

PROCESS FOR PREPARING PYRAZOLE DERIVATIVES

The instant invention is directed to a new process for manufacturing
5 pesticidally active materials as well as the intermediates thereof. More particularly,
the instant invention is directed to a process for manufacturing 1-aryl substituted
pyrazoles.

Many manufacturing processes have been described in the literature for
preparing such derivatives, for example in International Patent Publication Nos.
10 WO87/03781, WO93/06089 and WO94/21606; in European Patent Publication Nos.
0295117, 0403300, 0385809 and 0679650; US Patent Nos. 5232940 and 5236938;
and German Published Patent Application No. 19511269.

The Japp-Klingemann reaction, reviewed in *Org. React.*, Vol. 10, pages
143-178 (1959), known in the literature since 1887, is a process by which phenyl azo
15 compounds are formed from the reaction of diazonium salts with active methylene
compounds. Typically the phenyl azo compound is not isolated, but is reacted *in situ*
with base resulting in loss of a leaving group and formation of the corresponding
hydrazone. When the phenyl azo intermediate is properly substituted, a spontaneous
cyclization reaction occurs giving a 3,5-disubstituted-4-protio-pyrazole, that is, a 3,5-
20 disubstituted-4-unsubstituted pyrazole. If a 3,4,5-trisubstituted pyrazole is desired,
further manipulation is required in subsequent steps.

An object of the instant invention is to provide a new manufacturing process
for preparing arylpyrazole derivatives.

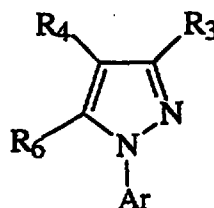
Another object of the instant invention is to provide a simple manufacturing
25 process, if possible, more simple than the existing process.

These objects are met in whole or in part by the instant invention.

This invention provides a new and more efficient process for the direct
preparation of 3,4,5-trisubstituted-1-arylpyrazoles. Surprisingly, it has been found
that the pyrazole ring cyclization of certain aryl azo intermediates proceeds such that
30 the leaving group (normally lost in these type of reactions) is reincorporated into the
pyrazole at C-4 thus giving immediate access to 3,4,5-trisubstituted-1-arylpyrazoles.
This offers advantages in reducing the number of reaction steps required to produce
the desired pesticidally active 3,4,5-trisubstituted-1-arylpyrazole derivatives, which in
turn means less waste chemical may be generated when manufacturing such
35 compounds; and less energy may be needed. This also helps to reduce the
manufacturing cost of the pesticidally active 1-aryl pyrazole derivatives.

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The present invention provides a process for preparing 1-arylpirazoles wherein:



(IV)

wherein:

Ar is optionally substituted phenyl or optionally substituted pyridyl;

R₃ is -C(O)R₈, -CN, -CO₂H, -C(O)NHR₈, -CHO, -C(O)CO₂R₈, -S(O)_mR₈,
 10 -C(O)CH₂Het, Het, -C(O)CH₂R₉, -C(O)(C₁-C₆ alkyl), -C(O)(C₁-C₆ haloalkyl),
 -C(O)styryl, halogen, -C(O)OR₈, -P(O)(OR₈)₂, -P(S)(OR₈)₂, -NO₂, R₉ or -S(O)_mstyryl;

R₄ is as defined for R₃ excluding -CN and halogen;

m is 0, 1 or 2;

R₆ is -NH₂, -OH or -CH₃;

15 R₈ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, R₉ or Het;

Het is a 5- or 6-membered heterocyclic ring, said ring having from one to three ring heteroatoms which are the same or different selected from the group consisting of nitrogen, sulfur and oxygen, each carbon atom of said ring being unsubstituted or being substituted by halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆
 20 haloalkoxy, cyano, nitro, amino, N-(C₁-C₆ alkyl)amino, N,N-di(C₁-C₆ alkyl)amino, OH, -S(O)_m(C₁-C₆ alkyl) or -S(O)_m(C₁-C₆ haloalkyl); and

R₉ is phenyl optionally substituted by one or more members selected from the group consisting of halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆
 haloalkoxy, cyano, nitro, amino, N-(C₁-C₆ alkyl)amino, N,N-di(C₁-C₆ alkyl)amino,
 25 -OH, -S(O)_m(C₁-C₆ alkyl) and -S(O)_m(C₁-C₆ haloalkyl);

said process comprising:

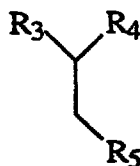
(a) reacting a compound having the formula:



(I)

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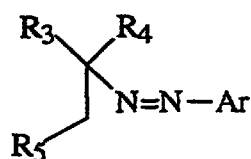
wherein Ar is as defined above and X is a compatible anion, with a compound having the formula:



(II)

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wherein R_3 and R_4 are as defined above and R_5 is $-CN$, $-C(O)OR_8$ or $-C(O)(C_1-C_6 \text{ alkyl})$, to afford the corresponding compound having the formula:



(III)

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wherein R_3 , R_4 , R_5 and Ar are as defined above; and

(b) subjecting the compound of formula (III) thus obtained to rearrangement to afford the corresponding compound of formula (IV).

In the specification the following terms have the general meanings given

15 below:

"alkyl" is branched or straight chain alkyl having from 1 to 6 carbon atoms;

"haloalkyl" is branched or straight chain alkyl having from 1 to 6 carbon atoms, bearing one or more halogen which are the same or different;

"alkoxy" is branched or straight chain alkoxy having from 1 to 6 carbon atoms;

20 "haloalkoxy" is branched or straight chain alkoxy having from 1 to 6 carbon atoms, bearing one or more halogen which are the same or different;

"halogen" means fluorine, chlorine, bromine or iodine.

In the definition above it will be understood that R_4 cannot represent $-CN$ or halogen because in formula (III) above, $-CN$ or halogen cannot migrate to the adjacent
25 carbon atom in the rearrangement step to give the compound of formula (IV) above.

X can be any anion compatible with the reaction conditions prevailing.

Examples of suitable groups include (HSO_4) , halogen, (BF_4) , $(ZnCl_3)$ and $(CoCl_3)$.

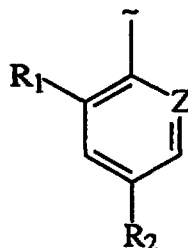
Preferably X is halogen or (HSO_4) .

When Ar is phenyl, it has from 0 to 5 substituents. When Ar is pyridyl, it has
30 from 0 to 4 substituents. Preferably, Ar has from 1 to 3 substituents. In any event, the

optional Ar substituents are preferably selected from the group consisting of halogen, CN, NO₂, haloalkyl, haloalkoxy, S(O)_mCF₃, SF₅ and R₁₀ wherein m is as defined above and R₁₀ is as defined below:

Preferably Ar is a group having the formula

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wherein:

- Z represents a trivalent nitrogen atom or a C-R₇ radical, the other three
 10 valences of the carbon atom forming part of the aromatic ring;
 R₁ and R₇ represent, independently of each other, a hydrogen or halogen atom, or CN or NO₂;
 R₂ represents halogen, haloalkyl, haloalkoxy, S(O)_mCF₃, SF₅ or R₁₀;
 and R₁₀ is phenyl optionally having from one to five substituents selected from
 15 the group consisting of halogen; alkyl; haloalkyl; cyanoalkyl; cyano; nitro; amino; hydrazino; alkoxy; haloalkoxy; haloalkylcarbonyl; formyl; alkylcarbonyl; thiocarbamoyl; carbamoyl; alkoxy carbonyl; SF₅; and R₈S(O)_m (preferably the 4-position substituent being halogen, haloalkyl or haloalkoxy); two adjacent phenyl substituents being optionally joined together form a 1,3-butadienylene
 20 (-CH=CH-CH=CH-), methylenedioxy (-O-CH₂-O-) or halomethylenedioxy (*e.g.*, -O-CF₂-O-) group so as to form a cyclic ring vicinal to the phenyl ring.

The following are also preferred embodiments of the invention, especially when Ar is one of the preferred groups depicted above:

- R₃ is -CN or -COR₈; and/or
 25 R₄ is -S(O)_mR₉, -S(O)_malkyl or -S(O)_mhaloalkyl; and/or
 R₅ is -CN; and/or
 R₆ is -NH₂.

The following value of the various substituents provide representative compounds of formulae (I) to (IV) above. In the Table that follows "Ph" means
 30 phenyl; "Pyr" means pyridyl; "Et" means ethyl.

Ar	X	R ₃	R ₄	R ₅	R ₆
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	COCH ₃	SO ₂ (4-Cl Ph)	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	SO ₂ (4-Cl Ph)	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	CO ₂ Et	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	SOCF ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	SOCH ₃	CN	NH ₂
2,6-Cl ₂ -4-OCF ₃ Ph	Cl	Cl	SOCF ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	SOEt	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	P(O)(OEt) ₂	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	Cl	CN	SO ₂ CF ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	SO(4-Cl Ph)	COCH ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	COCF ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	NO ₂	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	NO ₂	COCH ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	SO ₂ (2-thienyl)	COCH ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	COCH ₃	SO ₂ (2-thienyl)	CN	NH ₂
2,6-Cl ₂ -4-(4-Cl Ph) Ph	HSO ₄	CN	SOCF ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	Br	COCH ₃	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	Br	COPh	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	CO(2-furyl)	CN	NH ₂
2,6-Cl ₂ -4-CF ₃ Ph	HSO ₄	CN	SOCF ₃	CN	NH ₂
2,6-Cl ₂ -4-SF ₅ Ph	HSO ₄	COCH ₃	SO ₂ (4-Cl Ph)	CN	NH ₂
2,6-Cl ₂ -4-SF ₅ Ph	HSO ₄	CN	SO ₂ (4-Cl Ph)	CN	NH ₂
2,6-Cl ₂ -4-SF ₅ Ph	HSO ₄	CN	CO ₂ Et	CN	NH ₂
2,6-Cl ₂ -4-SF ₅ Ph	HSO ₄	CN	SOCF ₃	CN	NH ₂
2,6-Cl ₂ -4-SF ₅ Ph	HSO ₄	CN	SOCH ₃	CN	NH ₂
2,6-Cl ₂ -4-SF ₅ Ph	Cl	Cl	SOCF ₃	CN	NH ₂
2,6-Cl ₂ -4-SF ₅ Ph	HSO ₄	CN	SOEt	CN	NH ₂
2,6-Cl ₂ -4-SF ₅ Ph	HSO ₄	CN	P(O)(OEt) ₂	CN	NH ₂
2,6-Cl ₂ -4-(4CF ₃ Ph) Ph	HSO ₄	CN	SOCF ₃	CN	NH ₂
2,6-Cl ₂ -4-(4-OCF ₃ Ph) Ph	HSO ₄	CN	SOCF ₃	CN	NH ₂

Ar	X	R ₃	R ₄	R ₅	R ₆
2,6-Cl ₂ -4-O Ph	HSO ₄	CN	SOCF ₃	CN	NH ₂
2,6-Cl ₂ -4-(4-SCF ₃ Ph) Ph	HSO ₄	CN	SOCF ₃	CN	NH ₂

The process of the invention is generally conducted in two steps, although it may be carried out as a continuous process including the *in-situ* rearrangement of the compound of formula (III) to give a compound of formula (IV). This *in-situ* process may be preferred when the process forms part of a manufacturing process, as it may avoid the need for isolation of the intermediate of formula (II).

In the first step the diazonium salt (I) is reacted with a compound (II) in a solvent, with protic solvents such as methanol, ethanol and acetic acid being preferred.

The reaction is performed, optionally in the presence of a base, at a temperature between about 0° and about 120°C, preferably between about 0 and about 25°C, to give the azo product (III). When base is used in this step, it can be organic such as pyridine or triethylamine, or inorganic such as potassium carbonate or sodium hydroxide. When used, the amount of base is generally from about 1 to about 25 equivalents [based on the mole equivalents of the compound of formula (I)], with about 1 to 5 equivalents being preferred.

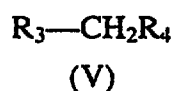
In the second step of the reaction sequence, the azo compound (III) is dissolved in a suitable solvent and optionally subjected to up to about 20 equivalents of a base, preferably up to about 5 equivalents, to give the rearranged pyrazole of formula (IV). The reaction temperature for this step is from about 0 to about 120°C, preferably from about 0 to about 25°C. The solvent can be protic such as methanol, ethanol or acetic acid, or preferably the solvent can be aprotic, such as dichloromethane, tetrahydrofuran, or toluene. Suitable bases may be organic (such as pyridine, triethylamine, or piperidine), inorganic (such as sodium hydroxide, potassium carbonate, sodium hydride) or organometallic (such as potassium t-butoxide, sodium methoxide, lithium diisopropylamide), with organic or organometallic bases being preferred.

The compound of formula (III) above is generally present in a molar excess. Preferably from about 1 to about 2 moles of the compound of formula (III) are present, more preferably from about 1.05 to about 1.1 moles.

Compounds of formula (III) in which Ar, R₃, R₄ and R₅ are as defined above, provided that when R₃ and R₅ are both cyano R₄ is not -C(O)OR₈, are novel and thus constitute a feature of the present invention.

Compounds of formula (II) may be prepared by the reaction of a compound of

formula (V):



5 wherein R_3 and R_4 are as defined above with a compound of the formula $\text{R}_5\text{CH}_2\text{L}$ wherein R_5 is as defined above and L is a leaving group, in the presence of a base. Examples of suitable leaving groups include halogen and tosylate (preferably halogen). The base is generally a strong base (*e.g.* sodium hydride or *n*-butyl lithium) and the reaction is generally performed in an aprotic solvent (*e.g.* tetrahydrofuran) at a
10 temperature from about -78°C to about 0°C . Compounds of formula (II), in which R_5 is cyano and R_3 and R_4 are as defined above, provided that when R_3 is $-\text{CN}$ then R_4 is not $-\text{C}(\text{O})\text{OR}_8$, are also novel and thus constitute a further feature of the present invention.

The following non-limiting examples illustrate the invention.

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Example 1

Preparation of 3-(4-chlorophenylsulfonyl)-4-cyanobutan-2-one

To a 300 mL reaction flask was added 2.4 g (59.3 mmole) sodium hydride (60% dispersion in oil) and 10 mL hexanes. The hexanes were removed by pipette
20 and replaced by 60 mL dry tetrahydrofuran (THF). The suspension was cooled to -15°C and a solution of 12.0 g (51.6 mmole) 4-chlorophenylsulfonyl acetone in 50 mL THF was added via addition funnel over 20 minutes maintaining the reaction temperature below -12°C . The resulting yellow solution was removed from the cold bath and stirred at room temperature for 30 min. The solution was recooled to -5°C
25 and 3.8 mL (54.1 mmole) bromoacetonitrile was added dropwise via addition funnel. After 5 min, the reaction mixture was removed from the cold bath and stirred at room temperature overnight. The reaction was quenched with 1 mL of saturated ammonium chloride and transferred with 100 mL of dichloromethane to a separatory funnel containing 100 mL brine. The organic layer was separated and the aqueous layer was
30 back extracted once with 50 mL more dichloromethane. The combined organics were then dried with sodium sulfate, filtered, concentrated, and chromatographed through a bed of silica gel using 1:1 hexane: dichloromethane. Isolation gave 8.2 g (59% yield) of 3-(4-chlorophenylsulfonyl)-4-cyanobutan-2-one, a yellow oil that was 90% pure by HPLC. ^1H NMR (CDCl_3) indicated desired product as the major component: δ 7.6
35 (m, 4H), 4.42 (dd, 1H), 2.78 (m, 2H), 2.48 (s, 3H).

Example 2

Preparation of 3-(4-chlorophenylsulfonyl)-3-[(2,6-dichloro-4-trifluoromethylphenyl)azo]-4-cyanobutan-2-one

To a 250 mL reaction flask was added 2.0 g (35.7 mmole) potassium hydroxide pellets followed by 30 mL water and 30 mL methanol. To this solution was added 6.9 g (25.5 mmole) of compound 3-(4-chlorophenylsulfonyl)-4-cyanobutan-2-one. Once homogeneous, 23.2 mmole of the hydrogensulfate diazonium salt of 2,6-dichloro-4-trifluoromethylaniline was added in one portion to the reaction medium. After stirring for 45 minutes at room temperature the reaction mixture was worked-up by adding water and dichloromethane. The layers were separated and the organic layer back extracted once with dichloromethane (50 mL). The combined organics were dried (Na₂SO₄), filtered, concentrated and chromatographed through silica gel using hexane:ethyl acetate mixture. Isolation gave 5.1 g (43%) the title compound as a glassy semi-solid which HPLC indicated was 98% pure and ¹HNMR indicated as desired product: δ 7.6 (m, 4H), 7.65 (s, 2H), 3.3 (dd, 2H), 2.42 (s, 3H).

Example 3

Preparation of 3-acetyl-5-amino-4-(4-chlorophenyl)sulfonyl-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole

Two drops of triethylamine were added to 0.51 g (1.0 mmole) 3-(4-chlorophenylsulfonyl)-3-(2,6-dichloro-4-trifluoromethylphenylazo)-4-cyanobutan-2-one dissolved in 10 mL dichloromethane. After stirring overnight at room temperature, the reaction was worked-up by adding additional dichloromethane and washing with water. The organic layer was separated, dried (Na₂SO₄), filtered and concentrated to give 0.55 g of the title compound that was 94% pure by HPLC, m.p. 158°C.

Example 4

Preparation of 2-(4-chlorophenylsulfonyl)succinonitrile

To a 500 mL reaction flask was added 2.0 g (51.0 mmole) sodium hydride (60% dispersion in oil) and 20 mL hexanes. The hexanes were removed by pipette and replaced by 90 mL dry tetrahydrofuran (THF). The suspension was cooled to 0°C and a solution of 10.0 g (46.4 mmole) 4-chlorophenylsulfonyl acetonitrile in 90 mL THF was added via addition funnel over 10 minutes maintaining the reaction temperature below 12°C. The resulting solution was removed from the cold bath and stirred at room temperature for 40 min. The solution was recooled to 0°C and 3.4 mL (48.7 mmole) bromoacetonitrile in 5 mL THF was added dropwise via addition

funnel. After 5 minutes, the reaction was removed from the cold bath and stirred at room temperature for two hours. The reaction was quenched with 1 mL of saturated ammonium chloride and concentrated to an oil which was transferred with 150 mL of dichloromethane to a separatory funnel containing 120 mL water. The organic layer
5 was separated and washed once more with 120 mL water and once with 120 mL brine. The organic layer was then dried (Na_2SO_4), filtered, concentrated, and chromatographed through a bed of silica gel using 85:15 hexane:ethyl acetate. Isolation gave 1.4 g (12% yield) of the title compound as a yellow powder that was 96% pure by HPLC, m.p. 130-137°C.

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Example 5

Preparation of 2-(4-chlorophenylsulfonyl)-

2-(2,6-dichloro-4-trifluoromethyl)phenylazo succinonitrile

To a 50 mL reaction flask was added 0.45 g (1.77 mmole) of 2-(4-
15 chlorophenylsulfonyl)succinonitrile in 15 mL methanol. Once homogeneous, 1.61 mmole of the hydrogensulfate diazonium salt of 2,6-dichloro-4-trifluoromethylaniline was added in one portion to the reaction medium. After stirring 45 min at room temperature the reaction mixture was worked-up by adding brine and dichloromethane. The layers were separated and the organic layer was dried
20 (Na_2SO_4), filtered, concentrated and chromatographed through silica gel using 90:10 hexane:ethyl acetate. Isolation gave 0.33 g (42%) of the title compound, a red crystalline solid which ^{19}F NMR indicated was over 95% pure, m.p. 45-50°C.

Example 6

Preparation of 5-amino-3-cyano-4-(4-chlorophenylsulfonyl)-

1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole

Three drops of triethylamine were added to 0.3 g (0.61 mmole) of 2-(4-
chlorophenylsulfonyl)-2-(2,6-dichloro-4-trifluoromethyl)phenylazo succinonitrile in
20 mL dichloromethane. After stirring two hours at room temperature the reaction
30 was worked-up by diluting with dichloromethane and partitioning from water. The layers were separated and the aqueous layer was back-extracted once with dichloromethane. The combined organics were dried (Na_2SO_4) filtered, concentrated and chromatographed through silica gel eluting with 90:10 hexane:ethyl acetate. Isolation gave 0.14 g (47% yield) of the title compound, 100% pure by HPLC as an
35 orange foam, m.p. 90-95°C.

Example 7

Preparation of ethyl 2,3-dicyano-2-(2,6-dichloro-4-trifluoromethyl)phenylazo propionate

22.1 Mmole of ethyl dicyanopropionate in 20 mL absolute ethanol was cooled
5 to 0°C, and 20.9 mmole of the hydrogensulfate diazonium salt of 2,6-dichloro-4-trifluoromethylaniline was added via addition funnel over 15 minutes. The reaction was warmed to room temperature and stirred overnight. The reaction was worked-up by adding water and dichloromethane. The layers were separated and the aqueous layer was back extracted once with dichloromethane. The combined organics were
10 washed once with brine and the organic layer was dried (Na₂SO₄), filtered, concentrated and chromatographed through silica gel using 90:10 hexane:ethyl acetate. Isolation gave 2.7 g (33%) of the title compound as a red viscous oil which contained 82% desired azo product and 13% of the corresponding hydrazone. ¹H NMR (CDCl₃) indicated desired product as the major component: d 7.70 (s, 2H), 4.44
15 (m, 2H), 3.58 (q, 2H), 1.39 (t, 3H).

Example 8

Preparation of 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-carboethoxypyrazole

20 To a 100 mL reaction flask was added 0.51 g (1.30 mmole) ethyl 2,3-dicyano-2-(2,6-dichloro-4-trifluoromethyl)phenylazo propionate in 20 mL tetrahydrofuran. The reaction was cooled to -78°C and 0.52 g (1.30 mmole) sodium hydride (60% dispersion in oil) was added in one portion. The reaction mixture warmed to room temperature overnight. Two grams of silica gel and 40 mL ethyl acetate were added to
25 the reaction mixture and the slurry was concentrated and chromatographed through silica gel eluting with 90:10 hexane:ethyl acetate (1 L) and 80:20 (2 L). Isolation gave 0.16 g (38% yield based on 82% pure starting material), a solid that was 99% pure by HPLC, m.p. 201.5-202.5°C.

Example 9

Preparation of hydrogensulfate diazonium salt of 2,6-dichloro-4-trifluoromethylaniline

30 To a 100 mL reaction flask was added 5.3 g (23.2 mmole) 2,6-dichloro-4-trifluoromethylaniline dissolved in 45 mL glacial acetic acid. The solution was cooled in an ice water bath and 3.8 g (30.1 mmole) nitrosylsulfuric acid was added in one portion. The reaction was removed from the ice bath and stirred at room temperature

for two hours. The resulting diazonium salt was used without purification.

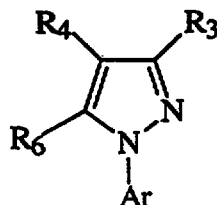
The compounds of formula (IV) prepared by the process of the present invention are useful as pesticides.

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While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited
10 solely by the scope of the following claims, including equivalents thereof.

WHAT IS CLAIMED IS:

1. A process for preparing a compound having the formula:



(IV)

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wherein:

- Ar is optionally substituted phenyl or optionally substituted pyridyl;
- 10 R₃ is -C(O)R₈, -CN, -CO₂H, -C(O)NHR₈, -CHO, -C(O)CO₂R₈, -S(O)_mR₈, -C(O)CH₂Het, Het, -C(O)CH₂R₉, -C(O)(C₁-C₆ alkyl), -C(O)(C₁-C₆ haloalkyl), -C(O)styryl, halogen, -C(O)OR₈, -P(O)(OR₈)₂, -P(S)(OR₈)₂, -NO₂, R₉ or -S(O)_mstyryl;
- R₄ is as defined for R₃ excluding -CN and halogen;
- m is 0, 1 or 2;
- 15 R₆ is -NH₂, -OH or -CH₃;
- R₈ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, R₉ or Het;
- Het is a 5- or 6-membered heterocyclic ring, said ring having from one to three ring heteroatoms which are the same or different selected from the group consisting of nitrogen, sulfur and oxygen, each carbon atom of said ring being unsubstituted or
- 20 being substituted by halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, cyano, nitro, amino, N-(C₁-C₆ alkyl)amino, N,N-di(C₁-C₆ alkyl)amino, OH, -S(O)_m(C₁-C₆ alkyl) or -S(O)_m(C₁-C₆ haloalkyl); and
- R₉ is phenyl optionally substituted by one or more members selected from the group consisting of halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆
- 25 haloalkoxy, cyano, nitro, amino, N-(C₁-C₆ alkyl)amino, N,N-di(C₁-C₆ alkyl)amino, -OH, -S(O)_m(C₁-C₆ alkyl) and -S(O)_m(C₁-C₆ haloalkyl);

said process comprising:

- (a) reacting a compound having the formula:



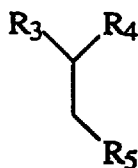
(I)

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wherein Ar is as defined above and X is a compatible anion, with a compound having the formula:

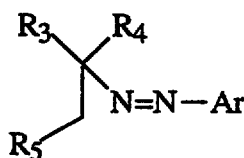


(II)



5

wherein R_3 and R_4 are as defined above and R_5 is $-\text{CN}$, $-\text{C}(\text{O})\text{OR}_8$ or $-\text{C}(\text{O})(\text{C}_1\text{-C}_6 \text{ alkyl})$, to afford the corresponding compound having the formula:



(III)

10

wherein R_3 , R_4 , R_5 and Ar are as defined above; and

(b) subjecting the compound of formula (III) thus obtained to rearrangement to afford the corresponding compound of formula (IV).

15

2. The process according to Claim 1, wherein Ar is phenyl having from 0 to 5 substituents or pyridyl having from 0 or 4 substituents, each substituent when present being selected from the group consisting of halogen, CN , NO_2 , $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_1\text{-C}_6$ haloalkoxy, $\text{S}(\text{O})_m\text{CF}_3$, SF_5 and R_{10} ; and R_{10} is phenyl optionally having from one to five substituents selected from the group consisting of

20 halogen, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, cyano($\text{C}_1\text{-C}_6$ alkyl), cyano, nitro, amino, hydrazino, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ haloalkoxy, ($\text{C}_1\text{-C}_6$ haloalkyl)carbonyl, formyl, ($\text{C}_1\text{-C}_6$ alkyl)carbonyl, thiocarbamoyl, carbamoyl, ($\text{C}_1\text{-C}_6$ alkoxy)carbonyl, SF_5 and $\text{R}_8\text{S}(\text{O})_m$, two adjacent phenyl substituents being optionally joined together to form a 1,3-butadienylene, methylenedioxy or halomethylenedioxy group.

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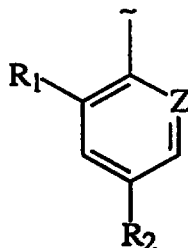
3. The process according to Claim 1 or Claim 2 wherein Ar has the formula:

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-14-



wherein:

Z is a trivalent nitrogen atom or a C-R₇ radical, the other three valences of the carbon atom forming part of the aromatic ring;

5 R₁ and R₇ are, independently of each other, hydrogen, halogen, CN or NO₂;
and

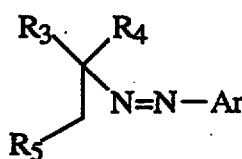
R₂ is halogen, C₁-C₆ haloalkyl, C₁-C₆ haloalkoxy, S(O)_mCF₃, SF₅ or R₁₀.

4. The process according to any one of the foregoing claims wherein R₃ is
10 -CN or -C(O)R₈.

5. The process according to any one of the foregoing claims wherein R₄ is
S(O)_mR₈ wherein R₈ is C₁-C₆ alkyl, C₁-C₆ haloalkyl or R₉.

15 6. A process according to any one of the foregoing claims wherein the
molar ratio of (I):(II) is from about 1:1 to about 1:2.

7. A process for preparing a compound having the formula:



(III)

wherein:

Ar is optionally substituted phenyl or optionally substituted pyridyl;

R₃ is -C(O)R₈, -CN, -CO₂H, -C(O)NHR₈, -CHO, -C(O)CO₂R₈, -S(O)_mR₈,
25 -C(O)CH₂Het, Het, -C(O)CH₂R₉, -C(O)(C₁-C₆ alkyl), -C(O)(C₁-C₆ haloalkyl),
-C(O)styryl, halogen, -C(O)OR₈, -P(O)(OR₈)₂, -P(S)(OR₈)₂, -NO₂, R₉ or -S(O)_mstyryl;

R₄ is as defined for R₃ excluding -CN and halogen;

m is 0, 1 or 2;

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R_5 is $-\text{CN}$, $-\text{C}(\text{O})\text{OR}_8$ or $-\text{C}(\text{O})(\text{C}_1-\text{C}_6 \text{ alkyl})$;

R_8 is C_1-C_6 alkyl, C_1-C_6 haloalkyl, R_9 or Het;

Het is a 5- or 6-membered heterocyclic ring, said ring having from one to three ring heteroatoms which are the same or different selected from the group consisting of nitrogen, sulfur and oxygen, each carbon atom of said ring being unsubstituted or being substituted by halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl,

C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, cyano, nitro, amino, $\text{N}-(\text{C}_1-\text{C}_6 \text{ alkyl})$ amino,

$\text{N,N-di}(\text{C}_1-\text{C}_6 \text{ alkyl})$ amino, OH , $-\text{S}(\text{O})_m(\text{C}_1-\text{C}_6 \text{ alkyl})$ or $-\text{S}(\text{O})_m(\text{C}_1-\text{C}_6 \text{ haloalkyl})$; and

R_9 is phenyl optionally substituted by one or more members selected from the group consisting of halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, cyano, nitro, amino, $\text{N}-(\text{C}_1-\text{C}_6 \text{ alkyl})$ amino, $\text{N,N-di}(\text{C}_1-\text{C}_6 \text{ alkyl})$ amino, $-\text{OH}$, $-\text{S}(\text{O})_m(\text{C}_1-\text{C}_6 \text{ alkyl})$ and $-\text{S}(\text{O})_m(\text{C}_1-\text{C}_6 \text{ haloalkyl})$;

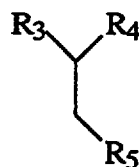
said process comprising reacting a compound having the formula:



(I)



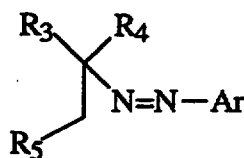
wherein Ar is as defined above and X is a compatible anion, with a compound having the formula:



(II)

wherein R_3 , R_4 and R_5 are as defined above.

8. A compound having the formula:



(III)

wherein:

Ar is optionally substituted phenyl or optionally substituted pyridyl;

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R_3 is $-C(O)R_8$, $-CN$, $-CO_2H$, $-C(O)NHR_8$, $-CHO$, $-C(O)CO_2R_8$, $-S(O)_mR_8$, $-C(O)CH_2Het$, Het , $-C(O)CH_2R_9$, $-C(O)(C_1-C_6 \text{ alkyl})$, $-C(O)(C_1-C_6 \text{ haloalkyl})$, $-C(O)styryl$, halogen, $-C(O)OR_8$, $-P(O)(OR_8)_2$, $-P(S)(OR_8)_2$, $-NO_2$, R_9 or $-S(O)_mstyryl$;

R_4 is as defined for R_3 excluding $-CN$ and halogen;

5 m is 0, 1 or 2;

R_5 is $-CN$, $-C(O)OR_8$ or $-C(O)(C_1-C_6 \text{ alkyl})$;

R_8 is $C_1-C_6 \text{ alkyl}$, $C_1-C_6 \text{ haloalkyl}$, R_9 or Het ;

Het is a 5- or 6-membered heterocyclic ring, said ring having from one to three ring heteroatoms which are the same or different selected from the group consisting of nitrogen, sulfur and oxygen, each carbon atom of said ring being unsubstituted or being substituted by halogen, $C_1-C_6 \text{ alkyl}$, $C_1-C_6 \text{ haloalkyl}$, $C_1-C_6 \text{ alkoxy}$, $C_1-C_6 \text{ haloalkoxy}$, cyano, nitro, amino, $N-(C_1-C_6 \text{ alkyl})\text{amino}$, $N,N\text{-di}(C_1-C_6 \text{ alkyl})\text{amino}$, OH , $-S(O)_m(C_1-C_6 \text{ alkyl})$ or $-S(O)_m(C_1-C_6 \text{ haloalkyl})$; and

R_9 is phenyl optionally substituted by one or more members selected from the group consisting of halogen, $C_1-C_6 \text{ alkyl}$, $C_1-C_6 \text{ haloalkyl}$, $C_1-C_6 \text{ alkoxy}$, $C_1-C_6 \text{ haloalkoxy}$, cyano, nitro, amino, $N-(C_1-C_6 \text{ alkyl})\text{amino}$, $N,N\text{-di}(C_1-C_6 \text{ alkyl})\text{amino}$, $-OH$, $-S(O)_m(C_1-C_6 \text{ alkyl})$ and $-S(O)_m(C_1-C_6 \text{ haloalkyl})$;

with the proviso that when R_3 is $-CN$ and R_5 is $-CN$, then R_4 cannot be $-C(O)OR_8$.

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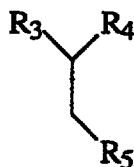
9. The compound according to Claim 8, which is:

3-(4-chlorophenylsulfonyl)-3-(2,6-dichloro-4-trifluoromethylphenylazo)-4-cyanobutan-2-one;

25 2-(4-chlorophenylsulfonyl)-2-(2,6-dichloro-4-trifluoromethyl)phenylazo succinonitrile; or

ethyl 2,3-dicyano-2-(2,6-dichloro-4-trifluoromethyl)phenylazo propionate.

10. A compound having the formula:

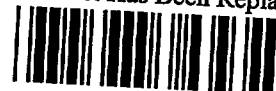


(II)

wherein:



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R_3 is $-C(O)R_8$, $-CN$, $-CO_2H$, $-C(O)NHR_8$, $-CHO$, $-C(O)CO_2R_8$, $-S(O)_mR_8$, $-C(O)CH_2Het$, Het , $-C(O)CH_2R_9$, $-C(O)(C_1-C_6 \text{ alkyl})$, $-C(O)(C_1-C_6 \text{ haloalkyl})$, $-C(O)styryl$, halogen, $-C(O)OR_8$, $-P(O)(OR_8)_2$, $-P(S)(OR_8)_2$, $-NO_2$, R_9 or $-S(O)_mstyryl$;

R_4 is as defined for R_3 excluding $-CN$ and halogen;

5 m is 0, 1 or 2;

R_5 is $-CN$;

R_8 is C_1-C_6 alkyl, C_1-C_6 haloalkyl, R_9 or Het ;

Het is a 5- or 6-membered heterocyclic ring, said ring having from one to three ring heteroatoms which are the same or different selected from the group consisting
 10 of nitrogen, sulfur and oxygen, each carbon atom of said ring being unsubstituted or being substituted by halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, cyano, nitro, amino, $N-(C_1-C_6 \text{ alkyl})$ amino, N,N -di(C_1-C_6 alkyl)amino, OH , $-S(O)_m(C_1-C_6 \text{ alkyl})$ or $-S(O)_m(C_1-C_6 \text{ haloalkyl})$; and

R_9 is phenyl optionally substituted by one or more members selected from the
 15 group consisting of halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, cyano, nitro, amino, $N-(C_1-C_6 \text{ alkyl})$ amino, N,N -di(C_1-C_6 alkyl)amino, $-OH$, $-S(O)_m(C_1-C_6 \text{ alkyl})$ and $-S(O)_m(C_1-C_6 \text{ haloalkyl})$;

with the proviso that when R_3 is $-CN$, then R_4 cannot be $-C(O)OR_8$.

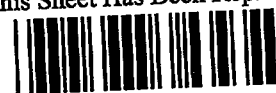
20 11. The compound according to Claim 10, which is:

3-(4-chlorophenylsulfonyl)-4-cyanobutan-2-one; or

2-(4-chlorophenylsulfonyl)succinonitrile.



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