim 11, wherein the reaction is carried out in the presence of an organic or inorganic base.

13. The process as claimed in claim 10, wherein the compound IV is used as a mixture of the free (neutral) compound of the formula IV and an alkali metal salt of the compound IV in a molar ratio of about 1:1.

14. The process as claimed in one or more of claims 10 to 13, wherein the compound of the formula IV is used in a molar ratio to the chlorosulfonyl isocyanate of 1.0:0.5 to 2.0:0.5.

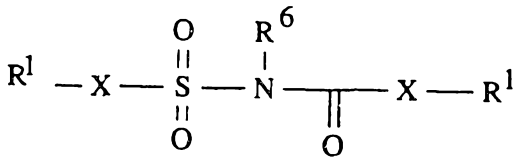
15. The process as claimed in one or more of claims 10 to 14, wherein the reaction is carried out in the presence of an inert organic solvent as far as possible without water.

16. A process for the preparation of a compound of the formula I, as defined in claim 1, which comprises

a) reacting a compound of the formula IV,

$$R^1\text{-}X\text{-}H \qquad (IV)$$

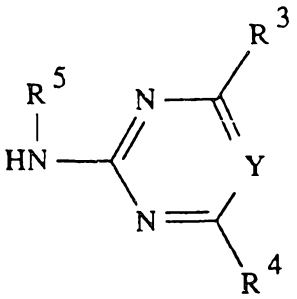
R^1 being defined as in formula I, with about half the molar amount of chlorosulfonyl isocyanate to give a compound of the formula II,



(II)

in which R^1, R^6 and X are defined as in formula I, and

b) subsequently reacting the compound obtained of the formula II with a compound of the formula III,

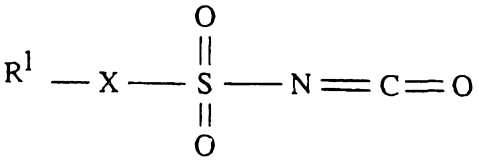


(III)

in which R^3, R^4, R^5 and Y are defined as in formula I.

17. The process as claimed in claim 16, wherein the process is carried out as a one-pot reaction without intermediate isolation of the compound of the formula II.

18. A process for the preparation of a compound of the formula V



(V)

which comprises reacting a salt of a compound of the formula IV

$$R^1\text{-}X\text{-}H \qquad \text{(IV)}$$

with chlorosulfonyl isocyanate in a molar ratio of at most 1:1.

19. The process as claimed in claim 18, wherein the reaction temperature is less than 100°C.

DATED this 5th day of March 1992.
HOECHST AKTIENGESELLSCHAFT

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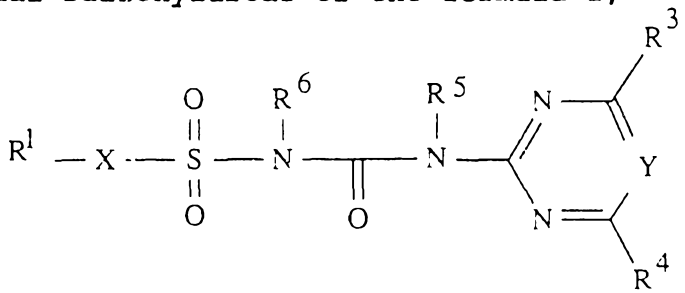
Abstract of the disclosure

Process for the preparation of sulfonylureas

Herbicidal sulfonylureas of the formula I,



(I)

in which X is -O-, -O-NR^2- or -SO_2-NR^2-, Y is -N- or CH,

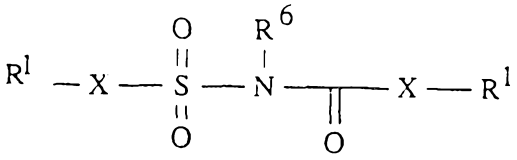
R^1 is (substituted) alkyl, (substituted) alkenyl or (substituted) alkynyl, or else, where X = O, (substituted) phenyl,

R^2 is H, alkyl, alkenyl, alkynyl or cycloalkyl,

R^3, R^4 are H, (substituted) alkyl or (substituted) alkoxy, halogen, alkylthio, alkylamino or dialkylamino and

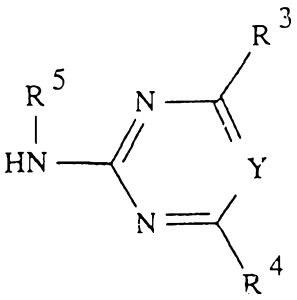
R^5, R^6 are H or alkyl, and their salts with acids or bases,

are prepared by reacting compounds of the formula II



(II)

with compounds of the formula III



(III).