

PATENT SPECIFICATION

(11) 1 359 756

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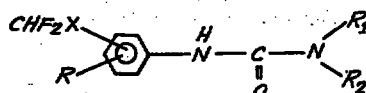


(54) N-ARYL-UREAS

(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Bruning, a body corporate recognised under German Law, of 6230 Frankfurt (M) 80, Hoechst, Germany, 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 N-aryl-ureas.

The present invention provides a compound of the general formula



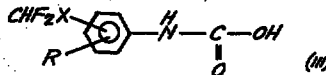
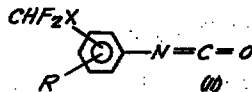
in which X represents an oxygen or sulphur atom; R represents a hydrogen or halogen, especially a chlorine or bromine, atom or an alkyl, especially a methyl, radical, or a difluoromethoxy or difluoromethylthio, especially a difluoromethoxy, radical;

R₁ represents an alkyl or alkoxy radical, preferably a methyl or methoxy radical, or the group $\text{CH}=\text{C}-\text{CH}-$



and R₂ represents a hydrogen atom or an alkyl radical, preferably a methyl radical.

The terms "alkyl" and "alkoxy" when used herein are to be taken each as denoting those radicals having from 1 to 4 carbon atoms. The present invention also provides a process for the manufacture of a compound of formula I wherein A an isocyanate of the formula (II), or a halide, amide or ester of the substituted carbamic acid (III) (for example the substituted carbamic acid phenyl ester)



is reacted with

a) a compound of the formula



IV

or,

b) an O-alkyl or N-alkyl-hydroxylamine, with subsequent alkylation of the reaction product or subsequent introduction of the $\text{CH}=\text{C}-\text{CH}-$ radical



when an O-alkyl hydroxylamine is used, or

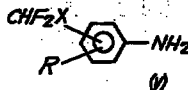
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c) hydroxylamine, with subsequent dialkylation of the reaction product, or monoalkylation of the OH group, or introduction of the $\text{CH}=\text{C}-\text{CH}-$ radical;

CH_3 ,

or

B. a substituted aniline of the formula

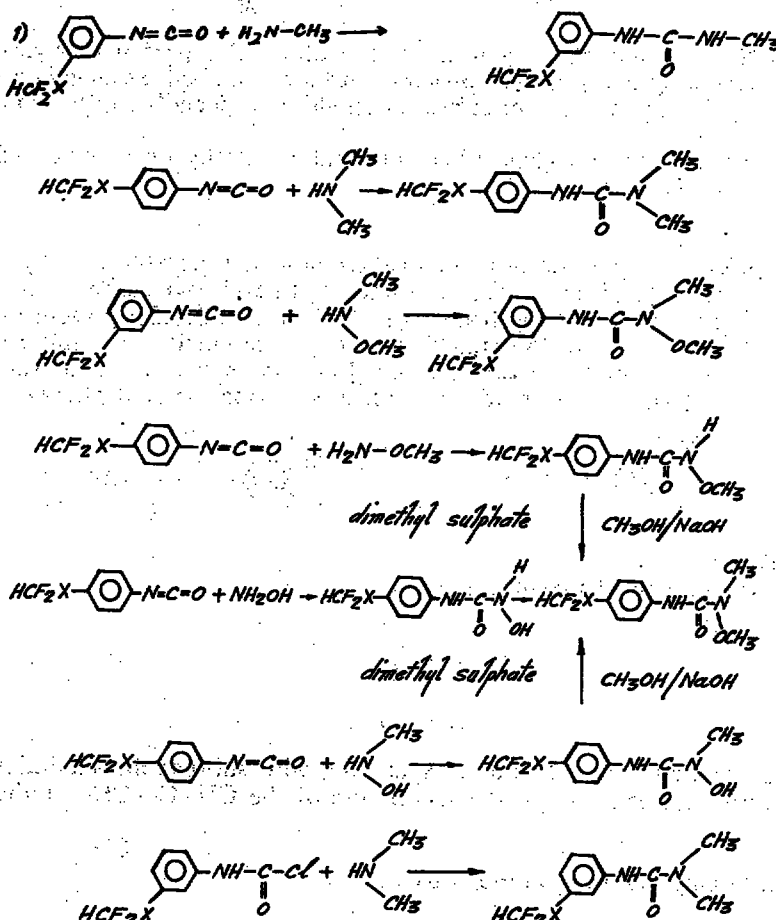


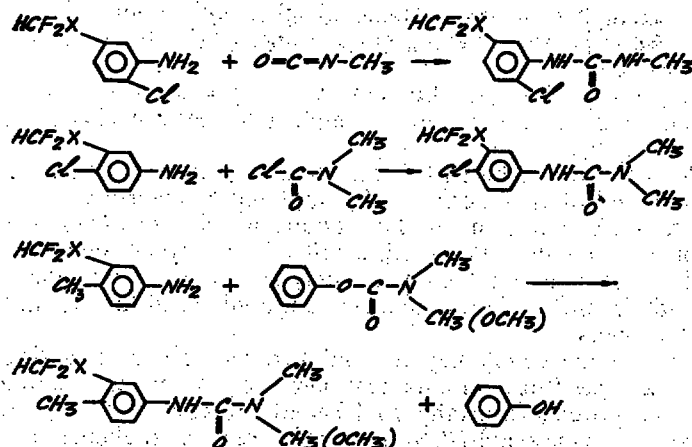
is reacted with

(a) an alkyl isocyanate or a dialkyl carbamic acid chloride, amide or ester (for example a phenyl ester) in which the alkyl substituents may be the same or different, or (b) an alkyl-alkoxy carbamic acid ester (for example an alkyl-alkoxy carbamic acid phenyl ester).

R , R_1 , R_2 , and X having the meanings given above, and alkyl and alkoxy being as hereinbefore defined, and when R_1 in the product represents an alkyl or alkoxy radical, optionally subjecting the reaction product to a subsequent halogenation, preferably bromination.

The present invention also provides a herbicide comprising a compound of formula I in admixture or conjunction with at least one solid or liquid additive for example a wetting agent, adhesive, dispersant, liquid or solid carrier grinding auxiliary, granulating agent, a further biocidally effective agent or a fertilizer. The course of the reaction for the manufacture of the above compounds can be illustrated by the following schemes starting from correspondingly substituted phenyl isocyanates, phenylcarbamic acid halides or anilines:





The difluoromethyl-thio-phenyl or difluoromethoxy-phenylisocyanates or carbamic acid derivatives are reacted with the amines or alkylated hydroxylamines derivatives at a temperature in the range for example of from 0°C to + 80°C, with or without diluent. Suitable diluents include benzene, toluene and dioxan.

The corresponding reactions with hydroxylamine are advantageously performed in a two-phase mixture consisting of water and an organic solvent immiscible with water, at a temperature of from about 0°C to + 40°C.

The alkylation may be effected with dialkyl sulphates, alkyl halides or alkyl toluene sulphonates, preferably in aqueous-alkaline suspension or in mixtures of aqueous alkali and an organic solvent. The alkali metal hydroxide solution and the alkylation agent are suitably added simultaneously with pH control. Alternatively, the urea can first be introduced into the reaction vessel together with the alkylation agent in an organic solvent and the alkali metal hydroxide solution can then be added, or, in the case of less alkali sensitive compounds, the reaction components can be added in the reverse order. The reaction temperature naturally depends on the reactivity of the alkylation agent used and is in the range of from 10 to 90°C.

Suitable starting compounds in the above reactions include;

- 3-difluoromethoxyphenyl isocyanate,
- 4-difluoromethoxyphenyl isocyanate,
- 4-chloro-3-difluoromethoxyphenyl isocyanate,
- 3-chloro-4-difluoromethoxyphenyl isocyanate and
- 3-methyl-4-difluoromethoxyphenyl isocyanate and

the corresponding thio compounds.

The isocyanates to be used may be obtained by known processes from the correspondingly substituted anilines formed in the reduction of the corresponding nitro-compounds (cf. Z. obsc. Chim. 39 (1969) Nr. 1, page 206). These nitro compounds may be obtained in known manner by reacting corresponding nitrophenols or nitrothiophenols with difluoro-chloromethane (cf. J. organ. Chem. 25, page 2009 (1960); Bull soc. Chim. Belges 74, page 270 (1965)).

Instead of the isocyanates the correspondingly substituted phenyl carbamic acid chlorides, amides or esters may also be used.

The compounds of the present invention are obtained in good yields and mostly are crystalline substances. They may be used in the form obtained or further purified by recrystallization from the usual organic solvents.

The products of the invention may be used for preventing the growth of undesired plants. They may be applied in the form of wettable powders, emulsion concentrates, dusting powders, or granules, either alone or, if desired, in combination with other herbicides, soil insecticides, or fertilizers.

Wettable powders are preparations that can be uniformly dispersed in water and contain, besides an inert substance, a wetting agent, for example a polyoxyethylated alkylphenol, polyoxyethylated oleyl- or stearylamine, alkyl- or alkylphenyl- sulphonate and a dispersing agent, for example the sodium salt of lignin-sulphonic acid, of 2,2'-dinaphthylmethane-6,6'-disulphonic acid, of dibutyl-naphthalene-sulphonic acid or sodium oleylmethyltauride.

Emulsion concentrates may be obtained by dissolving the active ingredient in an organic solvent, for example butanol, cyclohexanone, dimethylformamide,

xylene, or aromatic hydrocarbons having a higher boiling point. To obtain suspensions or emulsions in water having good properties, wetting agents as specified above are also added.

5 Dusting powders may be obtained by grinding the active ingredients with finely-divided solid substances, for example talc, natural clays, pyrophyllite or diatomaceous earths.

Granules may be produced by atomizing the active ingredient on to an absorptive granulated inert material, or by applying concentrates of the active ingredient to the surface or granulated inert material with the aid of an adhesive, for example polyvinyl alcohol, the sodium salt of polyacrylic acid or mineral oils. 10 Alternatively, suitable active ingredients may be made into granules, if desired in admixture with fertilizers, in the manner commonly used for the manufacture of granulated fertilizers.

Known herbicides which may be combined with the compounds of the invention are, for example (the non-chemical names are so-called "common names") urea derivatives: norea (N;(hexahydro-4,7-methanoindenyl)-N',N'-dimethyl urea), 15 cycluron (N-cyclooctyl-N',N'-dimethyl urea, methabenzthiazuron (N-(2-benzthiazolyl)N',N'-dimethyl urea), linuron, chloroxuron, monolinuron, fluometuron, diuron;

20 triazine derivatives: simazin, atrazin, ametryne, prometryne, desmetryne, methoprotlyne;

urazil derivatives: Lenacil (Trade Mark), bromacil;

pyrazone derivatives: 1-phenyl-4-amino-5-chloro-pyridazone (6);

25 growth-promoting preparations: 2,4-dichlorophenoxy-acetic acid, 4-chloro-2-methylphenoxy-acetic acid, 2,4,5-trichlorophenoxyacetic acid, 2-chloro-2-methylphenoxy-butyric acid, 2,3,6-trichloro-benzoic acid, 2-(2-methyl-4-chlorophenoxy)-propionic acid;

carbamic acid derivatives: barban, phenmedipham, triallate, diallate, vernolate, cycloate (N-ethyl-N-cyclohexylthioethyl-carbamate), molinate (hexahydro-

30 1H-azepine-carbamic acid thioethyl ester), EPTC (N,N-dipropylthioethyl-carbamate), chlorpropham and sweep;

dinitrophenol derivatives: dinitro-o-cresol, dinitro-sec.-butylphenol, (dinoseb), dinoseb acetate;

35 chlorinated aliphatic acids: sodium trichloroacetate and dalapon (sodium salt of 2,2-dichloropropionic acid), amiben (3-amino-2, 5-dichlorobenzoic acid), picloram (4-amino-3,5,6-trichloropyridinoethyl-propionamide);

amides: diphenamide, CDAA (N,N-diallyl-chloroacetamide, carbetamide (2-(phenylcarbonyl-hydroxy)-N-ethyl-propionamide), N-(1,1-dimethyl-propinyl)-3,5-dichloro-benzamide;

40 dipyridylum compounds: paraquat, diquat, morfamquat;

anilides: N-(3,4-dichlorophenyl)-methacrylamide, propanil, solan, monalide, 2-chl (methoxy-methyl)-acetanilide, propachlor, DCMA (methacryl-3,4-dichloro-anilide);

nitriles: dichlobenil, ioxynil;

45 other compounds: fluorenil, monosodium methyl-arsonate, trifluralin, endothall (3,6-endo-oxo-hexahydrophthalic acid), nitrofen (2,4-dichlorophenyl-4'-nitrophenyl ether), pyrichlor (2,3,4-trichloro-4-pyridinol) α -(2,2,2-trichloro-ethyl)-styrene, bensulide, aminotriazole, nitralin.

50 When the active ingredients of the present invention are mixed with fertilizers, preparations are obtained which have both a fertilizing and a herbicidal effect.

The herbicides of the present invention may be used in the form of commercial preparations in which they may be a major or minor component, for example the content of active ingredient may be in the range of from 10% to 95%, the balance being the usual herbicidal additives. However, when the compound of the present invention is mixed with other active ingredients and/or fertilizers, its content may be below the above range, for example down to 1% or even less. 55

The preparations may be applied in the dilutions generally used in controlling weeds, depending for example on the type of weed to be controlled, the crop plant, the climatic conditions, the season and the type of the soil. 60

In practice dilutions of from 0.001% to 1.0% are quite usual in the open field, higher or lower concentrations also being possible.

65 The compounds of the present invention have a good herbicidal effect, even against quite a number of weeds that are difficult to control, and are distinguished by their preserving properties for many crop plants, for example cereals, e.g.

wheat, barley, maize, rice or sorghum; leguminsae, e.g. soybean, kidney bean or pea; cotton, celery, and carrots.

The active ingredients can be applied in the pre-emergence and post-emergence process. They are superior to the closely related known urea derivatives, for example N-(trifluoromethoxy)-phenyl-N',N'-dimethyl or -N'-methyl-N'-methoxy ureas.

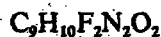
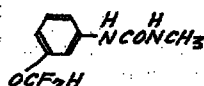
N-(trifluoromethylthio) phenyl-N',N'-dimethyl ureas and N-(trifluoromethoxy-phenyl-N',N'-dimethyl ureas are known herbicides (cf. Belgian Patent 719,350 and DOS 1,909,521).

The following Examples illustrate the invention:

Example 1.

3.5 Grams (0.11 mole) of methylamine were introduced into a solution of 18.5 grams (0.1 mole) of 3-difluoromethoxy-phenyl isocyanate in 30—50 ml of dry toluene and the reaction mixture was maintained at a temperature in the range of from 30 to 50°C by cooling. The mixture was maintained at said temperature for another hour. After cooling to 0 to +10°C and adding about 50 ml of petroleum ether, the crude crystalline product was filtered off with suction.

Yield: 21 grams melting point 92—93°C (from toluene)



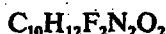
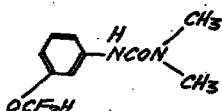
molecular weight 216

Analysis:	Calc.:	50 % C;	4.6 % H;	12.9 % N
	found:	50 % C;	4.8 % H;	12.6 % N

Example 2.

7.5 Grams (0.17 mole) of dimethylamine were introduced into a solution of 28 grams (0.15 mole) of 3-difluoromethoxyphenyl isocyanate in 60 ml of toluene, while the reaction temperature was maintained in the range of from 40 to 50°C. This temperature was maintained for another hour, the reaction mixture was cooled to 0 to +10°C and about 50 ml of petroleum ether were added. The crude crystalline product was filtered off with suction and washed with petroleum ether.

Yield: 31 grams melting point 115—116°C (from ethanol)



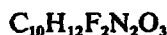
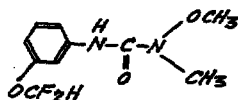
molecular weight 230

Analysis:	calc.:	52.1 % C;	5.2 % H;	12.3 % N
	found:	52.1 % C;	5.3 % H;	12.3 % N

Example 3.

10 Grams (0.17 mole) of O,N-dimethylhydroxyl amine were dropped at room temperature into a solution of 28 grams (0.15 mole) of 3-difluoromethoxy-phenyl isocyanate in 60 ml of dry toluene. The temperature of the reaction mixture was maintained below 40°C by cooling. After stirring for another hour and cooling of the reaction mixture to 0 to +10°C, petroleum ether was added. The crude product, separating in the form of a colorless viscous oil, was taken up in boiling cyclohexane. As after cooling and trituration no crystallization took place, the solvent was quantitatively removed under reduced pressure. The urea derivative remained behind as a nearly colorless, viscous oil.

Yield: 25 grams



molecular weight: 246

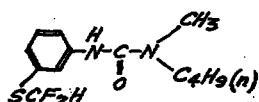
Analysis:	calc.:	48.7 % C;	4.9 % H;	11.4 % N
	found:	49.2 % C;	4.8 % H;	11.0 % N

Example 4.

14 Grams (0.15 mole) of N-methyl-N-butylamine were dropped into a solution of 28.2 grams (0.14 mole) of 3-difluoromethyl-thiophenyl isocyanate in 70 ml of dry toluene, while care was taken that temperature of the reaction mixture did not exceed about 40°C. The reaction mixture was stirred for one hour at 40°C, it was cooled to 0 to +10°C, the reaction product was filtered off with suction and washed with benzene.

Yield: 31 grams

melting point 94 — 95°C (from ethanol)



molecular weight 288

10

Analysis: calc.: 54.2% C; 6.3% H; 9.7% N
found: 54.1% C; 6.3% H; 9.6% N

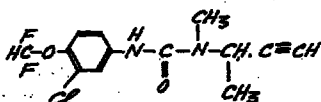
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Example 5.

15.8 Grams (0.17 mole) of methylamino-1-methylpropyne-(2) were dropped at 20 — 40°C into a solution of 33 grams (0.15 mole) of N-3-chloro-4-difluoromethoxy-phenyl isocyanate in 50 ml of dry toluene and the reaction mixture was maintained at 50°C for 3 hours. After cooling, about 50 ml of petroleum ether were added, the crystallizing crude product which separated after trituration was filtered off with suction and washed with a little petroleum ether.

Yield: 46 grams

melting point 91°C (from benzene/cyclohexane)



molecular weight 302.5

20

Analysis: Calc.: 51.6% C; 4.3% H; 9.3% N
found: 51.8% C; 4.5% H; 9.2% N

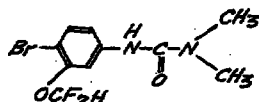
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Example 6.

12.3 Grams of anhydrous sodium acetate were added to a solution of 34.5 grams (0.15 mole) of N-3-difluoromethoxy-phenyl-N',N'-dimethyl urea in 100 ml of glacial acetic acid and at 70°C a solution of 24 grams (0.15 mole) of bromine in glacial acetic acid was added dropwise. Stirring of the reaction mixture was continued for another 30 minutes at the indicated temperature, whereupon the reaction mixture was cooled and poured into a large amount of ice-water. The separating oily reaction product completely crystallized after having been repeatedly washed with sodium hydrogen carbonate solution and water, the crystals were filtered off with suction and recrystallized from carbon tetrachloride.

Yield: 21 grams

melting point 138 — 139°C.



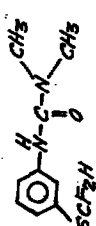
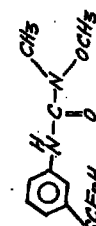
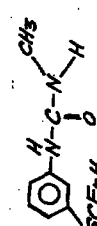
molecular weight 313

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Analysis: calc.: 38.3% C; 3.5% H; 9.0% N
found: 39.0% C; 3.4% H; 9.2% N

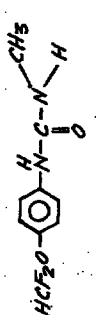
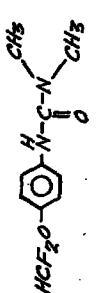
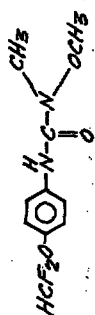
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TABLE I

Example No.		Prepared analog to Ex.	Melting point °C.	Analysis	
				Calc.	Found
7		2	145-146	48.7	C 48.9
				4.9	H 4.9
				11.4	N 11.6
				MW 246	
8		3	36	45.7	C 45.7
				4.6	N 4.4
				10.7	N 10.6
				MW 262	
9		1	110-111	46.5	C 46.8
				4.3	H 4.4
				12.1	N 12.2
				MW 232	

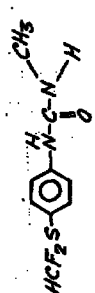
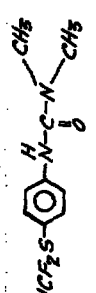
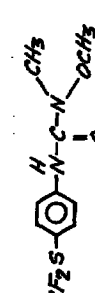
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TABLE I (Continued)

Example No.		Prepared analog to Ex.	Melting point °C.	Analysis		
				Calc.	Found	
10		1	105-106	50.0	C	49.0
				4.6	H	4.6
				12.9	N	11.8
11		2	113-115	52.2	C	52.0
				5.2	H	5.2
				12.2	N	12.1
12		3	93	48.7	C	48.9
				4.9	H	5.0
				11.4	N	11.4

K

TABLE I (Continued)

Example No.		Prepared analog to Ex.	Melting point °C.	Analysis	
				Calc.	Found
13		1	166	46.5	C 46.5
				4.3	H 4.7
				12.0	N 12.4
				MW 232	
14		2	119	48.7	C 48.7
				4.9	H 4.9
				11.4	N 11.4
				MW 246	
15		3	63	45.5	C 45.5
				4.6	H 4.5
				10.7	N 10.6
				MW 262	

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TABLE I (Continued)

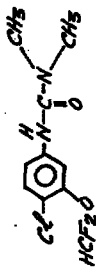
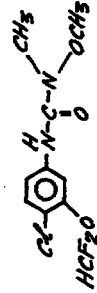
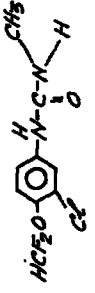
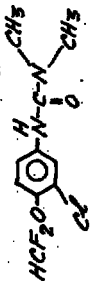
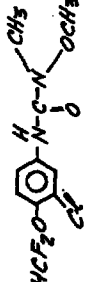
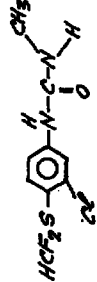
Example No.		Prepared analog to Ex.	Melting point °C.	Analysis	
				Calc.	Found
16	 MW 264.5	2	139	45.3	C 45.5
				4.2	H 4.4
				10.5	N 10.8
17	 MW 280.5	3	59	42.7	C 42.7
				3.9	H 4.1
				10.0	N 10.0
18	 MW 250.5	1	151	43.1	C 43.3
				3.6	H 3.7
				11.2	N 11.2

TABLE I (Continued)

Example No.		Prepared analog to Ex.	Melting point °C.	Analysis		
				Calc.		Found
19	 MW 264.5	2	90	45.3	C	44.9
				4.2	H	4.0
				10.6	N	11.0
20	 MW 280.5	3	71	42.7	C	43.1
				3.9	H	4.1
				10.0	N	10.1
21	 MW 266.5	1	111-112	40.5	C	40.4
				3.4	H	3.5
				9.8	N	10.1

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TABLE I (Continued)

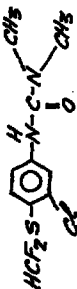
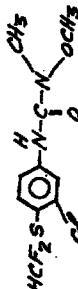
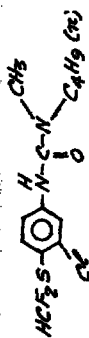
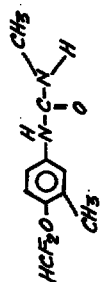
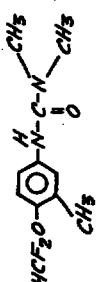
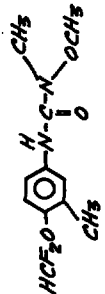
Example No.		Prepared analog to Ex.	Melting point °C.	Analysis		
				Calc.		Found
22		2	116-117	42.8	C	43.1
				3.9	H	3.9
				10.0	N	9.9
				MW 280.5		
23		3	Oil	40.5	C	40.9
				3.7	H	3.7
				9.5	N	9.2
				MW 296.5		
24		4	53	48.3	C	48.4
				5.3	H	5.5
				8.7	N	8.5
				MW 322.5		

TABLE I (Continued)

Example No.		Prepared analog to Ex.	Melting point °C.	Analysis		
				Calc.		Found
25	 MW 230	1	152	52.1	C	51.7
				5.2	H	5.3
				12.1	N	12.0
26	 MW 244	2	103	54.1	C	54.2
				5.7	H	6.1
				11.5	N	11.3
27	 MW 260	3	51	50.7	C	50.7
				5.4	H	5.5
				10.8	N	10.6

23

TABLE I (Continued)

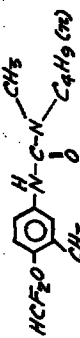
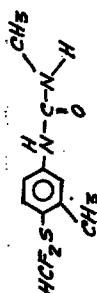
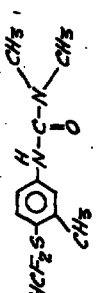
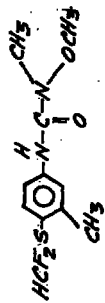
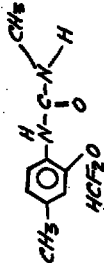
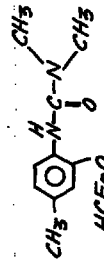
Example No.		Prepared analog to Ex.	Melting point °C.	Analysis		
				Calc.		Found
28		4	68	58.7	C	58.4
				7.0	H	7.6
				9.8	N	9.6
29		1	116	48.7	C	49.0
				4.9	H	4.9
				11.4	N	11.4
30		2	124	50.7	C	51.0
				5.4	H	5.7
				10.8	N	10.9

TABLE I (Continued)

Example No.		Prepared analog to Ex.	Melting point °C.	Analysis	
				Calc.	Found
31	 MW 276	3	49	47.8	47.9
				5.0	4.8
				10.1	10.5
32	 MW 230	1	149	52.1	52.9
				5.2	5.4
				12.1	11.7
33	 MW 244	2	66-67	53.7	54.2
				5.7	5.8
				11.5	11.8

25

TABLE I (Continued)

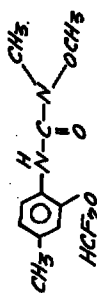
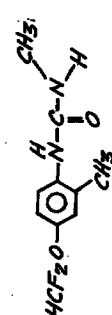
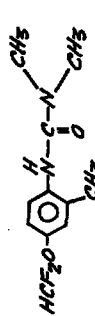
Example No.		Prepared analog to Ex.	Melting point °C.	Analysis	
				Calc.	Found
34	 MW 260	3	46-47	50.7	C 50.3
				5.4	H 5.5
				10.8	N 10.8
35	 MW 230	1	193	52.1	C 53.3
				5.2	H 5.3
				12.2	N 12.3
36	 MW 244	2	74	54.1	C 54.0
				5.7	H 5.9
				11.5	N 11.8

TABLE I (Continued)

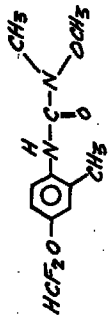
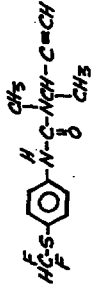
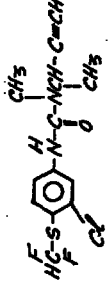
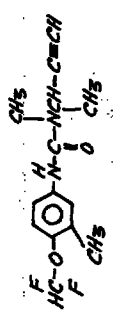
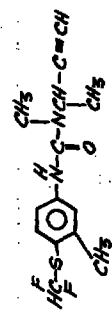
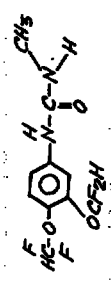
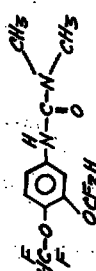
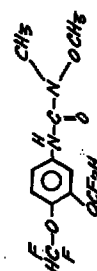
Example No.		Prepared analog to Ex.	Melting point °C.	Analysis		
				Calc.		Found
37	 MW 260	3	44	50.7 5.4 10.8	C H N	50.8 5.7 10.9
38	 MW 284	5	111-112	54.9 4.9 9.9	C H N	54.9 5.9 10.0
39	 MW 318.5	5	96	49.0 4.1 8.8	C H N	49.0 4.2 8.8

TABLE I (Continued)

Example No.		Prepared analog to Ex.	Melting point °C.	Analysis		
				Calc.		Found
40		5	71	59.5	C	59.4
				5.7	H	5.7
				9.9	N	9.9
41		5	94	56.3	C	56.7
				5.4	H	5.5
				9.4	N	9.6
42		1	125-126	42.5	C	42.5
				3.6	H	3.6
				9.9	N	9.9

Q

TABLE I (Continued)

Example No.		Prepared analog to Ex.	Melting point °C.	Analysis	
				Calc.	Found
43	 MW 296	2	67-68	44.6	44.6
				4.1	4.2
				9.5	9.3
44	 MW 312	3	Oil	42.3	42.2
				3.8	4.0
				9.0	9.2

Example 45.

A wettable powder readily dispersible in water was prepared by mixing 25 parts by weight of N-3-chloro-4-difluoromethoxy-phenyl-N',N'-dimethyl urea as active ingredient,

5 64 parts by weight of kaolin-containing quartz as inert substance,
10 parts by weight of the potassium salt of lignin-sulphonic acid,
1 part by weight of sodium oleylmethyl tauride as wetting and dispersing agent
and grinding the mixture obtained in a disc attrition mill.

10

Example 46.

A dusting powder having good herbicidal properties was prepared by mixing 10 parts by weight of N-3-chloro-4-difluoromethoxyphenyl-N'-methyl-N'-methoxy urea as active ingredient and

15

90 parts by weight of talcum as inert substance and grinding the mixture obtained in a disc attrition mill.

15

Example 47.

A granular preparation was prepared from 2.5 parts by weight of N-3-difluoromethoxy-phenyl-N',N'-dimethyl urea 0.5 part by weight of SiO₂

20

1.8 parts by weight of nonyl (ethoxy)₁₀ phenol as emulsifier and 95.2 parts by weight of sand as inert substance.

20

Example 48.

An emulsifiable concentrate was prepared from 15 parts by weight of N-4-difluoromethoxy-phenyl-N'-methyl urea 75 parts by weight of cyclohexanone as solvent and 10 parts by weight of nonyl (ethoxy)₁₀ phenol as emulsifier.

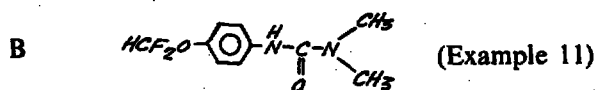
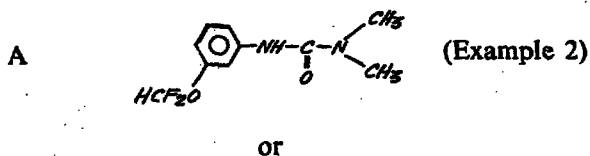
25

25

Example 49.

30 Seeds of different types of weeds and crop plants were sown in pots filled with soil and covered with a thin layer of soil. On the day of sowing the surface of the soil was sprayed with an aqueous suspension of a wettable powder containing as active ingredient

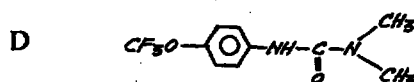
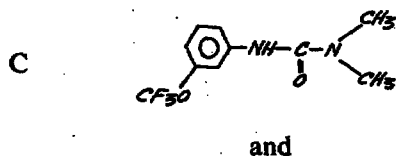
30



35

respectively, in different concentrations (pre-emergence process). As comparative substances the known compounds

35



40

were used. The results were evaluated 4 weeks later. They are summarized in the following Table 2 and defined as degree of damage to the weed or crop plant (0=no damage, 100=fully destroyed).

40

It can be seen that compounds A and B of the present invention had a comparable or even better effect on the weeds than the known compounds C and D. Also compounds A and B of the present invention did no harm or only little harm to the crop plants kidney beans, peas, soybeans, wheat, barley, maize and rice, while the known compounds C and D did too much harm to the crop plants (with the exception of compound C in peas). None of the compounds damaged cotton.

TABLE 2

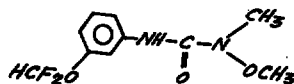
Results of a pre-emergence treatment:

Compound dose of active ingredient (kg/hectare)	A		B		C		D	
	0.3	1.25	0.3	1.25	0.3	1.25	0.3	1.25
Weeds:								
<i>Echinochloa crus-galli</i>	90	100	80	100	90	100	65	95
<i>Digitaria sanguinalis</i>	100	100	95	100	100	100	100	100
<i>Sinapis arvensis</i>	100	100	100	100	80	100	100	100
<i>Chenopodium album</i>	95	100	100	100	95	100	100	100
<i>Alopecurus myosuroides</i>	85	100	95	100	65	90	80	100
<i>Amaranthus retroflexus</i>	80	100	100	100	70	100	100	100
<i>Ipomoea purpurea</i>	70	100	60	95	60	100	35	95
<i>Poa annua</i>	80	100	90	100	75	90	95	100
<i>Stellaria media</i>	90	100	100	100	90	100	100	100
Crop plants:								
Kidney bean	0	25	0	20	20	80	20	70
Pea	0	30	0	10	0	30	30	75
Soybean	0	20	10	30	45	85	35	100
Wheat	0	30	0	20	55	90	85	100
Barley	0	25	0	20	40	80	70	100
Maize	0	35	0	0	30	65	55	85
Rice	0	20	0	30	50	90	45	75

Example 50.

The following compounds were tested in the manner described in Example 49:

E

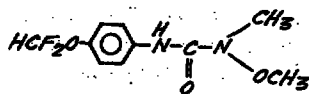


(Example 3)

and

31

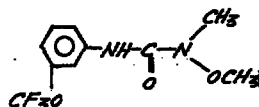
F



(Example 12)

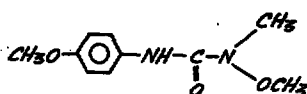
in comparison with

G



and

H



It was found that the compounds E and F of the present invention had a distinctly better herbicidal effect than the corresponding comparative compounds G and H. In the doses required for weed control compound E did little or no harm to the crop plants kidney beans, soybeans, wheat, maize, rice, carrots and celery. The same applies to compound F in soybean and cotton. In part the damage of comparative compounds G and H was also low in the aforesaid cultivations, but even with the highest dose (2.5 kg/hectare) a satisfactory herbicidal effect could not be obtained. The results are summarized in the following Table 3.

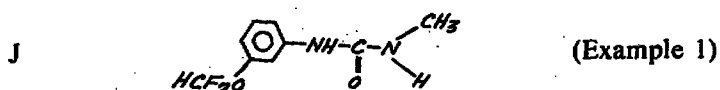
TABLE 3

Results of a pre-emergence process:

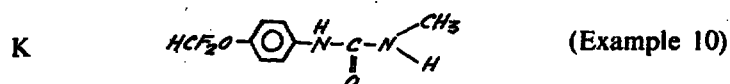
Compound dose of active ingredient (kg/hectare)	E		F		G		H	
	0.6	2.5	0.6	2.5	0.6	2.5	0.6	2.5
Weeds:								
<i>Echinochloa crus-galli</i>	95	100	80	100	10	40	20	60
<i>Digitaria sanguinalis</i>	50	80	90	100	30	80	30	75
<i>Sinapis arvensis</i>	100	100	100	100	80	100	80	100
<i>Chenopodium album</i>	100	100	100	100	70	100	65	95
<i>Alopecurus myosuroides</i>	100	100	80	100	10	55	50	95
<i>Amaranthus retroflexus</i>	100	100	90	100	70	95	40	95
<i>Ipomea purpurea</i>	100	100	70	95	0	0	0	60
<i>Poa annua</i>	95	100	80	100	40	80	60	95
<i>Stellaria media</i>	100	100	100	100	70	100	40	80
Crop plants:								
Kidney bean	0	20	—	—	0	10	—	—
Soybean	0	40	0	20	0	45	10	65
Cotton	—	—	0	0	—	—	0	45
Wheat	0	10	—	—	20	60	—	—
Maize	0	25	—	—	10	40	—	—
Rice	0	30	—	—	15	55	—	—
Carrot	0	10	—	—	0	15	—	—
Celery	0	15	—	—	0	0	—	—

Example 51.

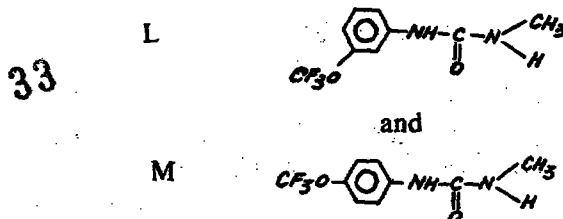
The following compounds were tested in a pre-emergence application.



and



in comparison with



5

The results are summarized in the following Table 4.

5

Compound J of the present invention was more effective, on the average, than comparative compound L and exhibited a selective effect in kidney bean, pea, wheat, barley, maize and soybean. The herbicidal effect of compound K was similar to that of comparative compound M, but unlike the latter, it showed little damage to the crops, wheat, barley, maize sorghum and rice.

10

10

TABLE 4

Results of a pre-emergence application:

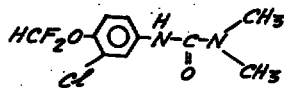
Compound dose of active ingredient (kg/hectare)	J		K		L		M	
	0.6	1.25	0.6	1.25	0.6	1.25	0.6	1.25
Weeds:								
Echinochloa crus-galli	85	100	60	85	45	80	60	85
Digitaria sanguinalis	90	100	80	85	70	90	75	80
Sinapis arvensis	100	100	100	100	85	100	100	100
Chenopodium album	95	100	90	100	60	90	80	85
Alopecurus myosuroides	90	100	75	85	75	85	80	95
Amaranthus retroflexus	95	100	95	100	90	100	90	100
Ipomoea purpurea	100	100	80	85	45	80	50	95
Poa annua	95	100	75	95	80	100	60	95
Stellaria media	100	100	100	100	80	95	100	100
Crop plants:								
Kidney bean	0	0	—	—	30	45	—	—
Pea	0	0	—	—	30	40	—	—
Wheat	0	25	0	0	65	70	65	95
Barley	0	15	0	0	30	60	50	55
Maize	0	0	0	0	40	50	40	55
Sorghum	0	25	0	20	60	70	70	75
Rice	—	—	0	0	—	—	45	50

Example 52.

In the same manner as described above the following compounds were tested in the pre-emergence application:

34

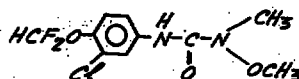
N



(Example 19)

and

O



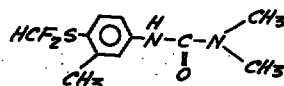
(Example 20)

Very low doses of both compounds (0.15 kg/hectare) destroyed the weeds *Ipomea purpurea*, *Sinapis arvensis*, *Echinochloa crus-galli*, *Poa annua*, *Anthemis arvensis*, *Alopecurus myosuroides*, *Lolium multiflorum*, *Digitaria sanguinalis*, *Amaranthus retroflexus*, *Chenopodium album* and *Mercurialis annua*; *Avena fatua* was destroyed by compound N with a dose of 0.3 kg/hectare and by compound O with a dose of 0.6 kg/hectare. Doses of 0.15 to 0.3 kg/hectare did little or no harm to the crop plants kidney bean, cotton, soybean, maize, wheat, and carrot.

Example 53.

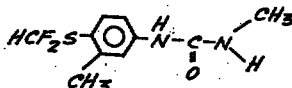
In a pre-emergence process the following compounds exhibited a good effect:

P



(Example 30)

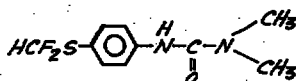
Q



(Example 29)

and

R



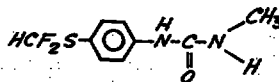
(Example 14)

In doses of 0.6 to 1.25 kg/hectare of active ingredient they destroyed the following weeds: *Ipomoea purpurea*, *Sinapis arvensis*, *Avena fatua*, *Echinochloa crus-galli*, *Poa annua* and *Anthemis arvensis*.

Example 54.

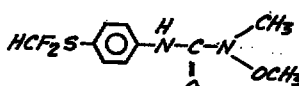
Compounds P, Q and R and the following compounds:

S



(Example 13)

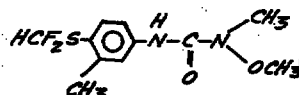
T



(Example 15)

and

U



(Example 31)

destroyed the same types of weeds when sprayed on the germinated plants which had developed two true leaves (post-emergence application).

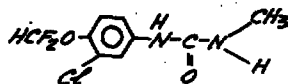
35

Compound

Example 55.

5

V



(Example 18)

5

was applied in the pre-emergence and post-emergence method in an amount of from 0.3 to 1.25 kg/hectare and destroyed the weeds *Ipomoea purpurea*, *Sinapis arvensis*, *Avena fatua*, *Echinochloa crus-galli*, *Poa annua* and *Anthemis arvensis*.

10

Example 56.

10

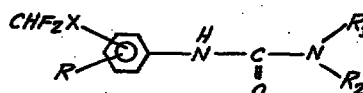
Compounds A, B, E, F, J, K, N, and O specified in the preceding examples were applied in the post-emergence method in doses of 0.15 to 1.25 kg/hectare. They controlled the weeds named in Example 55.

WHAT WE CLAIM IS:—

15

1. A compound of the formula

15



in which X represents an oxygen or sulphur atom;
R represents a hydrogen or halogen atom, or an alkyl or difluoromethoxy or difluoromethyl thio radical;
R₁ represents an alkyl or alkoxy radical or a

20

20

CH=C—CH—group,

CH₃R₂ represents a hydrogen atom or an alkyl radical.2. A compound as claimed in claim 1, wherein R₁ represents a methyl or methoxy radical.

25

3. A compound as claimed in claim 1 or claim 2, wherein R₂ represents a methyl radical.

25

4. A compound as claimed in claim 1, wherein R represents a hydrogen, chlorine or bromine atom or a methyl or difluoromethoxy radical.

5. A compound as claimed in claim 4, wherein R₁ represents a methyl or methoxy radical.

30

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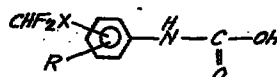
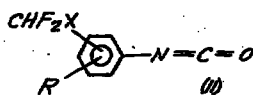
6. A compound as claimed in claim 4 or claim 5, wherein R₂ represents a methyl radical.

7. A compound as claimed in claim 1, and described in any one of Examples 1 to 44.

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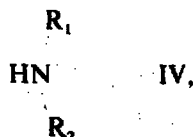
8. A process for the preparation of a compound as claimed in claim 1, wherein A an isocyanate of the formula II or a halide, amide or ester of the substituted carbamic acid III



is reacted with
a) a compound of the formula

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destroyed the same types of weeds when sprayed on the germinated plants which had developed two true leaves (post-emergence application).

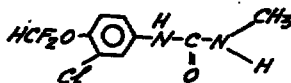
35

Compound

Example 55.

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V



(Example 18)

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was applied in the pre-emergence and post-emergence method in an amount of from 0.3 to 1.25 kg/hectare and destroyed the weeds *Ipomoea purpurea*, *Sinapis arvensis*, *Avena fatua*, *Echinochloa crus-galli*, *Poa annua* and *Anthemis arvensis*.

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Example 56.

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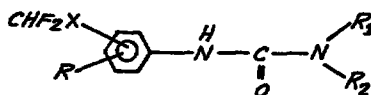
Compounds A, B, E, F, J, K, N, and O specified in the preceding examples were applied in the post-emergence method in doses of 0.15 to 1.25 kg/hectare. They controlled the weeds named in Example 55.

WHAT WE CLAIM IS:—

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1. A compound of the formula

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in which X represents an oxygen or sulphur atom;
R represents a hydrogen or halogen atom, or an alkyl or difluoromethoxy or difluoromethyl thio radical;
R₁ represents an alkyl or alkoxy radical or a

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20

$$\text{CH}=\text{C}-\text{CH}-\text{group,}$$

$$\text{CH}_2$$

R₂ represents a hydrogen atom or an alkyl radical.

2. A compound as claimed in claim 1, wherein R₁ represents a methyl or methoxy radical.

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3. A compound as claimed in claim 1 or claim 2, wherein R₂ represents a methyl radical.

4. A compound as claimed in claim 1, wherein R represents a hydrogen, chlorine or bromine atom or a methyl or difluoromethoxy radical.

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5. A compound as claimed in claim 4, wherein R₁ represents a methyl or methoxy radical.

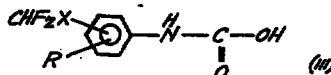
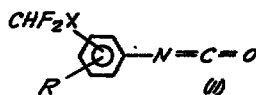
6. A compound as claimed in claim 4 or claim 5, wherein R₂ represents a methyl radical.

7. A compound as claimed in claim 1, and described in any one of Examples 1 to 44.

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8. A process for the preparation of a compound as claimed in claim 1, wherein A an isocyanate of the formula II or a halide, amide or ester of the substituted carbamic acid III



is reacted with

a) a compound of the formula

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R₁

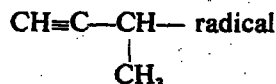
HN

IV,

R₂



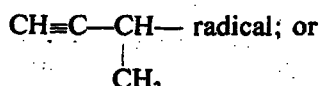
or
b) an O-alkyl- or N-alkyl-hydroxylamine, with subsequent alkylation of the reaction product or subsequent introduction of the



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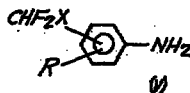
5 when an O-alkyl hydroxylamine is used or
c) hydroxylamine, with subsequent dialkylation of the reaction product, or monoalkylation of the OH group, or introductions of the

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B a substituted aniline of the formula

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is reacted with

a) an alkyl isocyanate or a dialkyl carbamic acid chloride, amide or ester (in which the alkyl substituents may be the same or different) or,
b) an alkyl-alkoxy carbamic acid ester,

15 R, R₁, R₂, and X having the meanings given in claim 1.

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9. A process as claimed in claim 8, wherein the carbamic acid ester is a phenyl ester.

10. A process as claimed in claim 8 or claim 9, wherein in the product R₁ represents an alkyl or alkoxy radical and the reaction product is subjected to a subsequent halogenation.

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11. A process as claimed in claim 10, wherein the halogenation is bromination.

12. A process as claimed in claim 8, wherein the starting material is 3-difluoromethoxyphenyl isocyanate, 4-difluoromethoxyphenyl isocyanate, 4-chloro-3-difluoromethoxyphenyl isocyanate, 3-chloro-4-difluoromethoxyphenyl isocyanate, 3-methyl-4-difluoromethoxyphenyl isocyanate, or a corresponding thio compound.

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13. A process as claimed in any one of claims 8 to 12, wherein R₁ represents a methyl or methoxy radical.

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14. A process as claimed in any one of claims 8 to 13, wherein R₂ represents a methyl radical.

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15. A process as claimed in claim 8 for the preparation of a compound as claimed in claim 4, wherein,

A an isocyanate of the formula II shown in claim 8 or a chloride, amide or ester of the substituted carbamic acid III shown in claim 8, is reacted with,

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a) a compound of the formula IV shown in claim 8, or

b) an O-alkyl or N-alkyl-hydroxylamine, with subsequent alkylation of the reaction product, or

c) hydroxylamine, with subsequent dialkylation of the reaction product, or

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B a substituted aniline of the formula V shown in claim 8, is reacted with
a) an alkyl isocyanate or a dialkyl carbamic acid chloride, amide or ester (in which the alkyl substituent may be the same or different) or

b) an alkyl-alkoxy carbamic acid ester, R₁, R₂ and X having the meaning given in claim 4.

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16. A process as claimed in claim 15, wherein the carbamic acid ester is a phenyl ester.

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17. A process as claimed in claim 15 or claim 16, wherein in the product R₁ represents an alkyl or alkoxy radical and the reaction product is subjected to a subsequent halogenation.

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18. A process as claimed in claim 17, wherein the halogenation is bromination.

19. A process as claimed in claim 15, wherein the starting material is 3-difluoromethoxyphenyl isocyanate, 4-difluoromethoxyphenyl isocyanate, 4-

chloro-3-difluoromethoxyphenyl isocyanate, 3-chloro-4-difluoromethoxyphenyl isocyanate, 3-methyl-4-difluoromethoxyphenyl isocyanate or a corresponding thio compound.

5 20. A process as claimed in any one of claims 15 to 19, wherein R₁ represents a methyl or methoxy radical.

21. A process as claimed in any one of claims 15 to 20, wherein R₂ represents a methyl radical.

22. A process as claimed in claim 8, and conducted substantially as described in any one of the Examples 1 to 44 herein or in the reaction scheme shown herein.

10 23. A compound as claimed in claim 1, whenever prepared by a process as claimed in any one of claims 8 to 14.

24. A compound as claimed in claim 4, whenever prepared by a process as claimed in any one of claims 15 to 22.

15 25. A herbicidal preparation containing a compound as claimed in any one of claims 1 to 3 and 23, in admixture or conjunction with at least one solid or liquid formulation additive.

26. A herbicidal preparation containing a compound as claimed in any one of claims 4 to 7 and 24 in admixture or conjunction with at least one solid or liquid formulation additive.

20 27. A herbicidal preparation as claimed in claim 26, and substantially as described in any one of Examples 45 to 48 herein.

28. A herbicidal preparation as claimed in claim 25 which also contains any one or more of the known herbicides specifically listed herein.

25 29. A herbicidal preparation as claimed in claim 26 or 27, which also contains any one or more of the known herbicides specifically listed herein.

30. A process for selectively controlling weeds in crop areas which comprises applying to the crop areas a compound as claimed in any one of claims 1 to 3 and 23, or a herbicidal preparation as claimed in claim 25 or claim 28.

30 31. A process for selectively controlling weeds in crop areas which comprises applying to the crop areas a compound as claimed in any one of claims 4 to 7 and 24, or a herbicidal preparation as claimed in any one of claims 26, 27 and 29.

32. A process as claimed in claim 30, wherein the crop is a cereal, legume, cotton, celery or carrots.

35 33. A process as claimed in claim 31, wherein the crop is a cereal, legume, cotton, celery or carrots.

34. A process as claimed in claim 30 or claim 32, wherein the dose of active ingredient is 0.15 to 2.5 kg/hectare.

35 35. A process as claimed in claim 31 or claim 33, wherein the dose of active ingredient is 0.15 to 2.5 kg/hectare.

40 36. A crop or soil which has been treated with a compound as claimed in any one of claims 1 to 3 and 23 or a preparation as claimed in claim 25 or claim 28.

37. A crop or soil which has been treated with a compound as claimed in any one of claims 4 to 7 and 24 or a preparation as claimed in claim 26, 27 and 29.

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