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**THIENYL- AND FURYLPIRROLE INSECTICIDAL
AND ACARICIDAL AGENTS**

BACKGROUND OF THE INVENTION

Insects and acarina destroy growing and harvested crops. In the United States alone, agronomic crops must compete with thousands of insect and acarid species. In particular, tobacco budworms, southern armyworms and two-spotted spider mites are especially devastating to crops.

Tobacco budworms cause tremendous economic losses in agronomic crops. In particular, budworms devastate cotton crops by feeding on green bolls. Control of budworms is complicated by their resistance to many common insecticides, including organophosphates, carbamates and pyrethroids. Also, budworm larvae are difficult to control with currently available insecticides once they reach the third instar.

Two-spotted spider mites attack many plant species, raspberry plants for example, by removing sap from leaves. When raspberry plants are heavily infested, canes and leaves become stunted. With a severe infestation, fruiting canes are damaged, resulting in reduced yield and fruit quality.

In spite of the commercial insecticides and acaricides available today, damage to crops, both growing and harvested, caused by insects and acarina still occurs. Accordingly, there is ongoing research

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to create new and more effective insecticides and acaricides.

5 Certain pyrrole compounds are known to possess acaricidal, fungicidal, insecticidal and/or antiinflammatory activity (see, e.g., United States Patent Numbers 4,267,184; 5,010,098; 5,102,904; 5,157,047; 5,162,308; 5,306,827; 5,286,741; 5,286,742 and 5,286,743, Japanese Patent Application JP-85-40874 filed on March 1, 1985, European Patent 10 Application EP-111452-A1 filed on June 20, 1984, and N. Ono et al, Journal of Heterocyclic Chemistry, 28, pages 2053-2055 (1991)). However, none of the pyrroles disclosed in those patents, patent applications and publication are within the scope of the present inven- 15 tion.

It is therefore an object of the present invention to provide compounds which are highly effective for controlling insects and acarina.

20 It is also an object of the present invention to provide a method for controlling insects and acarina.

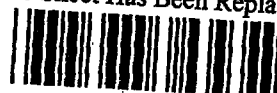
It is a further object of this invention to provide a method for protecting growing plants from attack by insects and acarina.

25 These and other objects of the present invention will become more apparent from the detailed description thereof set forth below.

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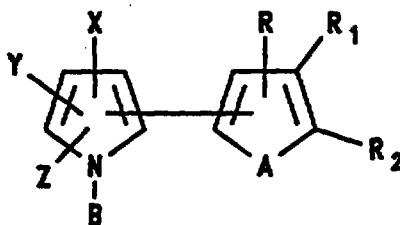
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SUMMARY OF THE INVENTION

The present invention describes thienyl- and furylpyrrole compounds which are useful as insecticidal and acaricidal agents for the control of insects and acarina and for the protection of plants from attack by insects and acarina.

The thienyl- and furylpyrrole compounds of the present invention have the following structural formula I:



(I)

wherein

R, R₁ and R₂ are each independently hydrogen, halogen, NO₂ or CHO, and when R₁ and R₂ are taken together with the carbon atoms to which they are attached, they may form a ring in which R₁R₂ is represented by the structure:



L, T, V and W are each independently hydrogen, halogen, CN or NO₂;

A is O or S;

X is CN, NO₂, C₁-C₆ haloalkyl, S(O)_mCF₂R₃ or C(S)NR₄R₅;
R₃ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

m is an integer of 0, 1 or 2;



R_4 and R_5 are each independently hydrogen,
 C_1-C_4 alkyl optionally substituted with one or
more halogen atoms, or
phenyl optionally substituted with one or more
5 halogen atoms,
 NO_2 groups,
CN groups,
 C_1-C_4 alkyl groups optionally sub-
stituted with one or more halogen
10 atoms, or
 C_1-C_4 alkoxy groups optionally sub-
stituted with one or more halogen
atoms;

Y is hydrogen, halogen, C_1-C_6 haloalkyl, $S(O)_mCF_2R_3$,
15 CN or
phenyl optionally substituted with one or more
halogen atoms,
 NO_2 groups,
CN groups,
20 C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;

Z is hydrogen, halogen or C_1-C_6 haloalkyl;

25 B is R_6 , OR_6 or CN;

R_6 is hydrogen, $C(O)R_7$, $CHR_8NHC(O)R_9$, CH_2SO ,
 $CHR_{10}OC(O)(CR_{11}R_{12})_nQ_1$,
 C_1-C_6 alkyl optionally substituted with one to
three halogen atoms,
30 one tri(C_1-C_4 alkyl)silyl,
one hydroxy,
one cyano,
one or two C_1-C_4 alkoxy groups optionally



- substituted with one to three halogen atoms,
one C_1-C_4 alkylthio,
one phenyl optionally substituted with one to
three halogen atoms, one to three C_1-C_4
alkyl groups or one to three C_1-C_4
alkoxy groups,
one phenoxy group optionally substituted
with one to three halogen atoms, one to
three C_1-C_4 alkyl groups or one to three
 C_1-C_4 alkoxy groups,
one benzyloxy group optionally substituted on
the phenyl ring with one to three
halogen atoms, one to three C_1-C_4 alkyl
groups or one to three C_1-C_4 alkoxy
groups,
one C_1-C_6 alkylcarbonyloxy group optionally
substituted with one to three halogen
atoms,
one C_2-C_6 alkenylcarbonyloxy group optionally
substituted with one to three halogen
atoms,
one phenylcarbonyloxy group optionally sub-
stituted with one to three halogen
atoms, one to three C_1-C_4 alkyl groups
or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkoxycarbonyl group option-
ally substituted with one to three
halogen atoms or one to three C_1-C_4
alkoxy groups, or
one benzylcarbonyloxy group optionally
substituted on the phenyl ring with one
to three halogen atoms, one to three
 C_1-C_4 alkyl groups or one to three C_1-C_4
alkoxy groups,
 C_3-C_6 alkenyl optionally substituted with one to



three halogen atoms or one phenyl group,
or

C_3-C_6 alkynyl optionally substituted with one to
three halogen atoms or one phenyl group;

5 R_7 is C_1-C_6 alkyl or C_3-C_6 cycloalkyl each optionally
substituted with one to three halogen
atoms,

one hydroxy,

one cyano,

10 one or two C_1-C_4 alkoxy groups
optionally substituted with one to
three halogen atoms,

one C_1-C_4 alkylthio,

one phenyl group optionally substituted
15 with one to three halogen atoms,
one to three C_1-C_4 alkyl groups or
one to three C_1-C_4 alkoxy groups,

one phenoxy group optionally substituted
with one to three halogen atoms,
20 one to three C_1-C_4 alkyl groups or
one to three C_1-C_4 alkoxy groups,

one benzyloxy group optionally
substituted on the phenyl ring with
one to three halogen atoms, one to
25 three C_1-C_4 alkyl groups or one to
three C_1-C_4 alkoxy groups,

one C_1-C_6 alkylcarbonyloxy group
optionally substituted with one to
three halogen atoms,

30 one C_2-C_6 alkenylcarbonyloxy group
optionally substituted with one to
three halogen atoms,

one phenylcarbonyloxy group optionally
substituted with one to three
35 halogen atoms, one to three C_1-C_4



- alkyl groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkoxy carbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or one benzyloxy carbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- C_2-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group,
- C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group,
- phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, phenoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,
- phenoxy optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,
- 1- or 2-naphthyl,
- 2-, 3-, or 4-pyridyl optionally substituted with one to three halogen atoms,



C_1-C_6 alkoxy optionally substituted with
one to three halogen atoms, or
 C_2-C_6 alkenyloxy optionally substituted
with one to three halogen atoms;

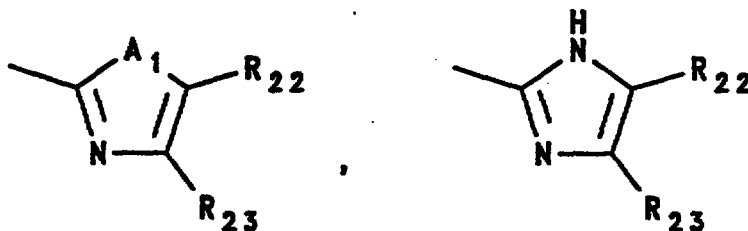
5 R_8 is hydrogen or C_1-C_4 alkyl;

R_9 is C_1-C_6 alkyl optionally substituted with
one to three halogen atoms,

phenyl optionally substituted with one
to three halogen atoms, CN groups, NO_2
10 groups, C_1-C_4 alkyl groups, C_1-C_4 alkoxy
groups or CF_3 groups,
2- or 3-thienyl, or
2- or 3-furyl;

15 Q is $\begin{array}{c} A_1 \\ | \\ C-R_{13} \end{array}$, $\begin{array}{c} A_1 \\ | \\ C-OR_{14} \end{array}$, $\begin{array}{c} A_1 \\ | \\ C-NR_{15}R_{16} \end{array}$, $\begin{array}{c} A_1 \\ | \\ P-(OR_{17})_2 \end{array}$, $\begin{array}{c} NR_{18} \\ | \\ C-NR_{19}R_{20} \end{array}$,
 $\begin{array}{c} NR_{18} \\ | \\ C-A_1R_{21} \end{array}$,

20



25

CN,

C_1-C_6 alkyl optionally substituted with one or
more halogen atoms, CN groups or phenyl
groups, or

30

phenyl optionally substituted with one or more
halogen atoms, C_1-C_4 alkyl groups, C_1-C_4
alkoxy groups, CN groups, NO_2 groups, CF_3
groups or $NR_{24}R_{25}$ groups;

A_1 is O or S;

R_{13} is C_1-C_6 alkyl or phenyl;

35



- R_{14} is C_1-C_6 alkyl;
- R_{15} and R_{16} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;
- R_{17} is C_1-C_4 alkyl;
- R_{18} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{19} or R_{21} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;
- R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl;
- R_{21} is C_1-C_4 alkyl or when taken together with R_{18} and the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;
- R_{22} and R_{23} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{22}R_{23}$ is represented by $-CH=CH-CH=CH-$;
- R_{24} and R_{25} are each independently hydrogen or C_1-C_4 alkyl;
- R_{10} is hydrogen or C_1-C_4 alkyl;
- R_{11} and R_{12} are each independently hydrogen, C_1-C_6 alkyl optionally substituted with one or more halogen atoms, C_1-C_6 alkoxy optionally substituted with one or more halogen atoms, C_1-C_6 alkylthio optionally substituted with one or more halogen atoms, or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1-C_4 alkyl groups optionally substituted

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5 with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms, or
when R₁₁ and R₁₂ are taken together with the atom
to which they are attached may form a C₃-C₆
cycloalkyl group optionally substituted with one
to three C₁-C₄ alkyl groups, C₂-C₆ alkenyl groups
or phenyl groups, or R₁₁ or R₁₂ may be taken
together with R₂₆ and the atoms to which they are
10 attached to form a 4- to 7-membered heterocyclic
ring;

n is an integer of 0, 1, 2, 3 or 4;

15 Q₁ is $\begin{array}{c} \text{O} \\ | \\ \text{A}_2\text{R}_{26}, \text{P}-(\text{OR}_{27})_2, \text{NR}_{28}\text{R}_{29}, \text{CR}_{30}\text{R}_{31}\text{C}(\text{O})\text{R}_{32}, \text{or} \\ \text{C}_3\text{-C}_6 \text{ cycloalkyl optionally substituted with one} \\ \text{or more C}_1\text{-C}_6 \text{ alkyl groups,} \\ \text{C}_2\text{-C}_6 \text{ alkenyl groups, or} \\ \text{phenyl groups optionally substituted with one} \\ \text{or more halogen atoms,} \\ \text{NO}_2 \text{ groups,} \\ \text{CN groups,} \\ \text{C}_1\text{-C}_4 \text{ alkyl groups optionally substi-} \\ \text{tuted with one or more halogen} \\ \text{atoms, or} \\ \text{C}_1\text{-C}_4 \text{ alkoxy groups optionally substi-} \\ \text{tuted with one or more halogen} \\ \text{atoms;} \end{array}$

A₂ is O or S(O)_p;

p is an integer of 0, 1 or 2;

30 R₂₆ is hydrogen,

C₁-C₆ alkyl

C₂-C₆ alkenyl,

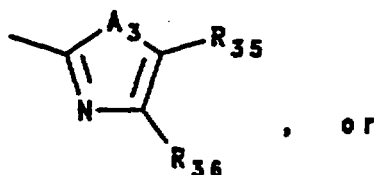
C₂-C₆ alkynyl,

35 phenyl optionally substituted with one or more
halogen atoms,



NO₂ groups,
 CN groups,
 C₁-C₄ alkyl groups optionally substituted
 with one or more halogen atoms, or
 5 C₁-C₄ alkoxy groups optionally substituted
 with one or more halogen atoms,
 C(O)R₃₃ provided p is 0,
 C(O)R₃₄ provided p is 0,
 (CH₂CH₂O)_qR₃₃, or.

10



15

R₂₆ may be taken together with either R₁₁ or R₁₂
 and the atoms to which they are attached to form a
 4- to 7-membered heterocyclic ring;

A₃ is O or S;

R₃₃ is C₁-C₆ alkyl,

20

C₂-C₆ alkenyl,

C₂-C₆ alkynyl, or

phenyl optionally substituted with one or more
 halogen atoms,

NO₂ groups,

25

CN groups,

C₁-C₄ alkyl groups optionally substituted
 with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted
 with one or more halogen atoms;

30

q is an integer of 1, 2 or 3;

R₃₄ is OR₃₇ or NR₃₈R₃₉;

R₃₇ is C₁-C₆ alkyl or

phenyl optionally substituted with one or more
 halogen atoms,

35

NO₂ groups,



- CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;
- 5 R₃₈ and R₃₉ are each independently hydrogen or C₁-C₄ alkyl;
- R₃₅ and R₃₆ are each independently hydrogen or C₁-C₄ alkyl, or
10 when taken together may form a ring wherein
R₃₅R₃₆ is represented by -CH=CH-CH=CH-;
- R₂₇ is C₁-C₄ alkyl;
R₂₈ is hydrogen,
C₁-C₆ alkyl,
15 C₂-C₆ alkenyl,
C₂-C₆ alkynyl, or
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
20 CN groups,
C₁-C₄ alkyl groups optionally
substituted with one or more
halogen atoms, or
C₁-C₄ alkoxy groups optionally
25 substituted with one or more
halogen atoms, or
- R₂₈ may be taken together with either R₁₁ or R₁₂
and the atoms to which they are attached to form a
4- to 7-membered heterocyclic ring;
- 30 R₂₉ is hydrogen,
C₁-C₆ alkyl,
C₂-C₆ alkenyl,
C₂-C₆ alkynyl,
phenyl optionally substituted with one or more
35 halogen atoms,



- NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
5 C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms,
C(A₄)R₄₀,
CN,
SO₂R₄₁, or
10 C(O)CHR₄₂NHR₄₃;
A₄ is O or S;
R₄₀ is OR₄₄, CO₂R₄₄, NR₄₅R₄₆,
C₁-C₆ alkyl optionally substituted with one to
three halogen atoms,
15 C₂-C₆ alkenyl,
C₂-C₆ alkynyl, or
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
20 CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;
25 R₄₄ is C₁-C₆ alkyl optionally substituted with one
phenyl group, or
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
30 CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;
35 R₄₅ and R₄₆ are each independently hydrogen or C₁-C₄

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- alkyl;
- 5 R_{41} is $NR_{47}R_{48}$,
 C_1-C_6 alkyl,
 C_2-C_6 alkenyl,
 C_2-C_6 alkynyl, or
 phenyl optionally substituted with one or more
 halogen atoms,
 NO_2 groups,
 CN groups,
- 10 C_1-C_4 alkyl groups optionally substituted
 with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
 with one or more halogen atoms;
- 15 R_{47} and R_{48} are each independently hydrogen or C_1-C_4
 alkyl;
- R_{42} is hydrogen,
 C_1-C_4 alkyl optionally substituted with
 one hydroxy group,
 one SR_{49} group,
20 one $C(O)NH_2$ group,
 one NH_2 group,
 one $NHC(=NH)NH_2$ group,
 one CO_2H group,
 one phenyl group optionally substituted with
25 one hydroxy group,
 one 3-indolyl group or
 one 4-imidazolyl group;
- R_{49} is hydrogen or C_1-C_4 alkyl;
- 30 R_{43} is $C(A_4)R_{50}$;
 R_{50} is C_1-C_6 alkyl optionally substituted with one or
 more halogen atoms,
 C_1-C_6 alkoxyalkyl,
 C_1-C_6 alkylthio,
35 phenyl optionally substituted with one or more
 halogen atoms,



- NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
5 C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms,
OR₄₄,
CO₂R₄₄ or
NR₄₅R₄₆;
10 R₃₀ and R₃₁ are each independently hydrogen,
C₁-C₆ alkyl optionally substituted with one or
more halogen atoms,
C₁-C₆ alkoxy optionally substituted with one or
more halogen atoms,
15 C₁-C₆ alkylthio optionally substituted with
one or more halogen atoms,
phenyl optionally substituted with one or more
halogen atoms,
CN groups,
20 NO₂ groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms, or
25 when R₃₀ and R₃₁ are taken together with the atom
to which they are attached may form a C₃-C₆
cycloalkyl group optionally substituted with one
to three C₁-C₄ alkyl groups, C₂-C₆ alkenyl groups
or phenyl groups;
30 R₃₂ is OR₅₁, NR₄₇R₄₈, C₁-C₄ alkyl or
phenyl optionally substituted with one or more
halogen atoms,
CN groups,
NO₂ groups,
35 C₁-C₄ alkyl groups optionally substituted

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with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms; and

R_{51} is C_1-C_4 alkyl or

5 phenyl optionally substituted with one or more
halogen atoms,

CN groups,

NO_2 groups,

10 C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;

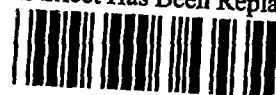
provided that when A is S, X is $S(O)_mCF_2R_3$ and Z is
hydrogen, then Y is hydrogen, halogen, C_1-C_6 haloalkyl,
15 $S(O)_mCF_2R_3$ or CN; and further provided that when the
pyrrole ring is substituted with hydrogen at each of
the pyrrole carbon atoms adjacent to the ring nitrogen
atom, then X cannot be CN or NO_2 .

20 This invention also relates to compositions
containing those compounds and methods for using those
compounds and compositions. Advantageously, it has
been found that the thienyl- and furylpyrrole compounds
of the present invention, and compositions containing
them, are effective insecticidal and acaricidal agents
25 for the control of insects and acarina and for the
protection of plants from attack by insects and
acarina. The compounds of the present invention are
especially useful for the control of tobacco budworms
and southern armyworms.

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DETAILED DESCRIPTION OF THE INVENTION

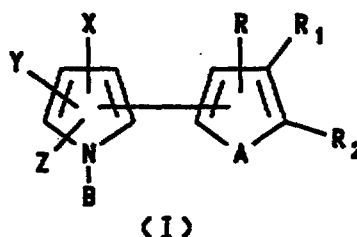
Advantageously, the present invention pro-
vides a method for controlling insects and acarina by
contacting said insects and acarina, their breeding
35 ground, food supply or habitat with an insecticidally



or acaricidally effective amount of a formula I, thienyl- or furylpyrrole compound.

The present invention also provides a method for protecting growing plants from attack by insects and acarina by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a formula I, thienyl- or furylpyrrole compound.

The thienyl- and furylpyrrole compounds of the present invention have the following structural formula I:



Wherein R, R₁, R₂, A, X, Y, Z and B are as described hereinabove for formula I.

Preferred formula I thienyl- and furylpyrrole compounds of the present invention are those wherein R, R₁ and R₂ are each independently hydrogen, halogen or NO₂, and when R₁ and R₂ are taken together with the carbon atoms to which they are attached, they may form a ring in which R₁R₂ is represented by the structure:



L, T, V and W are each independently hydrogen, halogen, CN or NO₂;

A is O or S;

X is CN, NO₂, C₁-C₆ haloalkyl, S(O)_mCF₂R₃ or C(S)NR₄R₅;

R₃ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;



m is an integer of 0, 1 or 2;

R_4 and R_5 are each independently hydrogen,

C_1-C_4 alkyl optionally substituted with one or more halogen atoms, or

5 phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

10 C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is hydrogen, halogen, C_1-C_6 haloalkyl, $S(O)_mCF_2R_3$, CN or

15 phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

20 C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or C_1-C_6 haloalkyl;

B is R_6 or CN;

25 R_6 is hydrogen, $C(O)R_7$, or

C_1-C_6 alkyl optionally substituted with one to three halogen atoms,

one cyano,

one C_1-C_4 alkoxy group,

30 one C_1-C_6 alkylcarbonyloxy group,

one phenylcarbonyloxy group, or

one benzylcarbonyloxy group; and

R_7 is phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups or CF_3 groups.

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Another group of preferred formula I insecti-
cidal and acaricidal agents are those wherein
R, R₁ and R₂ are each independently hydrogen, halogen
or NO₂, and when R₁ and R₂ are taken together
with the carbon atoms to which they are
attached, they may form a ring in which R₁R₂
is represented by the structure:



L, T, V and W are each independently hydrogen, halogen,
CN or NO₂;

A is O or S;

X is CN, NO₂ or C₁-C₆ haloalkyl;

Y is hydrogen, halogen, C₁-C₆ haloalkyl or phenyl
optionally substituted with one or more

halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

Z is hydrogen, halogen or C₁-C₆ haloalkyl;

B is R₆ or CN;

R₆ is hydrogen, C(O)R₇ or

C₁-C₆ alkyl optionally substituted with one to
three halogen atoms,

one cyano,

one C₁-C₄ alkoxy group,

one C₁-C₆ alkylcarbonyloxy group,

one phenylcarbonyloxy group, or

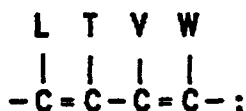
one benzylcarbonyloxy group; and

R₇ is phenyl optionally substituted with one or more



halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups or CF_3 groups.

More preferred formula I thienyl- and furyl-pyrrole compounds of this invention are those wherein
 5 R, R_1 and R_2 are each independently hydrogen, halogen or NO_2 , and when R_1 and R_2 are taken together with the carbon atoms to which they are attached, they may form a ring in which R_1R_2 is represented by the structure:



L, T, V and W are each independently hydrogen, halogen, CN or NO_2 ;

15 A is O or S;

X is CN, NO_2 or C_1-C_6 haloalkyl;

Y is hydrogen, halogen, C_1-C_6 haloalkyl or phenyl optionally substituted with one or more halogen atoms,

20 NO_2 groups,
CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

25 C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is halogen or C_1-C_6 haloalkyl;

B is R_6 or CN;

R_6 is hydrogen, $C(O)R_7$ or

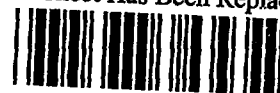
30 C_1-C_6 alkyl optionally substituted with one to three halogen atoms,

one cyano,

one C_1-C_4 alkoxy group,

one C_1-C_6 alkylcarbonyloxy group,

35 one phenylcarbonyloxy group, or



one benzylcarbonyloxy group; and

R_7 is phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups or CF_3 groups.

5 Another group of more preferred formula I thienyl- and furylpyrrole compounds of this invention which are effective insecticidal and acaricidal agents are those wherein

10 R , R_1 and R_2 are each independently hydrogen, halogen or NO_2 , and when R_1 and R_2 are taken together with the carbon atoms to which they are attached, they may form a ring in which R_1R_2 is represented by the structure: $-CH=CH-CH=CH-$;

A is O or S;

15 X is CN or NO_2 ;

Y is halogen, CF_3 or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

20 CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

25 Z is hydrogen, halogen or CF_3 ; and

B is hydrogen or C_1-C_6 alkyl substituted with one C_1-C_4 alkoxy group.

Most preferred formula I insecticidal and acaricidal agents are those wherein

30 R , R_1 and R_2 are each independently hydrogen, halogen or NO_2 ;

A is O or S;

X is CN or NO_2 ;

Y is halogen, CF_3 or

35 phenyl optionally substituted with one or more



halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted

5 with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted

with one or more halogen atoms;

Z is CF₃; and

B is hydrogen or C₁-C₆ alkyl substituted with one C₁-C₄

10 alkoxy group.

Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine. The term "C₁-C₆ haloalkyl" is defined as a C₁-C₆ alkyl group substituted with one or more halogen atoms.

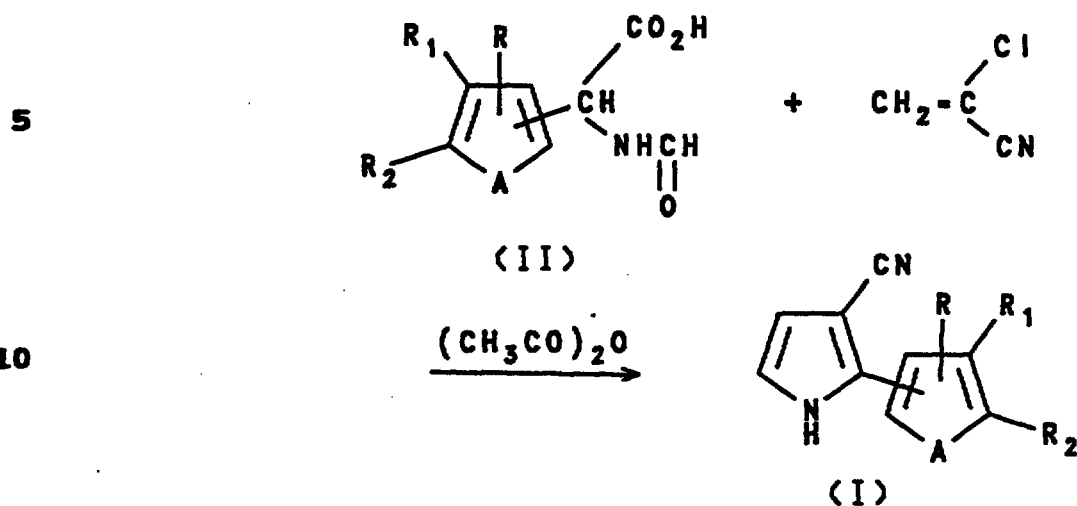
15 Advantageously, it has been found that the formula I compounds of the present invention are especially useful for the control of tobacco budworms, southern armyworms and two-spotted spider mites.

Thienyl- and furylpyrrole compounds of
20 formula I wherein X is CN and Y, Z and B are hydrogen may be prepared by reacting an N-formyl(thienyl or furyl)glycine of formula II with 2-chloroacrylonitrile and acetic anhydride as shown in Flow Diagram I.

25

30

35

FLOW DIAGRAM I

15 Certain compounds of formula I wherein X is
CN, Y is C₁-C₆ haloalkyl and Z and B are hydrogen may
be prepared by reacting the appropriately substituted
thienyl- or furylglycine of formula III with a C₁-C₆
haloalkyl acid anhydride to form an oxazolinone inter-
20 mediate of formula IV and reacting said formula IV
intermediate with 2-chloroacrylonitrile as shown in
Flow Diagram II.

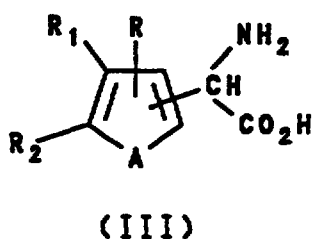
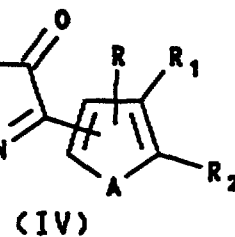
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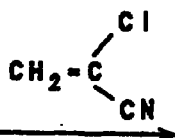
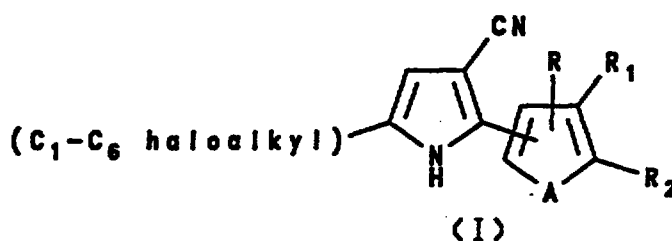
35

FLOW DIAGRAM II

5

 C_1-C_6 haloalkyl acid
anhydride $(C_1-C_6 \text{ haloalkyl})$ 

10



15

Formula I compounds wherein X and Y are C_1-C_6 haloalkyl and Z and B are hydrogen may be prepared by reacting an oxazolinone of formula IV with a bromoalkene of formula V as shown in Flow Diagram III.

20

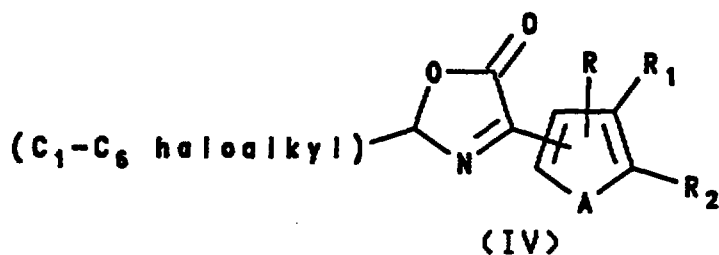
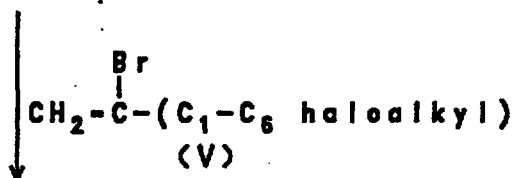
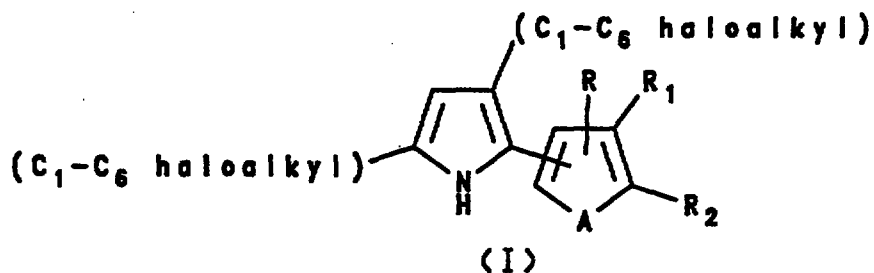
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- 25 -

FLOW DIAGRAM III

20 4-Cyano-2-(thienyl- or furyl)pyrrole compounds may be prepared by reacting acrylonitrile with an N-(trimethylsilyl)methyl-5-methyl-(thienyl- or furyl)thioimide of formula VI in the presence of tetrabutylammonium fluoride to form a 2-(thienyl- or

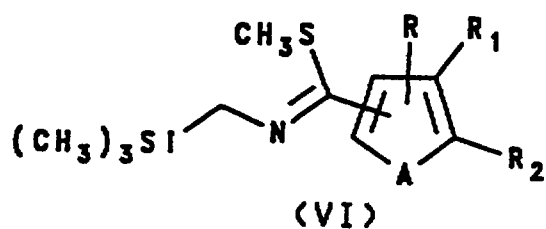
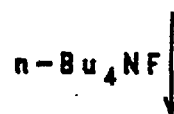
25 furyl)-1-pyrroline-4-carbonitrile intermediate of formula VII and reacting said formula VII intermediate with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and pyridine as shown below in Flow Diagram IV.

30

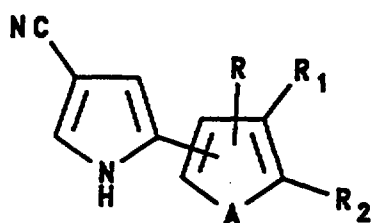
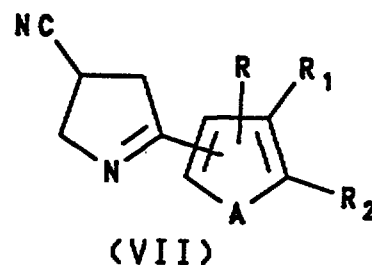
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FLOW DIAGRAM IV

5



10



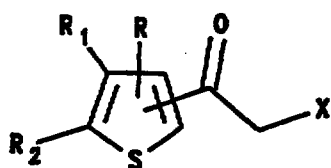
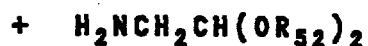
15

3-Cyano or nitro-2-thienylpyrrole compounds may be prepared as shown below in Flow Diagram V.

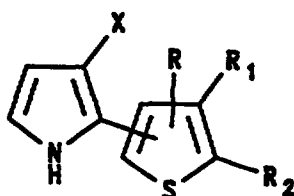
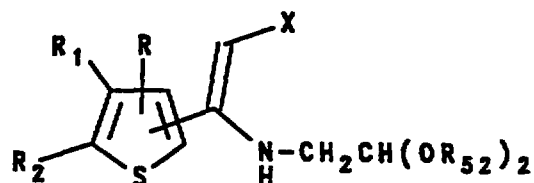
20

FLOW DIAGRAM V

25



30



wherein

R, R₁ and R₂ are each independently hydrogen, halogen

35



- 27 -

or NO_2 , and when R_1 and R_2 are taken together with the carbon atoms to which they are attached, they may form a ring in which R_1R_2 is represented by the structure:



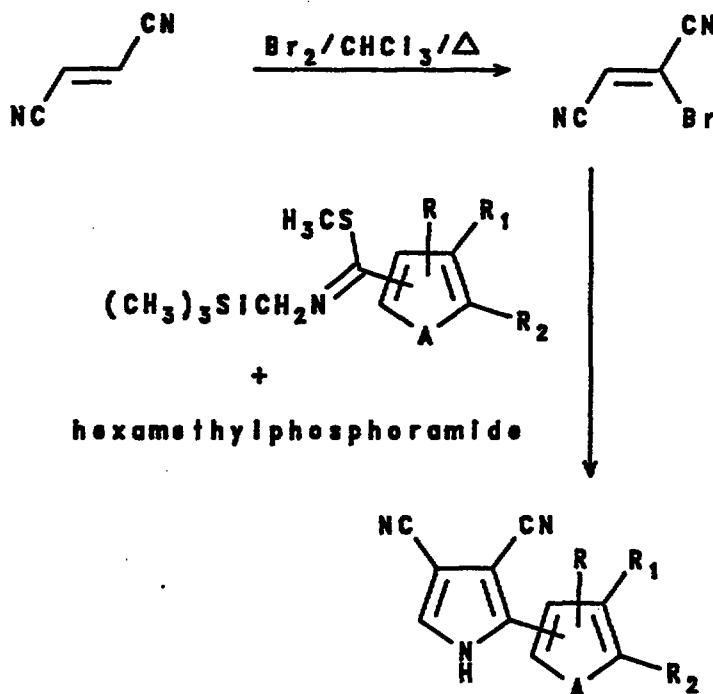
L, T, V and W are each independently hydrogen, halogen, CN or NO_2 ;

X is CN or NO_2 ; and

R_{52} is C_1 - C_4 alkyl.

2-(Thienyl- or furyl)pyrrole-3,4-dicarbonitrile compounds may be prepared as shown below in Flow Diagram VI.

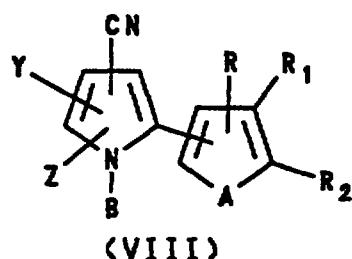
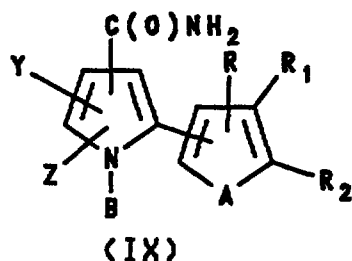
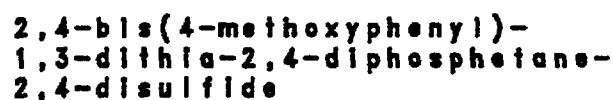
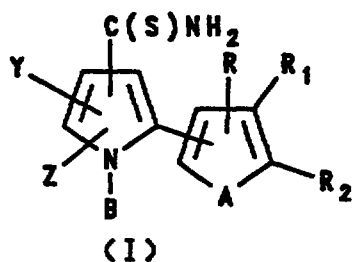
FLOW DIAGRAM VI



Formula I compounds wherein X is $\text{C}(\text{S})\text{NH}_2$ may be prepared by reacting the appropriately substituted formula VIII (thienyl- or furyl)pyrrole-carbonitrile with an excess of hydrogen peroxide and sodium

hydroxide to give the appropriately substituted formula IX (thienyl- or furyl)pyrrole carboxamide and reacting said formula IX carboxamide with a reagent capable of introducing the thioxo group, such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide as shown below in Flow Diagram VII.

FLOW DIAGRAM VII



wherein

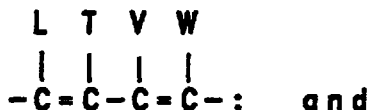
A, B, Y and Z are as described hereinabove for formula I;

R, R₁ and R₂ are each independently hydrogen, halogen



or NO_2 , and when R_1 and R_2 are taken together with the carbon atoms to which they are attached, they may form a ring in which R_1R_2 is represented by the structure:

5



L, T, V and W are each independently hydrogen, halogen, CN or NO_2 .

10

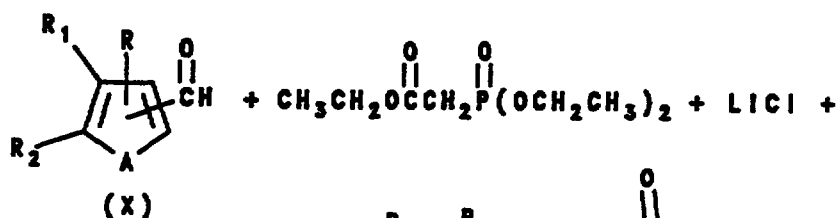
4-(Thienyl- or furyl)pyrrole-3-thiocarboxamide compounds may be prepared by reacting the appropriately substituted formula X aldehyde with triethyl phosphonoacetate, lithium chloride and triethylamine to form the ester of formula XI. The formula XI ester is
 15 reacted with a strong base such as sodium hydride and tosylmethyl isocyanide to form a formula XII ethyl 4-(thienyl- or furyl)pyrrole-3-carboxylate which is hydrolyzed with an alkali metal hydroxide such as
 20 potassium hydroxide to form a formula XIII 4-(thienyl- or furyl)pyrrole-3-carboxylic acid. The formula XIII carboxylic acid is reacted with a tri(C_1 - C_4 alkyl)amine to form a first mixture. The first mixture is reacted with thionyl chloride and N,N-dimethylformamide to give a second mixture. The second mixture is reacted with a
 25 formula XIV amine compound to give the formula XV 4-(thienyl- or furyl)pyrrole-3-carboxamide and reacting the formula XV carboxamide with a reagent capable of introducing the thioxo group, such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide,
 30 to give the desired 4-(thienyl- or furyl)pyrrole-3-thiocarboxamide. The above reaction schemes are shown below in Flow Diagram VIII.

35

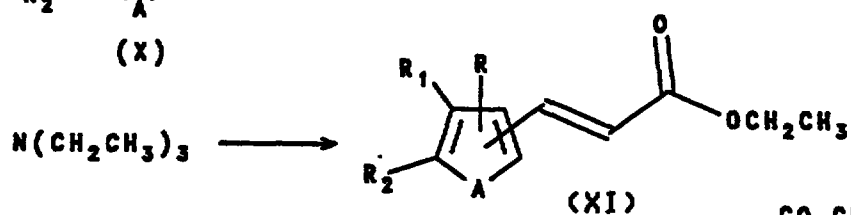


FLOW DIAGRAM VIII

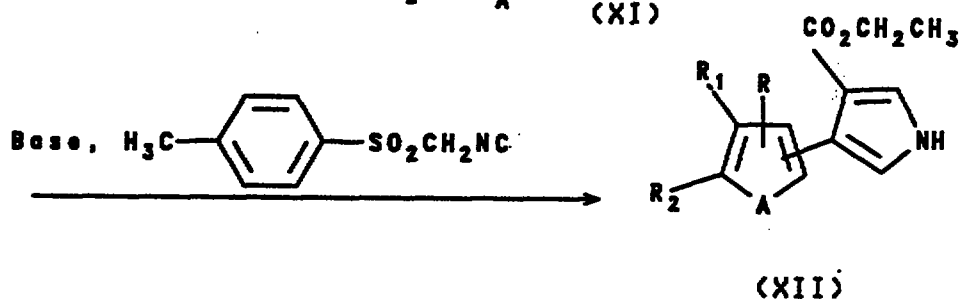
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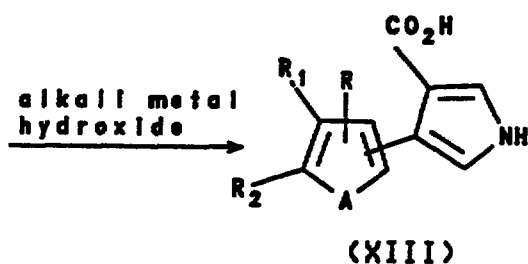
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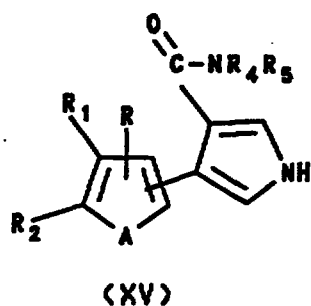


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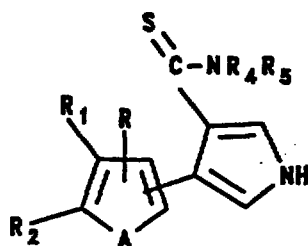
1. tri(C1-C4 alkyl)amine
 2. SOCl₂, N,N-dimethylformamide
 3. HNR₄R₅
- (XIV)

25

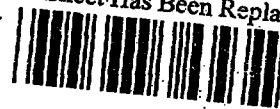


2,4-bis(4-methoxyphenyl)-
1,3-dithia-2,4-diphosphatane-
2,4-disulfide

30



35

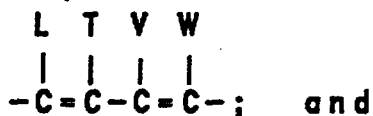


wherein

A, R₄ and R₅ are as described hereinabove for formula I;

5 R, R₁ and R₂ are each independently hydrogen, halogen or NO₂, and when R₁ and R₂ are taken together with the carbon atoms to which they are attached, they may form a ring in which R₁R₂ is represented by the structure:

10



L, T, V and W are each independently hydrogen, halogen, CN or NO₂.

15

2-(Thienyl- and furyl)-1-hydroxypyrrole-3-carbonitrile compounds may be prepared by reacting a formula XVI ester with an acetal of cyanopropionaldehyde in the presence of sodium hydride to form an acetal of formula XVII and reacting the formula XVII acetal with hydroxylamine hydrochloride as shown in

20

Flow Diagram IX.

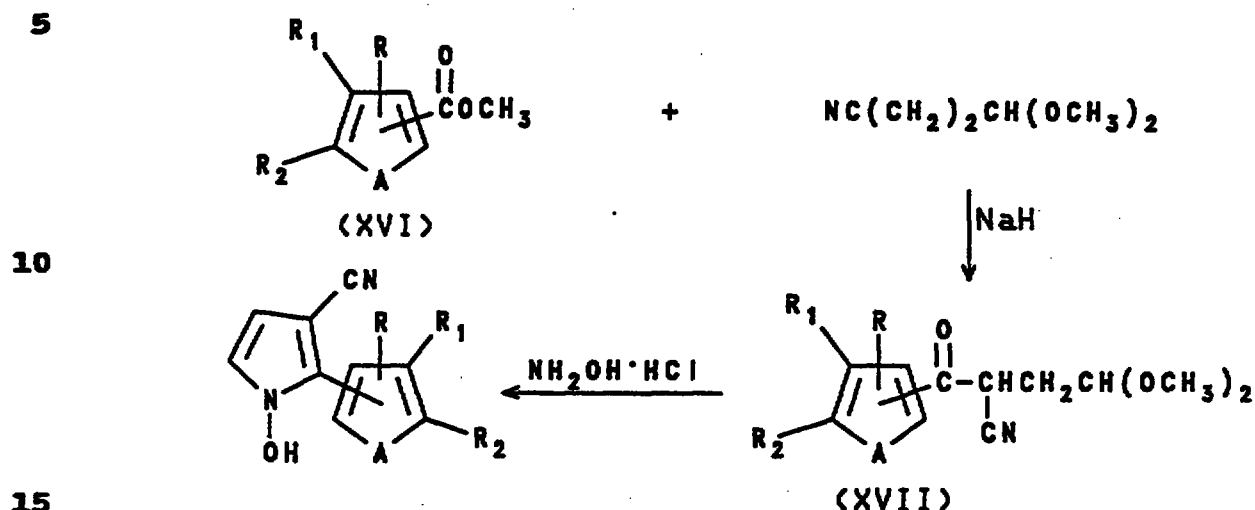
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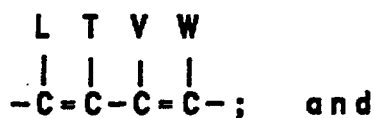
- 32 -

FLOW DIAGRAM IX

wherein

A is O or S;

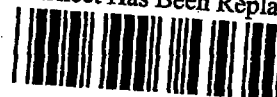
20 R, R₁ and R₂ are each independently hydrogen, halogen or NO₂, and when R₁ and R₂ are taken together with the carbon atoms to which they are attached, they may form a ring in which R₁R₂ is represented by the structure:



L, T, V and W are each independently hydrogen, halogen, CN or NO₂.

30 5-(Thienylpyrrole-2,3-dicarbonitrile compounds of formula I may be prepared by reacting a formula XVIII oxime with sodium oxalacetate to form a formula XIX intermediate which is reacted with hydrochloric acid in the presence of an alcohol to form a

35 formula XX 5-thienyl-1-hydroxypyrrole-3-carboxylate.



- 33 -

The formula XX carboxylate is reacted with methyl iodide and potassium t-butoxide to give a formula XXI 5-thienyl-1-methoxypyrrole-3-carboxylate. Saponification of the formula XXI carboxylate gives a formula XXII 5-thienyl-1-methoxypyrrole-3-carboxylic acid which is reacted with chlorosulfonyl isocyanate and N,N-dimethylformamide to give the formula I 5-thienylpyrrole-2,3-dicarbonitrile. The above reaction scheme is shown in Flow Diagram X.

5

10

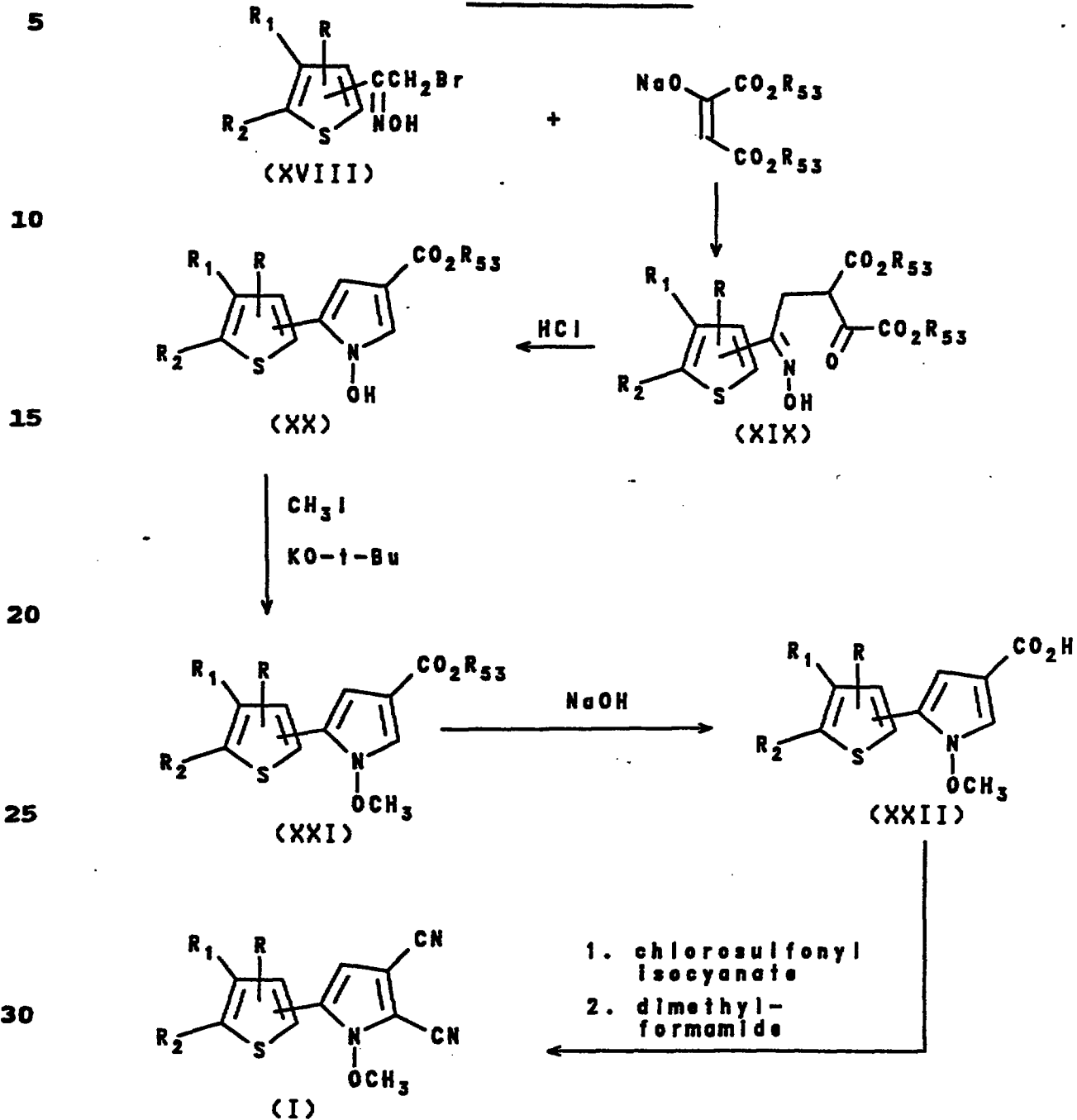
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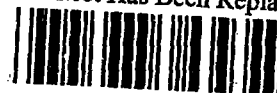
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FLOW DIAGRAM X



wherein

R, R₁ and R₂ are each independently hydrogen, halogen or NO₂, and when R₁ and R₂ are taken together with the carbon atoms to which they are attached, they may form a ring in which R₁R₂ is represented by the structure:

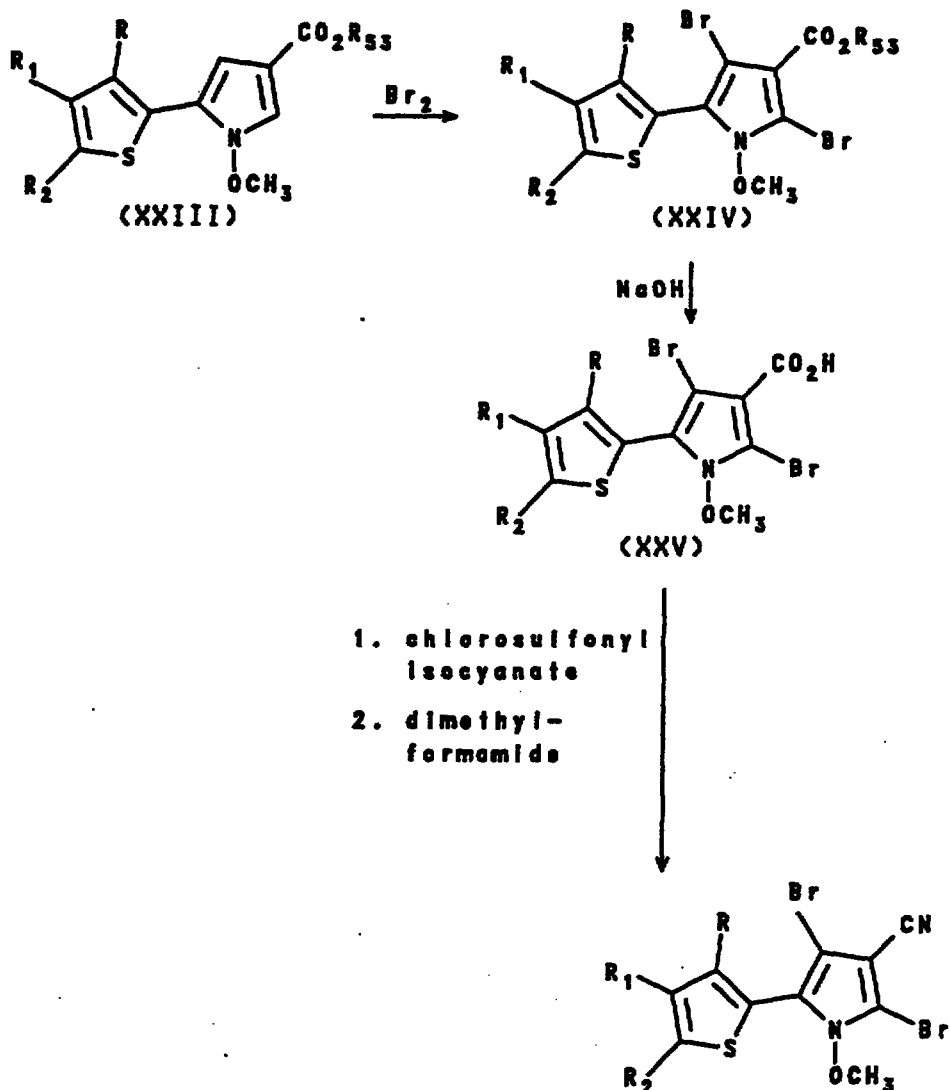


L, T, V and W are each independently hydrogen, halogen, CN or NO₂; and

R₅₃ is C₁-C₆ alkyl or C₃-C₆ cycloalkyl.

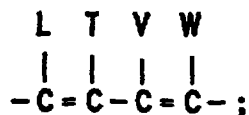
2,4-Dibromo-5-(2-thienyl)-1-methoxypyrrole-3-carbonitrile compounds of the present invention may be prepared by reacting a formula XXIII 5-(2-thienyl)-1-methoxypyrrole-3-carboxylate with bromine to form a formula XXIV 2,4-dibromo-5-(2-thienyl)-1-methoxypyrrole-3-carboxylate. Saponification of the formula XXIV carboxylate gives a formula XXV acid which is reacted with chlorosulfonyl isocyanate and dimethylformamide to give the desired 2,4-dibromo-5-(2-thienyl)-1-methoxypyrrole-3-carbonitrile. The above reaction scheme is shown in Flow Diagram XI.

FLOW DIAGRAM XI



wherein

R and R₁ are each independently hydrogen, halogen or NO₂, and when R₁ is taken together with R₂ and the carbon atoms to which they are attached, they may form a ring in which R₁R₂ is represented by the structure:

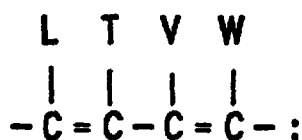


R₂ is halogen, and when taken together with R₁ and the



carbon atoms to which they are attached, they may form a ring in which R_1R_2 is represented by the structure:

5



L, T, V and W are each independently hydrogen, halogen, CN or NO_2 ; and

10

R_{53} is $\text{C}_1\text{-C}_6$ alkyl or $\text{C}_3\text{-C}_6$ cycloalkyl.

Similarly, 2,4-dibromo-5-(3-thienyl)-1-methoxypyrrole-3-carbonitrile compounds may be prepared as shown in Flow Diagram XII.

15

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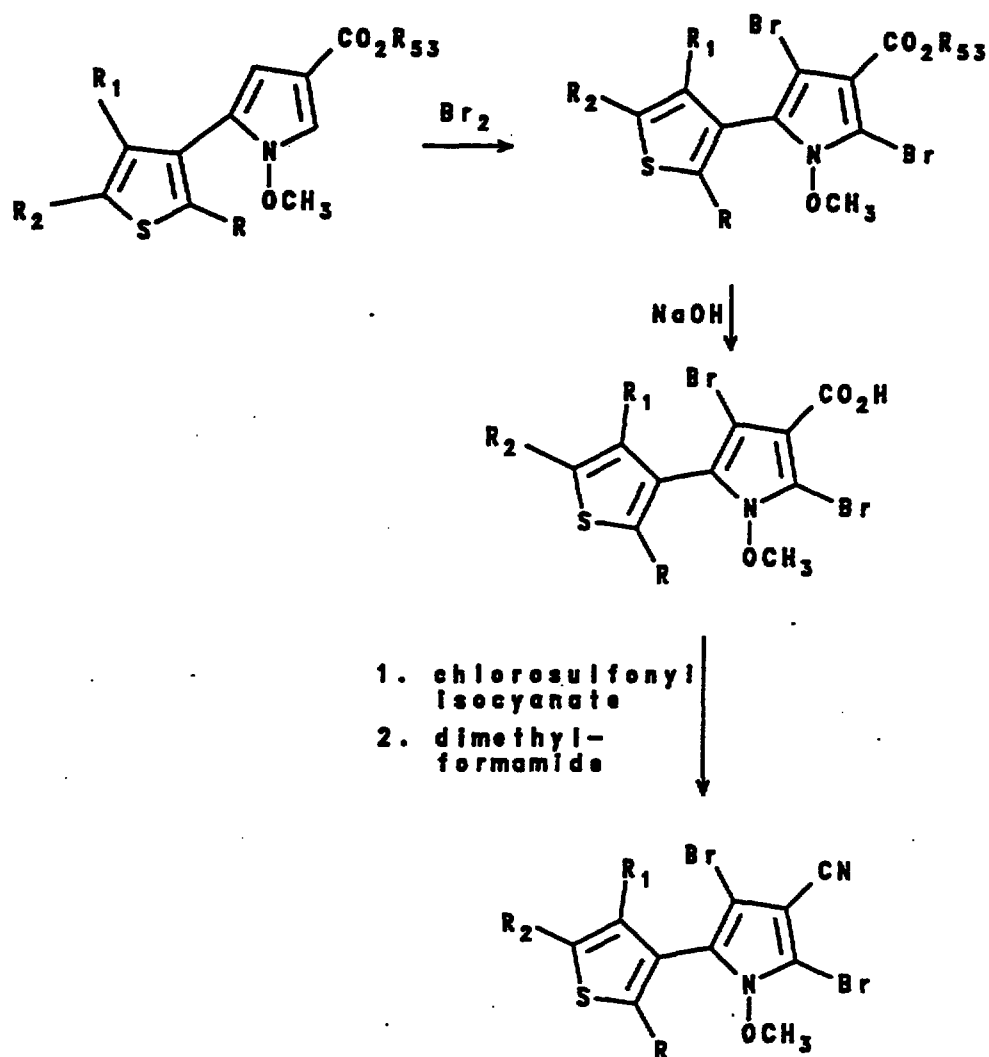
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FLOW DIAGRAM XII



wherein

R_1 is hydrogen, halogen or NO_2 , and when R_1 is taken together with R_2 and the carbon atoms to which they are attached, they may form a ring in which R_1R_2 is represented by the structure:



R and R_2 are each independently halogen, and when R_2 is



taken together with R_1 and the carbon atoms to which they are attached, they may form a ring in which R_1R_2 is represented by the structure:

5



L, T, V and W are each independently hydrogen, halogen, CN or NO_2 ; and

10

R_{53} is $\text{C}_1\text{-C}_6$ alkyl or $\text{C}_3\text{-C}_6$ cycloalkyl.

4-Bromo-2-($\text{C}_1\text{-C}_6$ haloalkyl)-5-(2-thienyl)-1-methoxypyrrole-3-carbonitrile compounds of the present invention may be prepared as shown in Flow Diagram XIII.

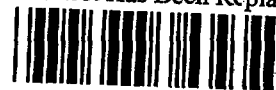
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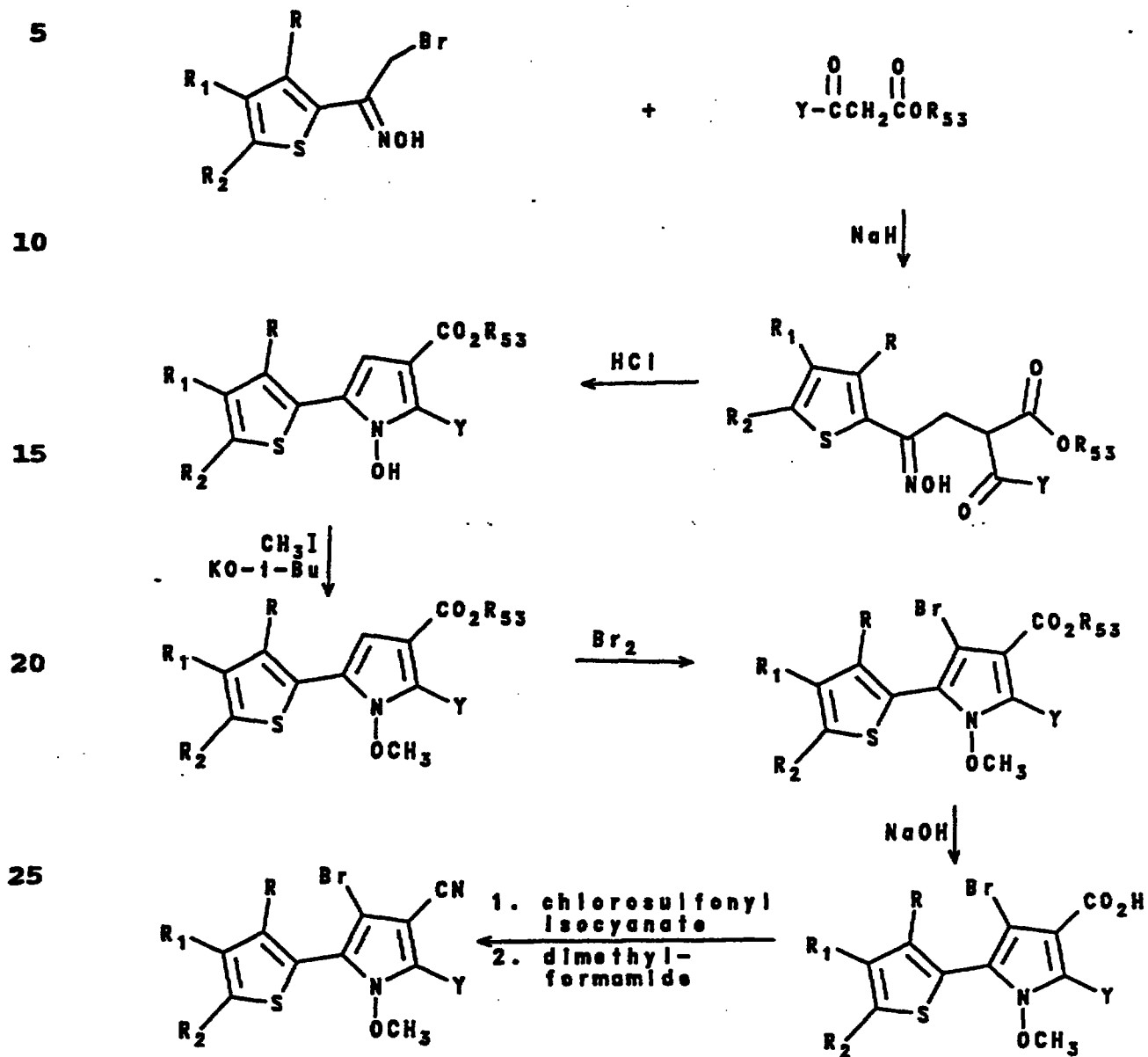
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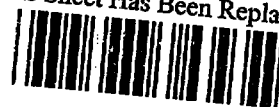


- 40 -

FLOW DIAGRAM XIII



wherein Y is C_1 - C_6 haloalkyl and R, R_1, R_2 and R_{53} are as described in Flow Diagram XI.



Similarly, 4-bromo-2-(C₁-C₆ haloalkyl)-5-(3-thienyl)-1-methoxypyrrole-3-carbonitrile compounds may be prepared as shown in Flow Diagram XIV.

FLOW DIAGRAM XIV

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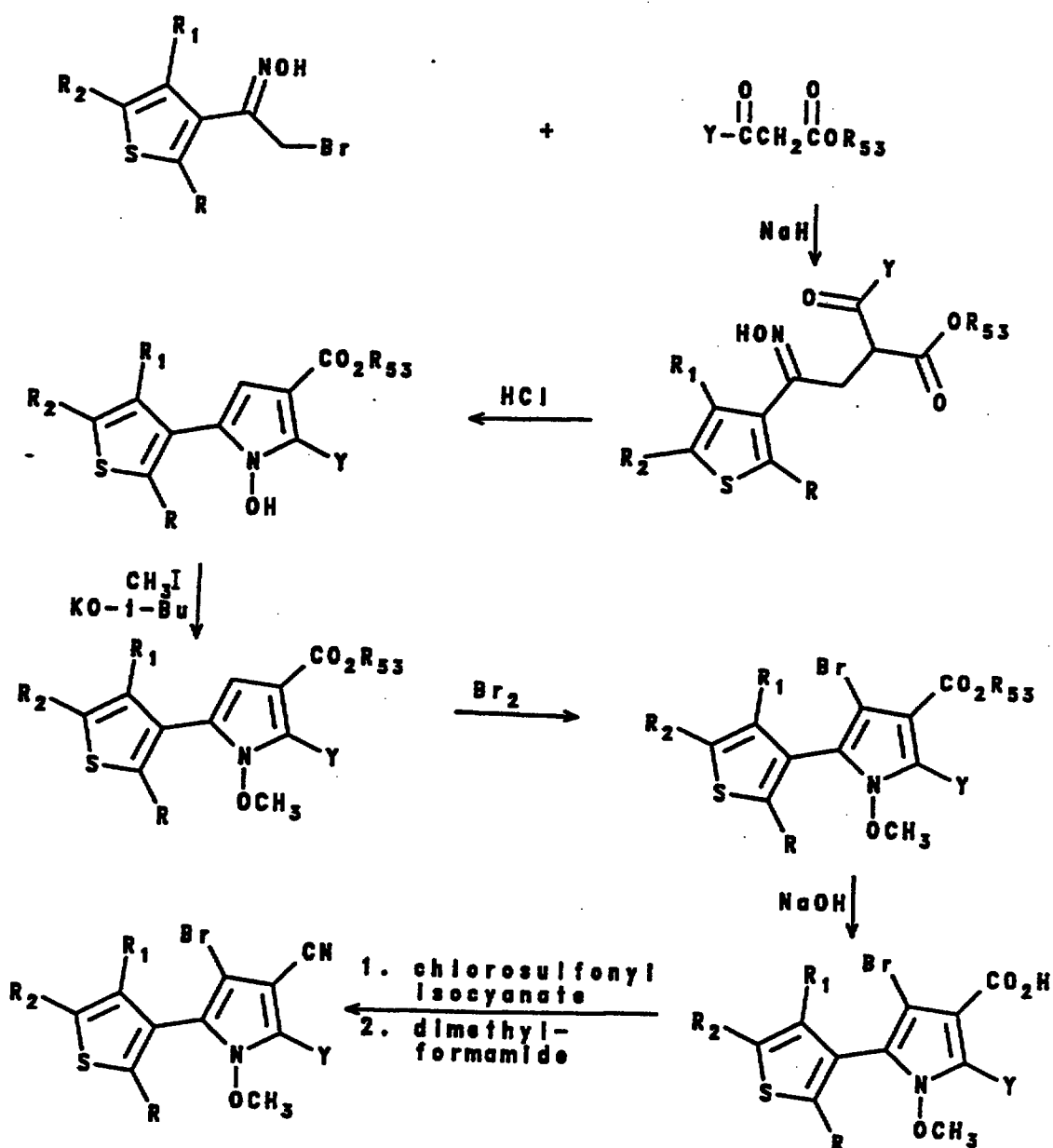
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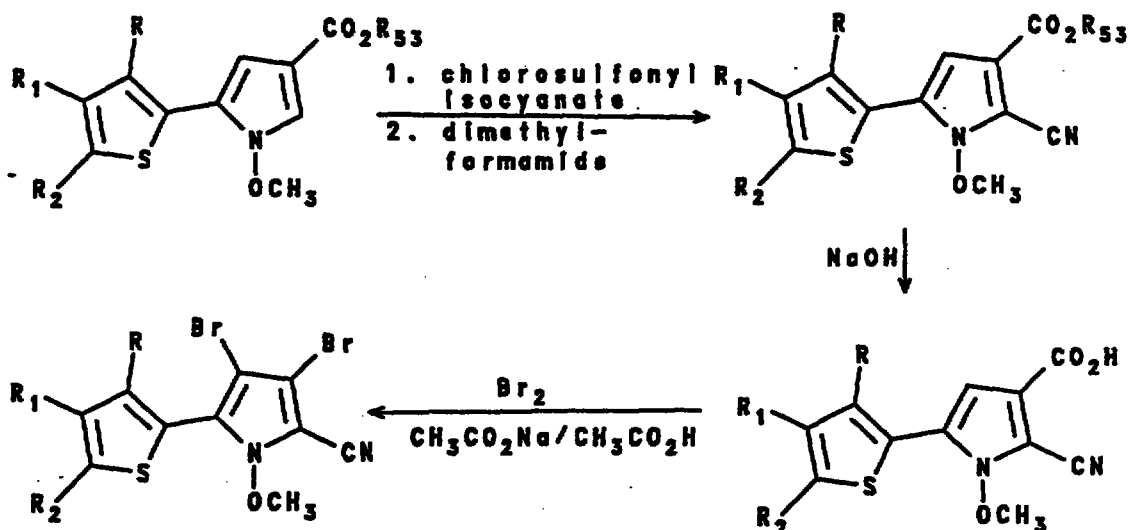




wherein Y is C₁-C₆ haloalkyl and R, R₁, R₂ and R₅₃ are as described in Flow Diagram XII.

3,4-Dibromo-5-(2-thienyl)-1-methoxypyrrole-2-carbonitrile compounds may be prepared by reacting a 5-(2-thienyl)-1-methoxypyrrole-3-carboxylate with chlorosulfonyl isocyanate and dimethylformamide to give a 2-cyano-5-(2-thienyl)-1-methoxypyrrole-3-carboxylate. Saponification and bromination of the 2-cyano-5-(2-thienyl)-1-methoxypyrrole-3-carboxylate compound gives the desired 3,4-dibromo-5-(2-thienyl)-1-methoxypyrrole-2-carbonitrile as shown in Flow Diagram XV.

FLOW DIAGRAM XV

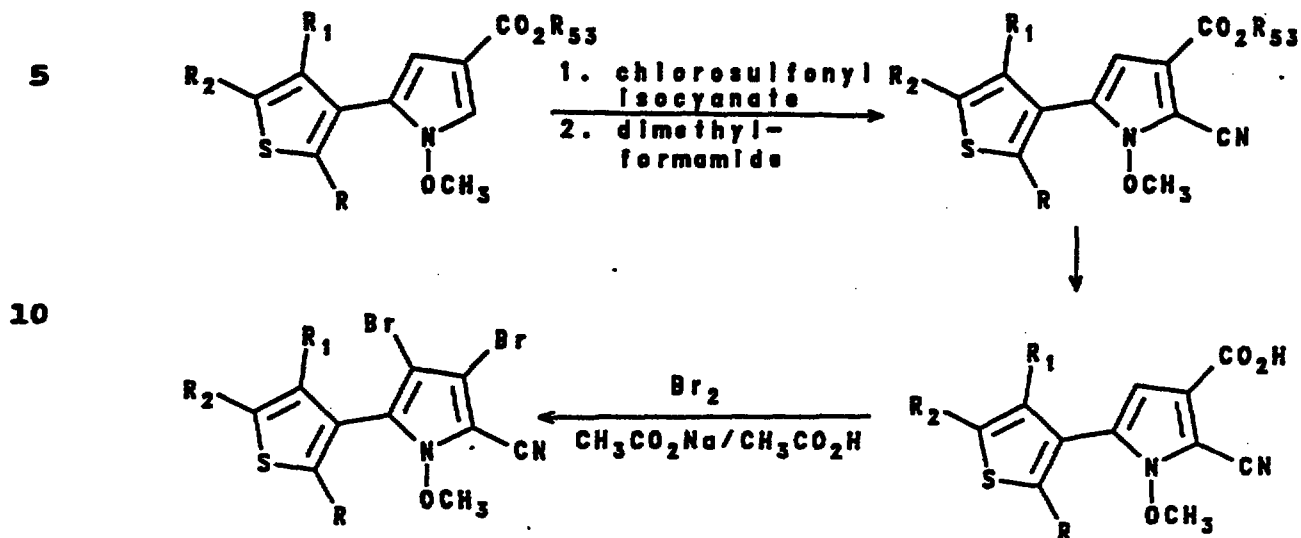


wherein R, R₁, R₂ and R₅₃ are as described in Flow Diagram XI.

Similarly, 3,4-dibromo-5-(3-thienyl)-1-methoxypyrrole-2-carbonitrile compounds may be prepared as shown in Flow Diagram XVI.

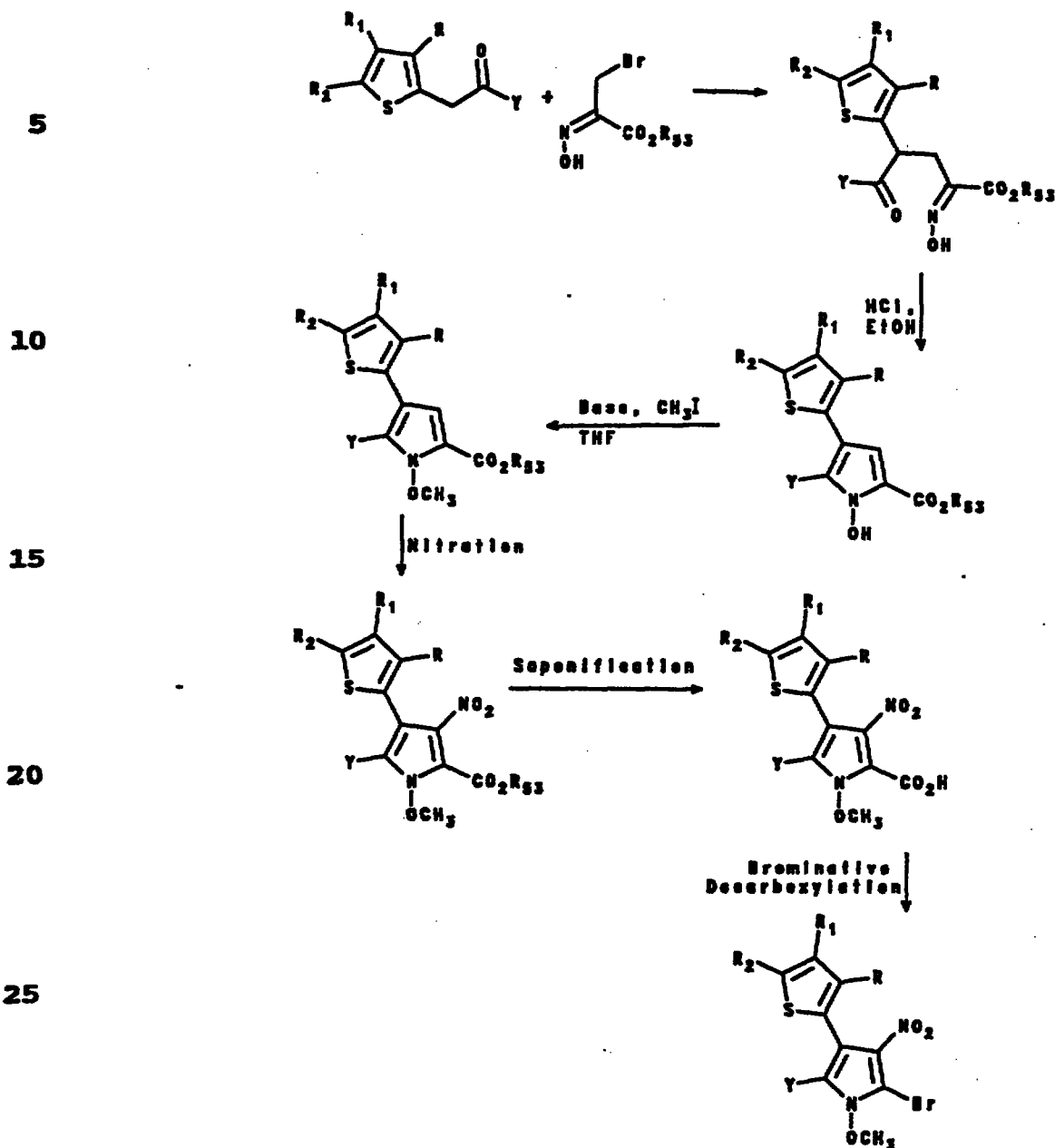


FLOW DIAGRAM XVI



Formula I 2-bromo-3-nitro-5-(C₁-C₆ haloalkyl)-4-(2-thienyl)-1-methoxypyrrole compounds may be prepared as shown in Flow Diagram XVII.

FLOW DIAGRAM XVII

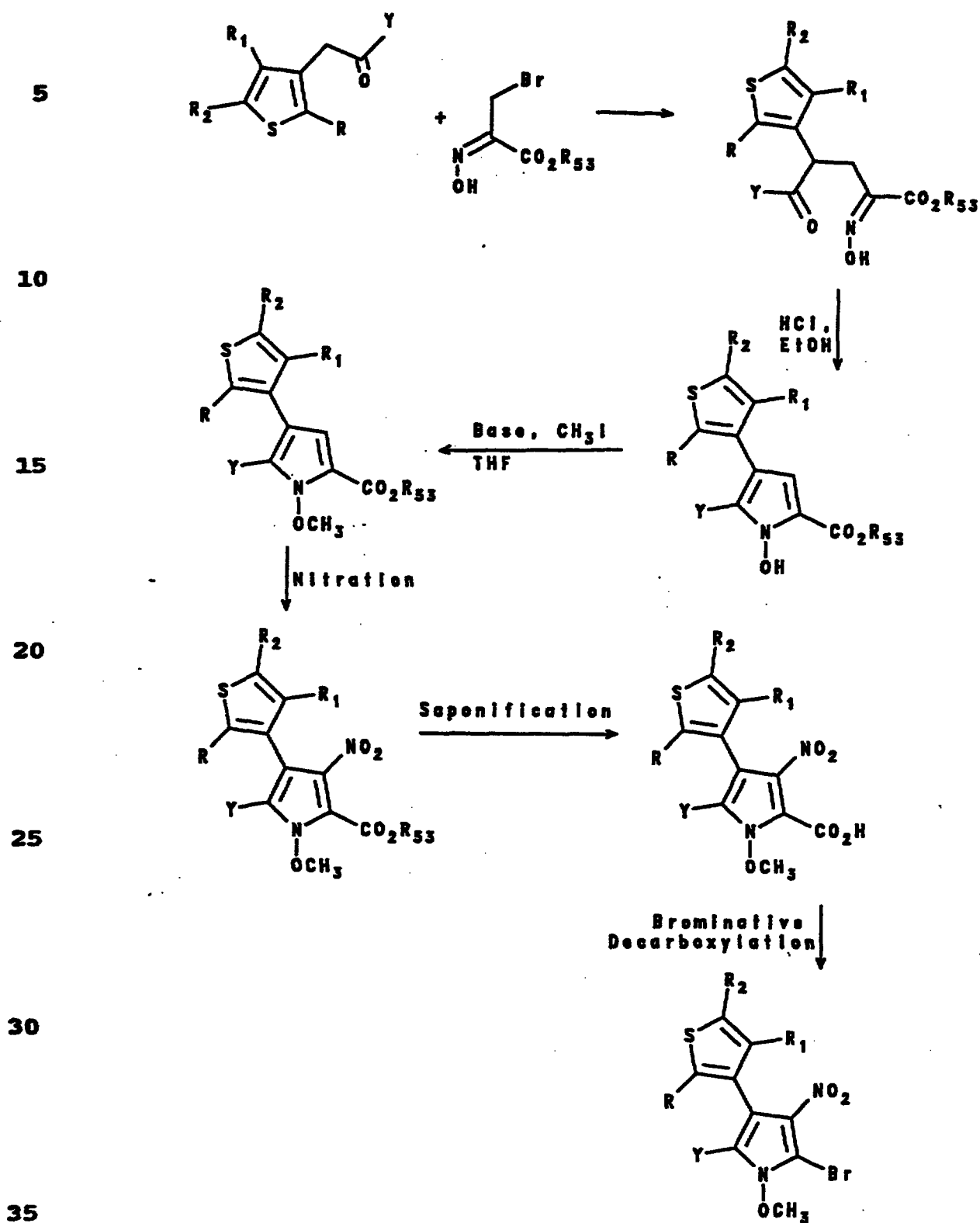


wherein Y is C_1 - C_6 haloalkyl and R, R_1 , R_2 and R_{53} are as described in Flow Diagram XI.

Similarly, 2-bromo-3-nitro-5-(C_1 - C_6 haloalkyl)-4-(3-thienyl)-1-methoxypyrrole compounds may be prepared as shown in Flow Diagram XVIII.



- 45 -

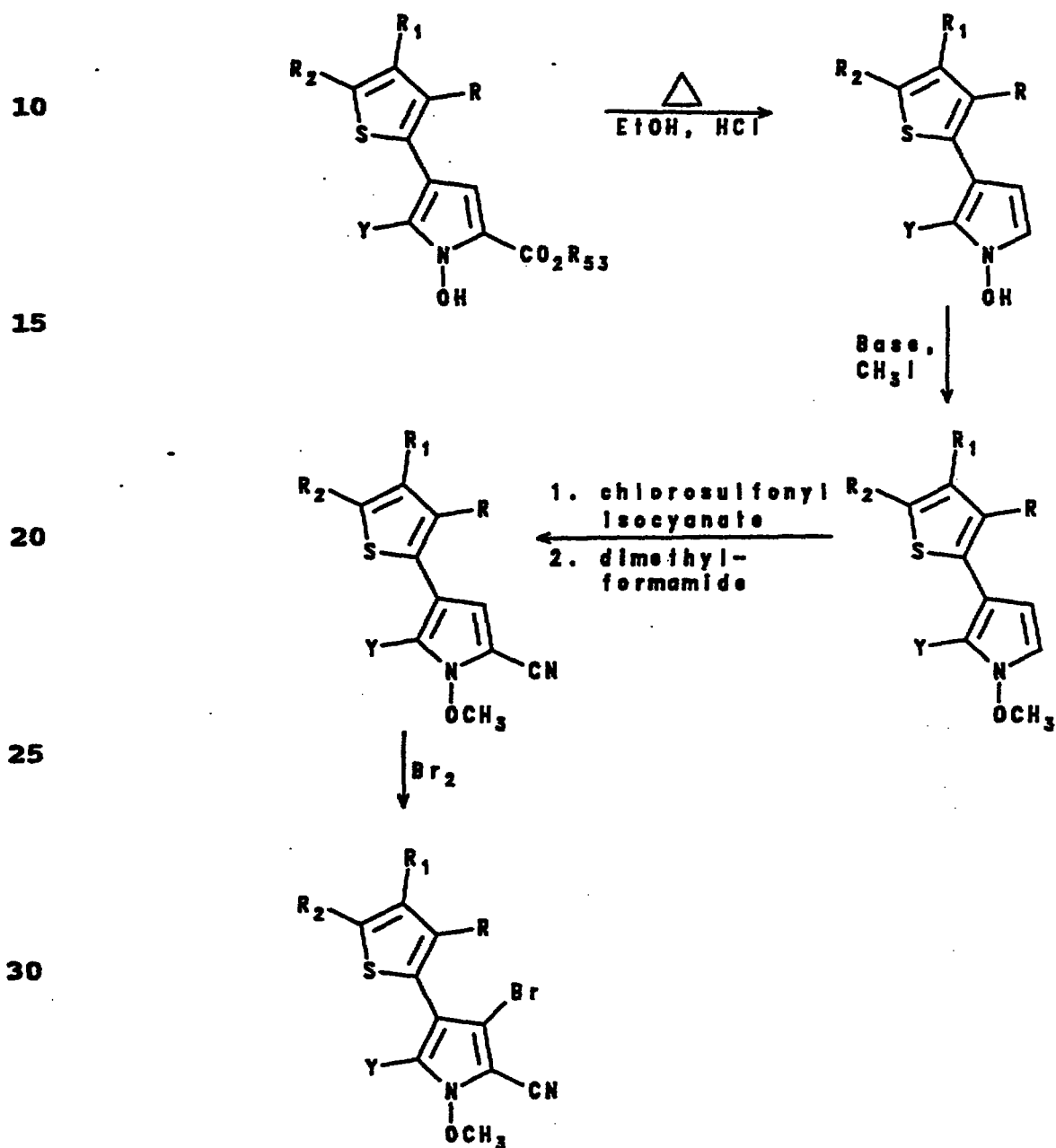
FLOW DIAGRAM XVIII



wherein Y is C₁-C₆ haloalkyl and R, R₁, R₂ and R₅₃ are as described in Flow Diagram XII.

3-Bromo-5-(C₁-C₆ haloalkyl)-4-(2-thienyl)-1-methoxypyrrole-2-carbonitrile compounds may be prepared as shown in Flow Diagram XIX.

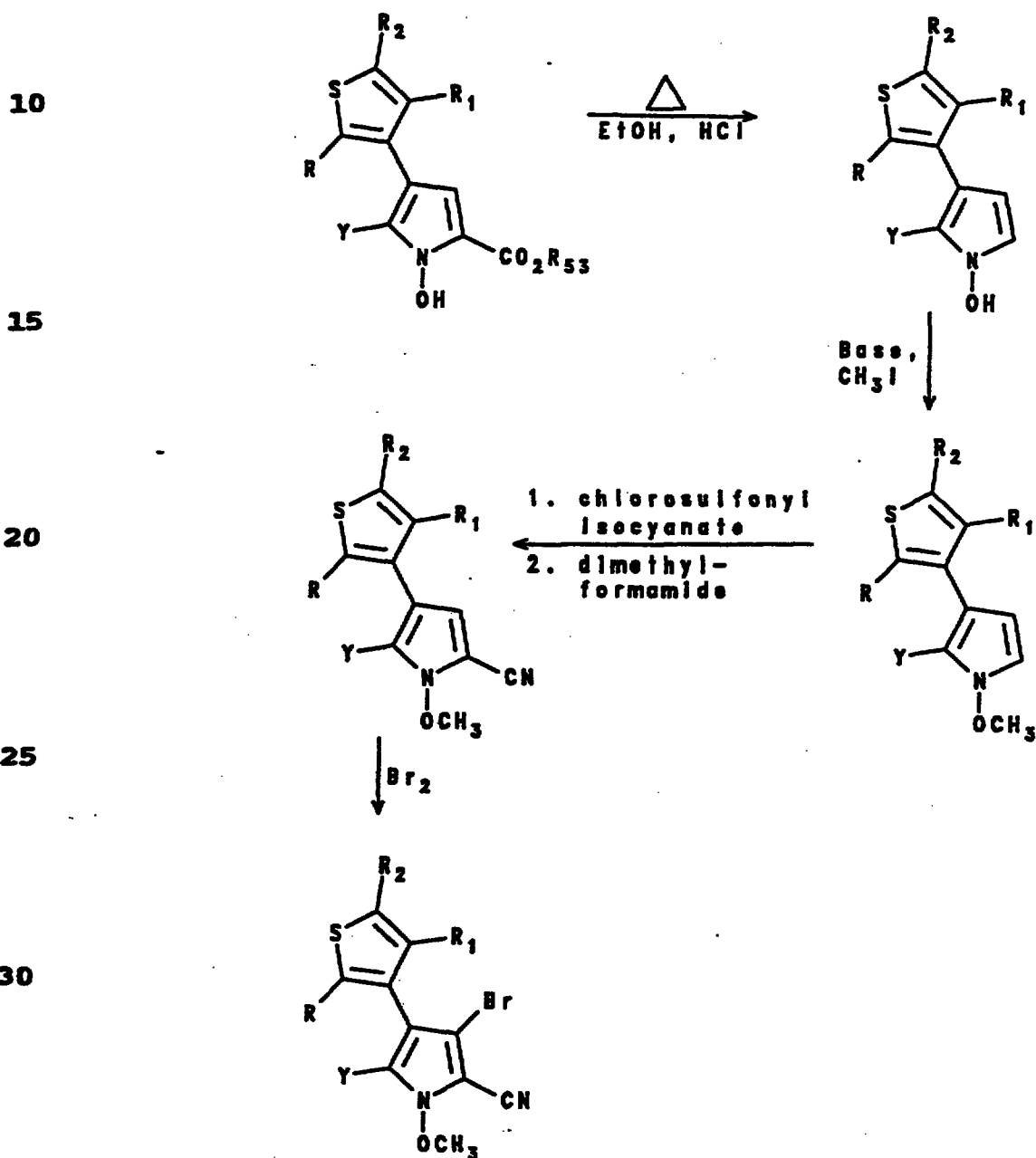
FLOW DIAGRAM XIX



wherein Y is C₁-C₆ haloalkyl and R, R₁, R₂ and R₅₃ are as described in Flow Diagram XI.

Similarly, 3-bromo-5-(C₁-C₆ haloalkyl)-4-(3-thienyl)-1-methoxypyrrole-2-carbonitrile compounds may be prepared as shown in Flow Diagram XX.

FLOW DIAGRAM XX





wherein Y is C₁-C₆ haloalkyl and R, R₁, R₂ and R₅₃ are as described in Flow Diagram XII.

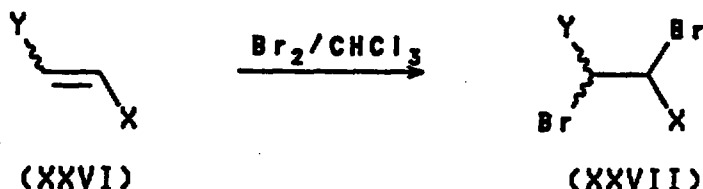
4-Aryl-3-(nitro and cyano)-5-(C₁-C₆ haloalkyl)-2-(2- and 3-thienyl and -furyl)pyrrole compounds may be prepared by reacting a substituted or unsubstituted beta-(nitro or cyano)styrene of formula XXVI with bromine to form a (substituted or unsubstituted-phenyl)-1,2-dibromo-2-(nitro or cyano)ethane of formula XXVII which is then subjected to a dehalogenation treatment using a base such as pyridine to form a substituted or unsubstituted (nitro or cyano)bromostyrene of formula XXVIII. Reaction of the bromostyrene with a formula XXIX oxazolinone in the presence of a tri(C₁-C₄ alkyl)amine gives the desired 4-aryl-3-(nitro or cyano)-5-(C₁-C₆ haloalkyl)-2-(2- or 3-thienyl or -furyl)pyrrole. The above reaction scheme is shown in Flow Diagram XXI.



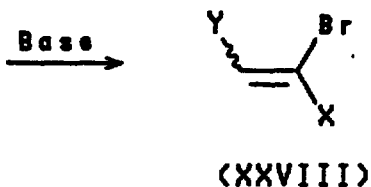
- 49 -

FLOW DIAGRAM XXI

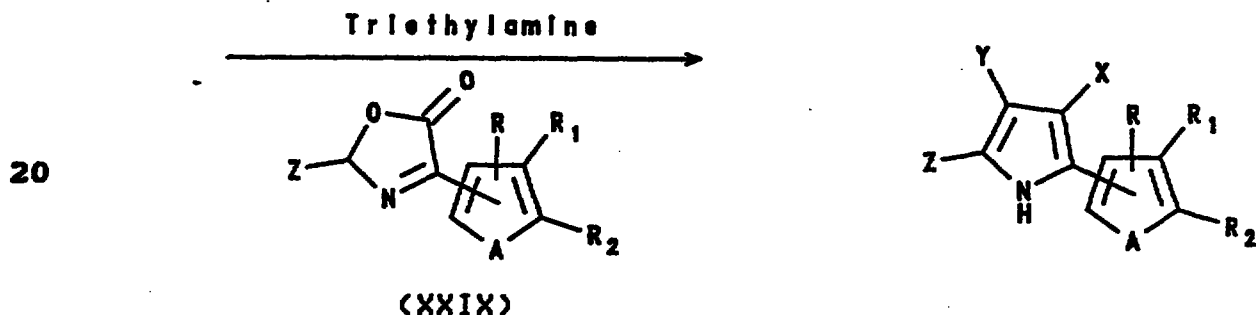
5



10



15



25

wherein

X is CN or NO₂;

Y is phenyl optionally substituted with one or more halogen atoms,

30

NO₂ groups,

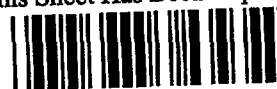
CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

35

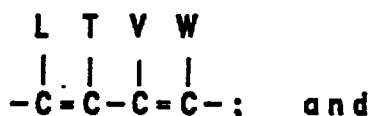
Z is C₁-C₆ haloalkyl;



- 50 -

A is O or S;

R, R₁ and R₂ are each independently hydrogen, halogen or NO₂, and when R₁ and R₂ are taken together with the carbon atoms to which they are attached, they may form a ring in which R₁R₂ is represented by the structure:

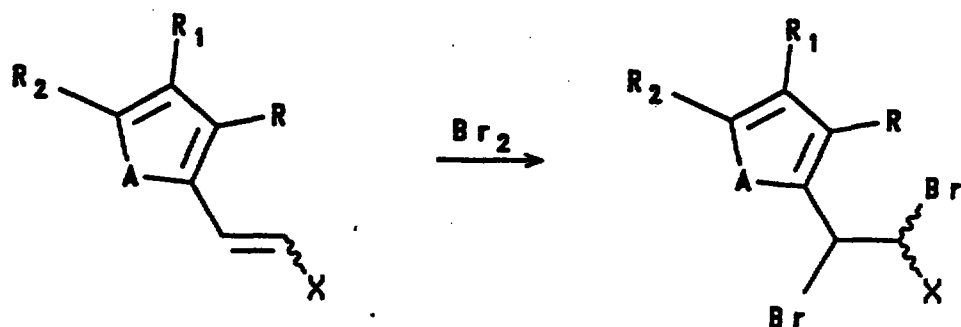


L, T, V and W are each independently hydrogen, halogen, CN or NO₂.

Similarly, 4-(2-thienyl and -furyl)-3-(nitro and cyano)-5-(C₁-C₆ haloalkyl)-2-arylpyrrole compounds may be prepared as shown in Flow Diagram XXII and 4-(3-thienyl and -furyl)-3-(nitro and cyano)-5-(C₁-C₆ haloalkyl)-2-arylpyrrole compounds may be prepared as shown in Flow Diagram XXIII.

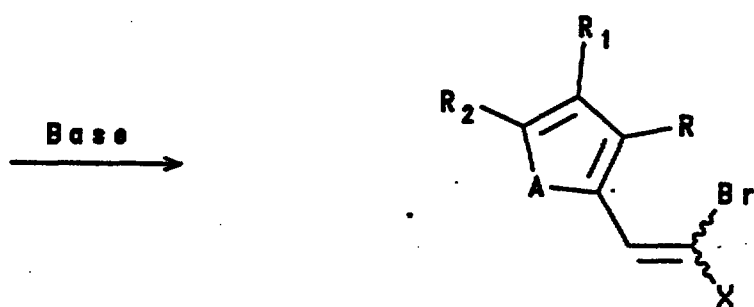
FLOW DIAGRAM XXII

5

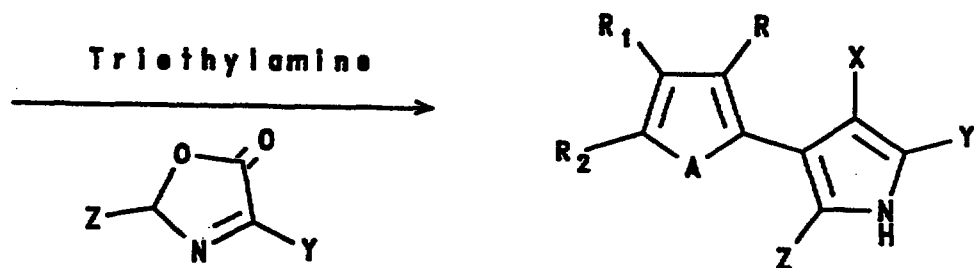


10

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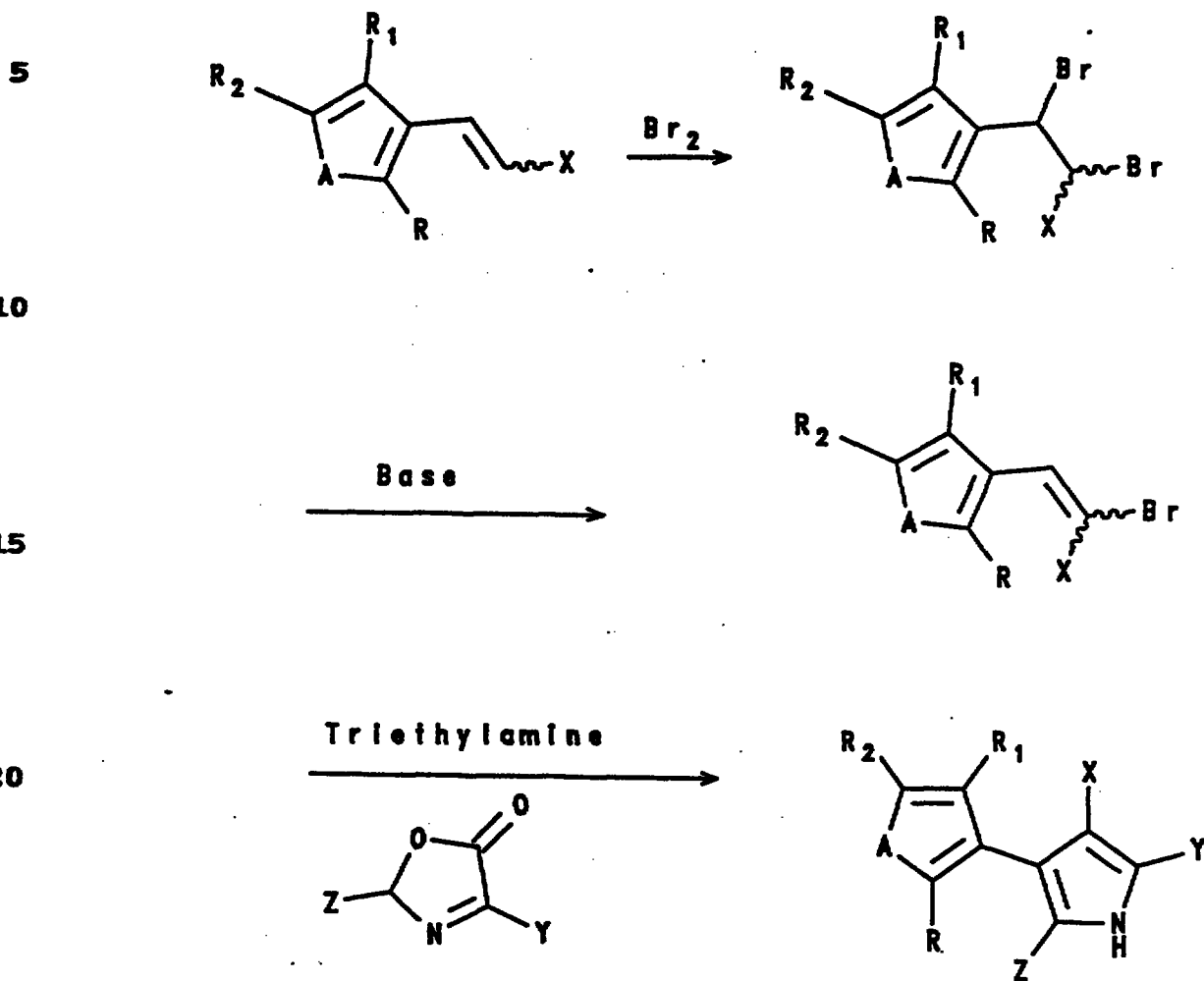


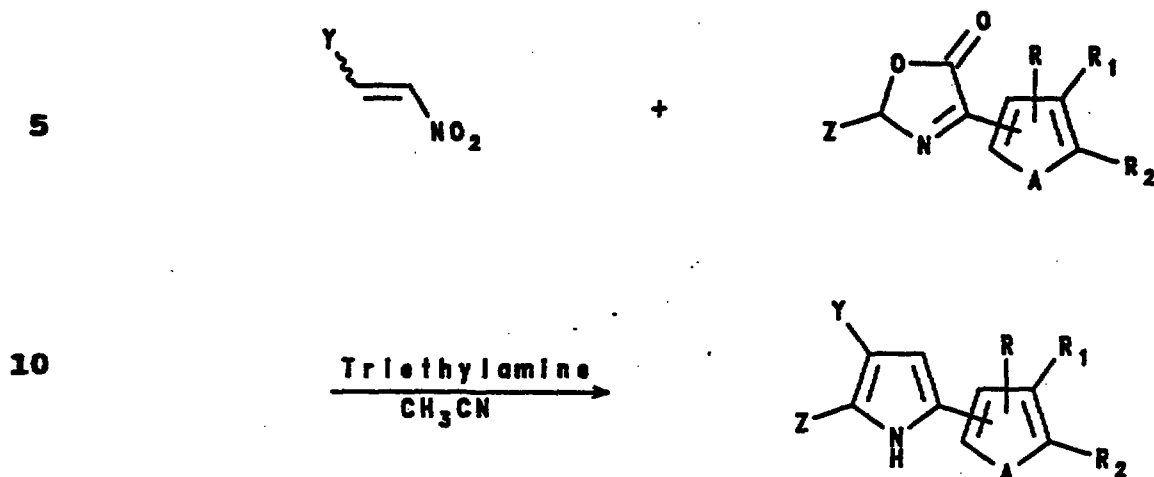
25

wherein A, X, Y and Z are as described in Flow Diagram XXI and R, R_1 and R_2 are as described in Flow Diagram XI.

30

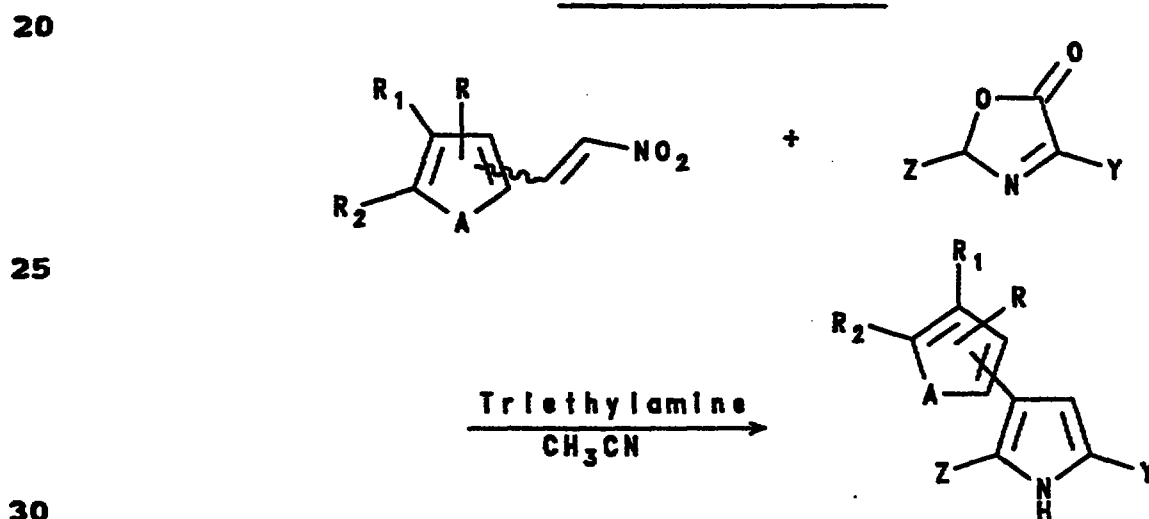
35

FLOW DIAGRAM XXIII

FLOW DIAGRAM XXIV

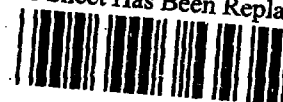
wherein Y, Z, A, R, R₁ and R₂ are as described in Flow Diagram XXI.

15 Similarly, 3-(2- and 3-thienyl and -furyl)-2-(C₁-C₆ haloalkyl)-5-arylpyrrole compounds may be prepared as shown in Flow Diagram XXV.

FLOW DIAGRAM XXV

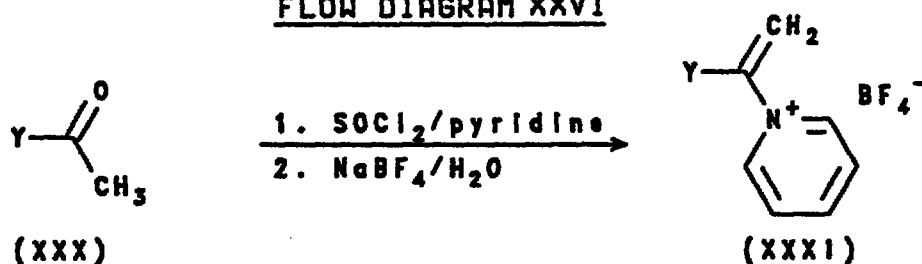
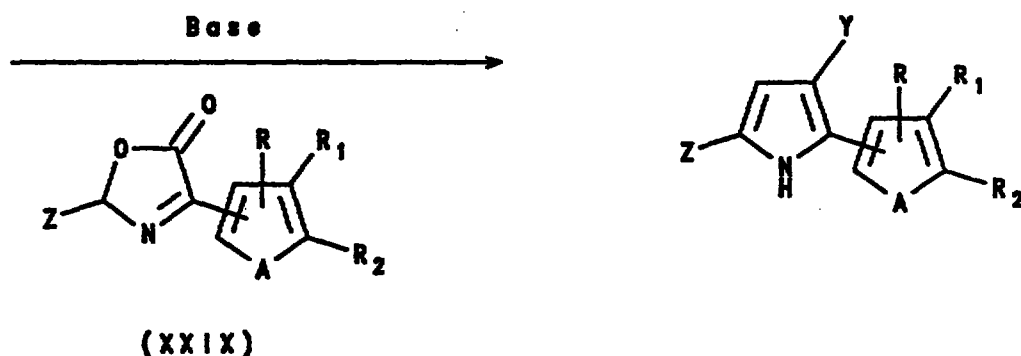
wherein Y, Z, A, R, R₁ and R₂ are as described in Flow Diagram XXI.

35 5-(C₁-C₆ Haloalkyl)-3-aryl-2-(2- and 3-thienyl and -furyl)pyrrole compounds may be prepared by reacting a substituted or unsubstituted acetophenone of



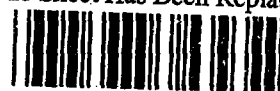
formula XXX with a thionyl halide in the presence of an organic base such as pyridine. Thereafter, the reaction mixture is treated with aqueous sodium tetrafluoroborate to give a formula XXXI N- α -(substituted or unsubstituted)styrylpyridinium tetrafluoroborate. The formula XXXI styrylpyridinium tetrafluoroborate is then reacted with a formula XXIX oxazolinone in the presence of a base, such as pyridine to form the desired 5-(C₁-C₆ haloalkyl)-3-aryl-2-(2- or 3-thienyl or -furyl)-pyrrole compound. The above reaction scheme is shown in Flow Diagram XXVI.

FLOW DIAGRAM XXVI

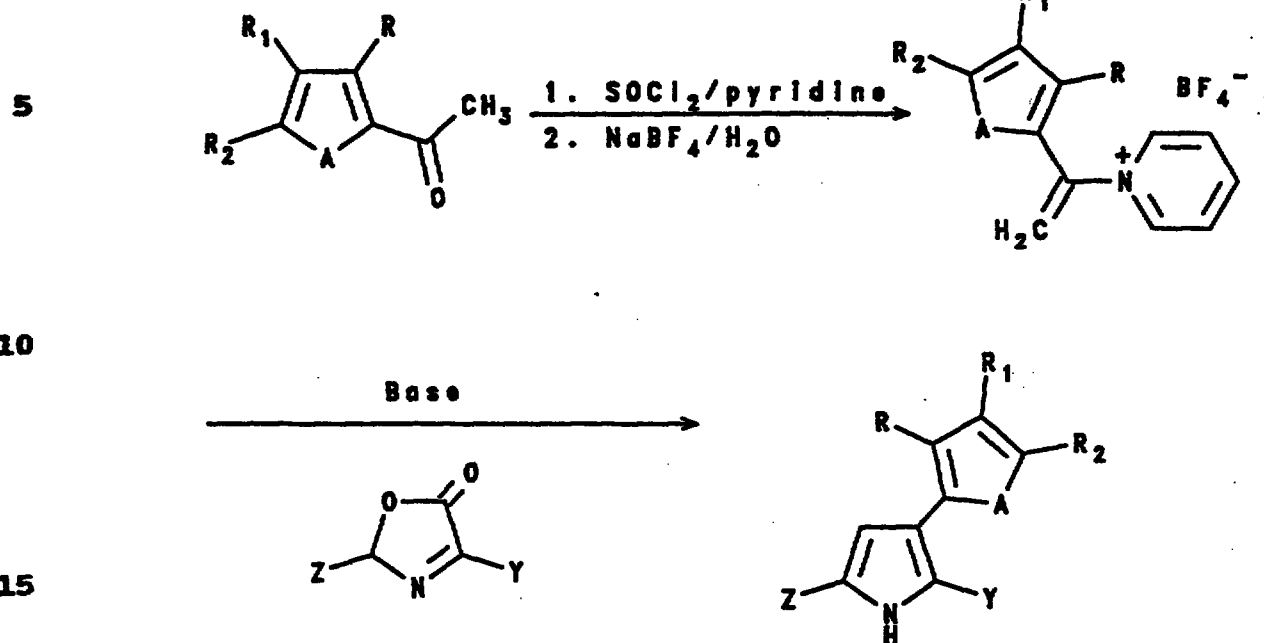


wherein Y, Z, A, R, R₁ and R₂ are as described in Flow Diagram XXI.

Similarly, 5-(C₁-C₆ haloalkyl)-2-aryl-3-(2-thienyl and -furyl)pyrrole compounds may be prepared as shown in Flow Diagram XXVII and 5-(C₁-C₆ haloalkyl)-2-aryl-3-(3-thienyl and -furyl)pyrrole compounds may be prepared as shown in Flow Diagram XXVIII.



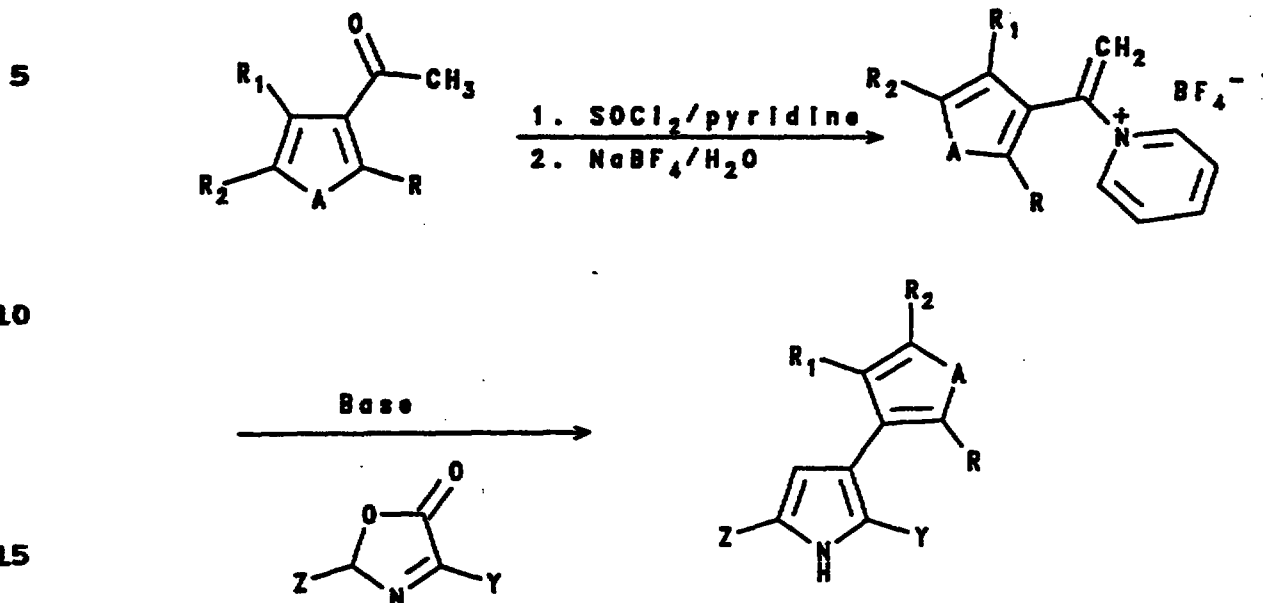
- 55 -

FLOW DIAGRAM XXVII

wherein A, Z and Y are as described in Flow Diagram XXI
and R, R_1 and R_2 are as described in Flow Diagram XI.



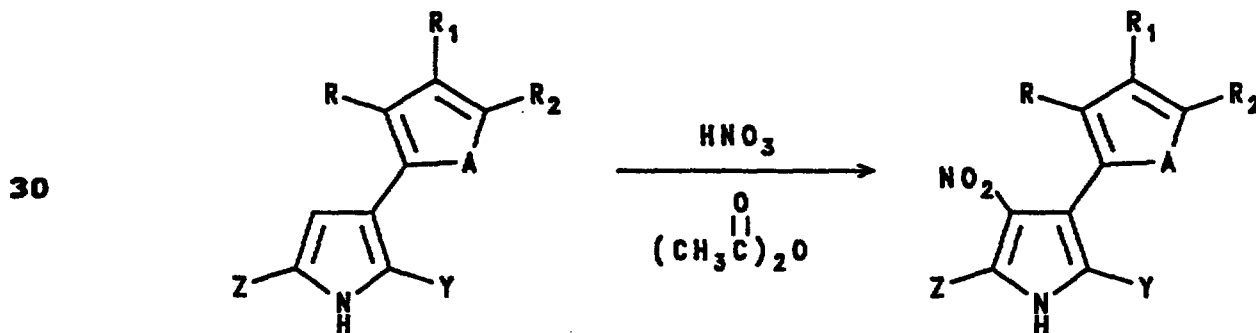
FLOW DIAGRAM XXVIII



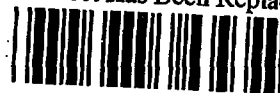
wherein A, Z and Y are as described in Flow Diagram XXI and R, R₁ and R₂ are as described in Flow Diagram XII.

20 5-(C₁-C₆ haloalkyl)-2-aryl-4-nitro-3-(2-thienyl)pyrrole compounds may be prepared by reacting a 5-(C₁-C₆ haloalkyl)-2-aryl-3-(2-thienyl)pyrrole compound with nitric acid and acetic anhydride as shown in Flow Diagram XXIX.

FLOW DIAGRAM XXIX



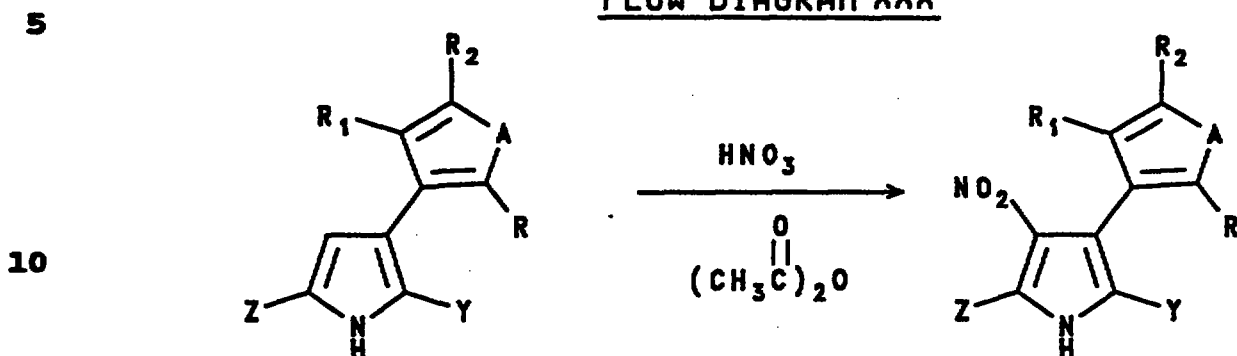
35 wherein A, Z and Y are as described in Flow Diagram XXI and R, R₁ and R₂ are as described in Flow Diagram XI.



- 57 -

Similarly, 5-(C₁-C₆ haloalkyl)-2-aryl-4-nitro-3-(3-thienyl)pyrrole compounds may be prepared as shown in Flow Diagram XXX.

FLOW DIAGRAM XXX



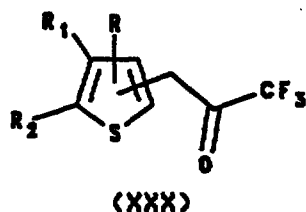
wherein A, Z and Y are as described in Flow Diagram XXI and R, R₁ and R₂ are as described in Flow Diagram XII.

2,3,5-Tris(trifluoromethyl)-4-(2- and 3-thienyl)pyrrole compounds of the present invention may be prepared by reacting a formula XXX 3-(2- or 3-thienyl)-1,1,1-trifluoro-2-propanone with hydroxylamine hydrochloride to form a formula XXXI oxime. The formula XXXI oxime is then reacted in a pressure bottle with liquid hexafluoro-2-butyne in the presence of at least a ten mole percent amount of a base such as an alkali metal alkoxide in a solvent at an elevated temperature to form a formula XXXII 3-(2- or 3-thienyl)-5a-hydroxy-2,4-a,5b-tris(trifluoromethyl)-1-pyrroline. The formula XXXII pyrroline is then reacted with hydrochloric acid in an alcohol to form the desired 2,3,5-tris(trifluoromethyl)-4-(2- or 3-thienyl)pyrrole compound. The above reaction scheme is shown in Flow Diagram XXXI.

35

FLOW DIAGRAM XXXI

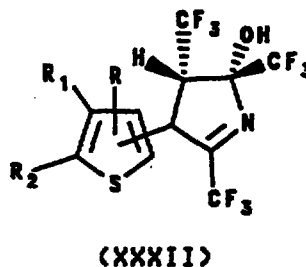
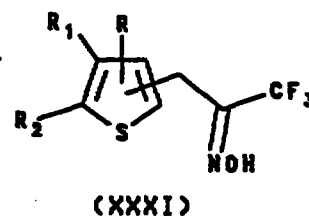
5



+



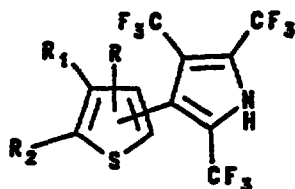
10



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25

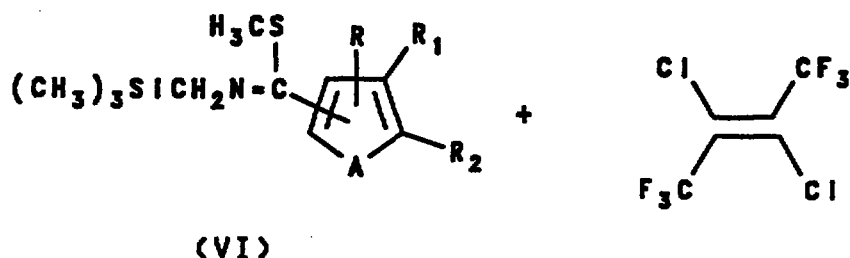
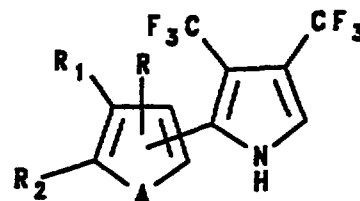
3,4-Bis(trifluoromethyl)-2-(2- and 3-thienyl and -furyl)pyrrole compounds may be prepared by reacting an N-(trimethylsilyl)methyl-5-methyl(thienyl- or furyl)thioimide of formula VI with 2,3-dichlorohexafluorobutene as shown below in Flow Diagram XXXII.

30

35



FLOW DIAGRAM XXXII



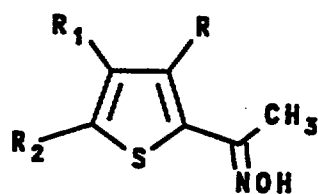
2,3-Bis(trifluoromethyl)-4-halo-5-(2-thienyl)pyrrole compounds may be prepared by reacting an oxime of formula XXXIII with hexafluoro-2-butyne in the presence of a base such as an alkali metal alkoxide to form the vinyl oxime of formula XXXIV and the 2-(2-thienyl)-4,5-trans-bis(trifluoromethyl)-1-pyrrolin-5-ol of formula XXXV. The formula XXXIV vinyl oxime is then heated to form the formula XXXVI 2-(2-thienyl)-4,5-bis(trifluoromethyl)-1-pyrrolin-4-ol. The formula XXXV pyrrolin-5-ol or formula XXXVI pyrrolin-4-ol is then reacted with hydrochloric acid in an alcohol to obtain a 5-(2-thienyl)-2,3-bis(trifluoromethyl)pyrrole compound. The 5-(2-thienyl)-2,3-bis(trifluoromethyl)pyrrole is then reacted with a halogenating agent to obtain the desired 2,3-bis(trifluoromethyl)-4-halo-5-(2-thienyl)pyrrole. The above reaction scheme is shown in Flow Diagram XXXIII.



- 60 -

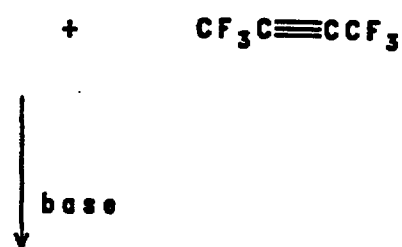
FLOW DIAGRAM XXXIII

5

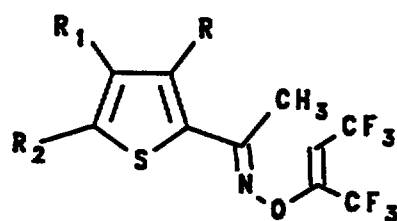


(XXXIII)

10

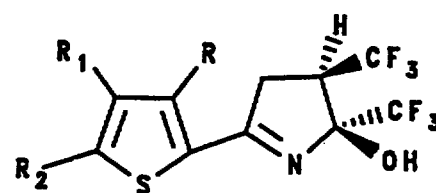


15



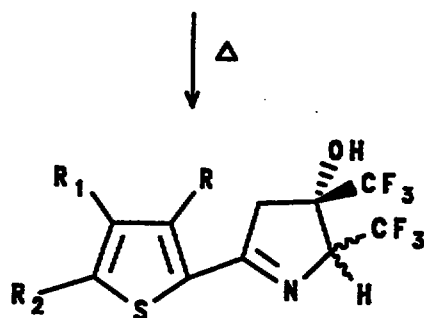
(XXXIV)

+



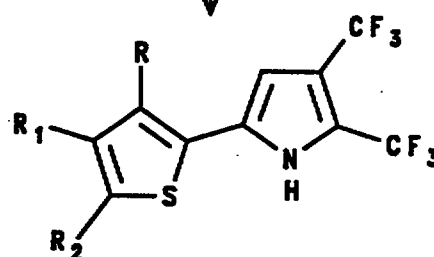
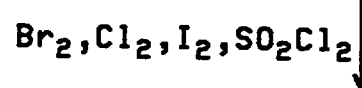
(XXXV)

20

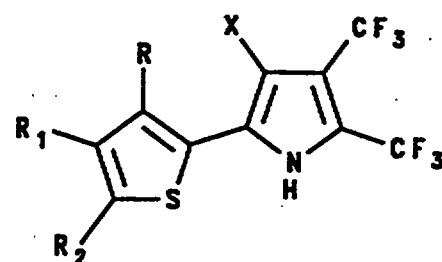


(XXXVI)

25



30



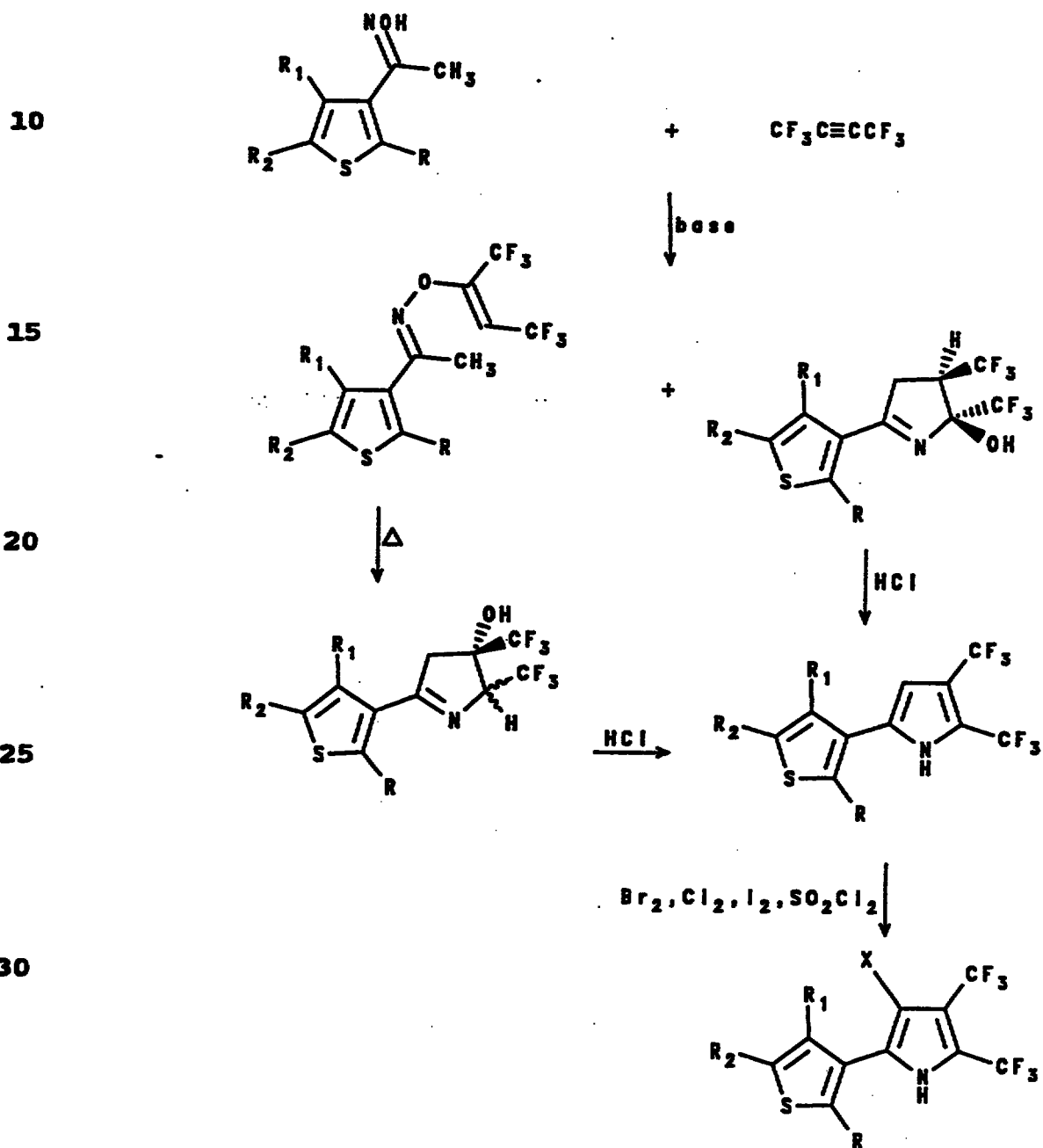
35



wherein X is Cl, Br or I and R, R₁ and R₂ are as described in Flow Diagram XI.

Similarly, 2,3-Bis(trifluoromethyl)-4-halo-5-(3-thienyl)pyrrole compounds may be prepared as shown in Flow Diagram XXXIV.

FLOW DIAGRAM XXXIV



wherein X is Cl, Br or I and R, R₁ and R₂ are as described in Flow Diagram XII.

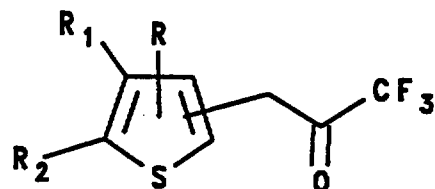
2,5-Bis(trifluoromethyl)-3-(2- and 3-thienyl)pyrrole compounds may be prepared as shown in Flow Diagram XXXV.

FLOW DIAGRAM XXXV

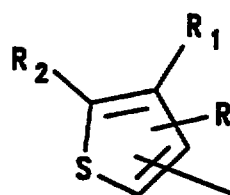
10



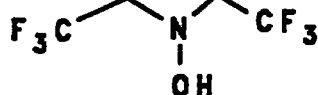
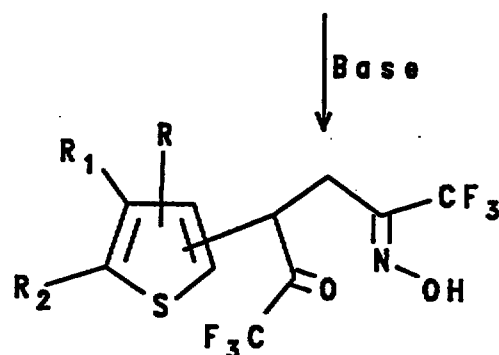
+



15



20

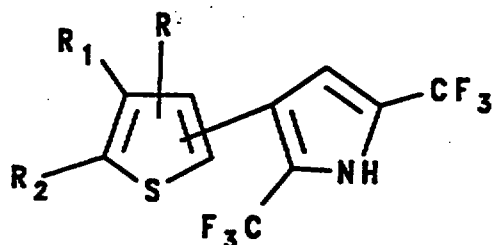


Base

25

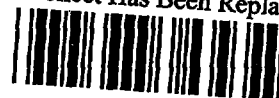
Zn/CH₃CO₂H

30



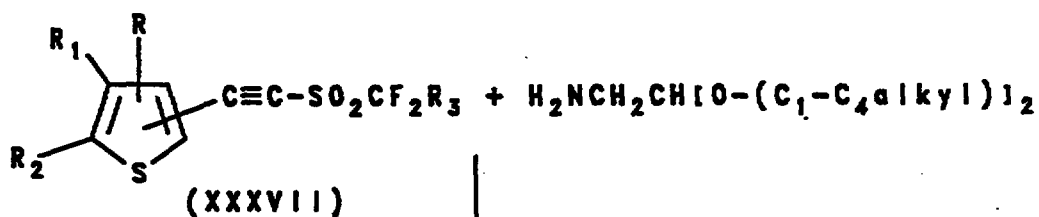
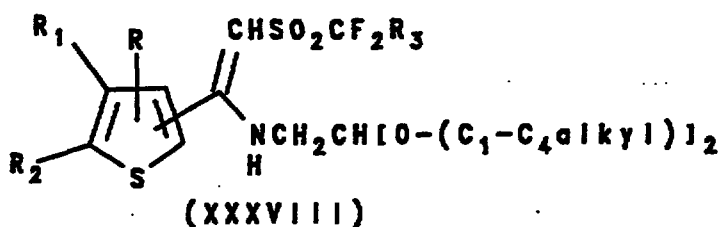
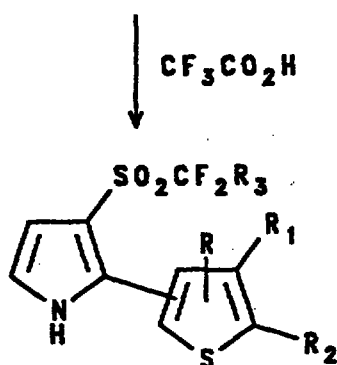
3-(Haloalkylsulfonyl)-2-(2- and 3-thienyl)-pyrrole compounds may be prepared by reacting a (2- or 3-thienyl)ethynyl haloalkylsulfonyl compound of formula

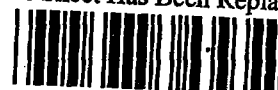
35



XXXVII with an aminoacetaldehyde di(C₁-C₄ alkyl)acetal to form a {{α-[(haloalkylsulfonyl)methylene](2- or 3-thienyl)}amino}acetaldehyde di(C₁-C₄ alkyl)acetal of formula XXXVIII. The formula XXXVIII acetal is then
5 reacted with excess trifluoroacetic acid to obtain the desired 3-(haloalkylsulfonyl)-2-(2- or 3-thienyl)-pyrrole compound. The above reaction scheme is shown in Flow Diagram XXXVI.

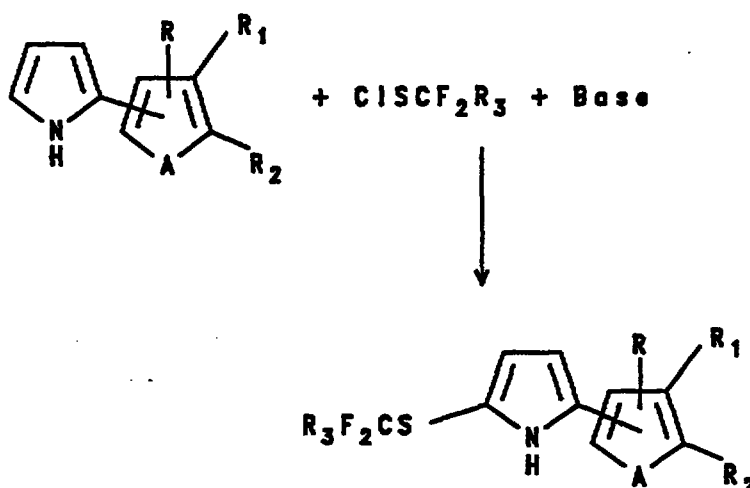
10
FLOW DIAGRAM XXXVI





5-(Haloalkylthio)-2-(2- and 3-thienyl and -furyl)pyrrole compounds may be prepared by reacting a 2-(2- or 3-thienyl or -furyl)pyrrole compound with a haloalkylsulfonyl chloride compound in the presence of a base as shown in Flow Diagram XXXVII.

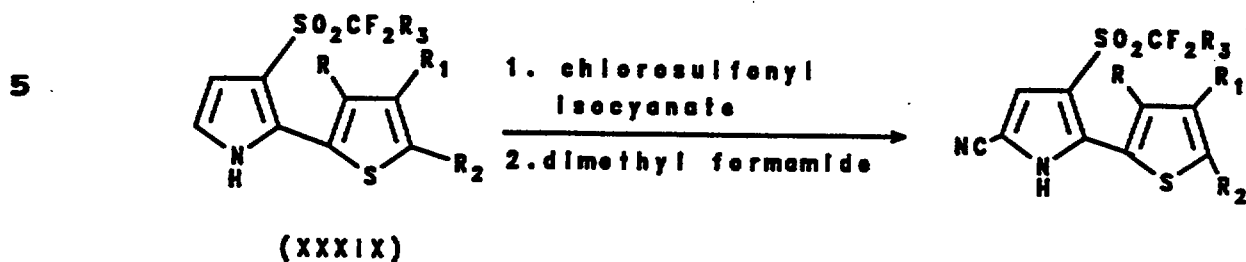
FLOW DIAGRAM XXXVII



4-(Haloalkylsulfonyl)-5-(2-thienyl)pyrrole-2-carbonitrile compounds may be prepared by reacting a 3-(haloalkylsulfonyl)-2-(2-thienyl)pyrrole compound of formula XXXIX with chlorosulfonyl isocyanate in the presence of a solvent to form a reaction mixture. The reaction mixture is then treated with dimethylformamide to obtain the desired 4-(haloalkylsulfonyl)-5-(2-thienyl)pyrrole-2-carbonitrile compound. The above reaction scheme is shown in Flow Diagram XXXVIII.



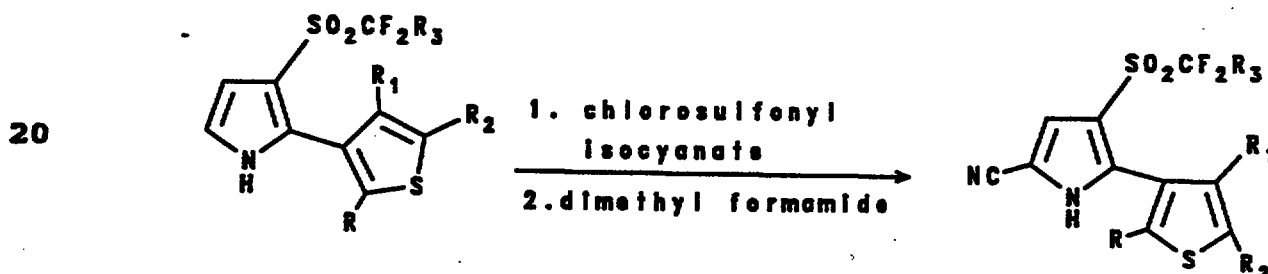
FLOW DIAGRAM XXXVIII



10 wherein R_3 is as described above for formula I and R , R_1 and R_2 are as described in Flow Diagram XI.

Similarly, 4-(haloalkylsulfonyl)-5-(3-thienyl)pyrrole-2-carbonitrile compounds may be prepared as shown in Flow Diagram XXXIX.

FLOW DIAGRAM XXXIX



25 wherein R_3 is as described above for formula I and R , R_1 and R_2 are as described in Flow Diagram XII.

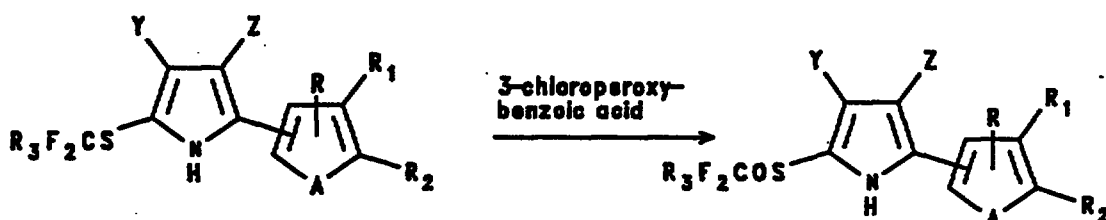
5-(Haloalkylsulfonyl)-2-(2- and 3-thienyl and -furyl)pyrrole compounds may be prepared by reacting a 5-(haloalkylthio)-2-(2- or 3-thienyl or -furyl)pyrrole compound with an oxidizing agent such as 3-chloroperoxybenzoic acid as shown in Flow Diagram XL.

30

35

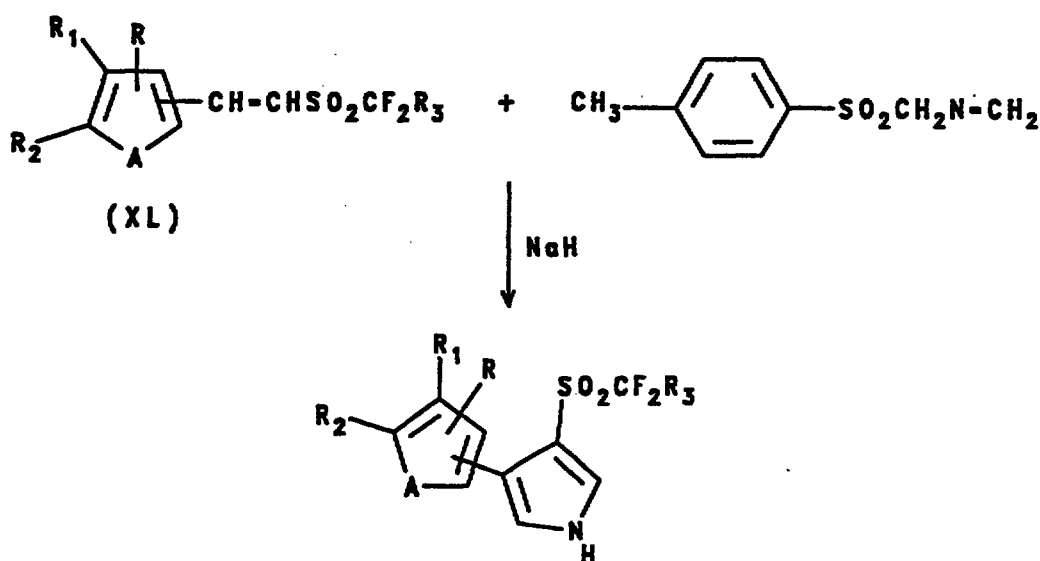


- 66 -

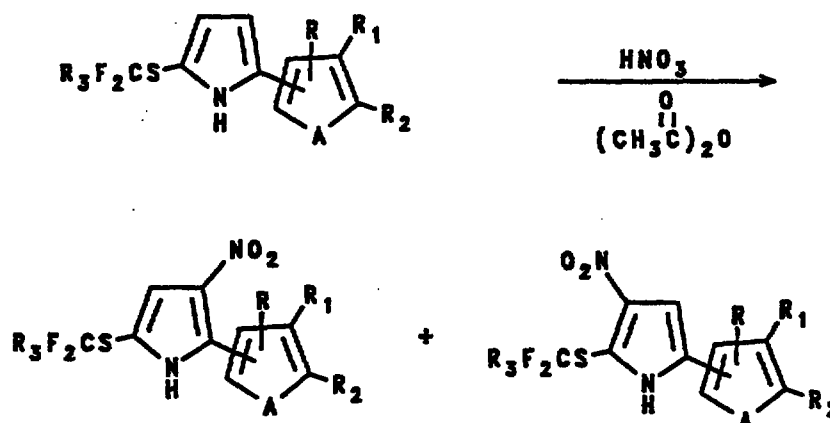
FLOW DIAGRAM XL

10 wherein A and R_3 are as described above for formula I;
 R, R_1 and R_2 are as described in Flow Diagram V and Y
 and Z are each independently hydrogen or halogen.

3-(2-And 3-thienyl and -furyl)-4-(halo-
 alkylsulfonyl)pyrrole compounds may be prepared by
 15 reacting a haloalkylsulfone of formula XL with N-methy-
 lene-1-(p-tolylsulfonyl)methylamine in the presence of
 a base such as sodium hydride as shown in Flow Diagram
 XLI.

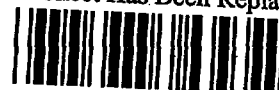
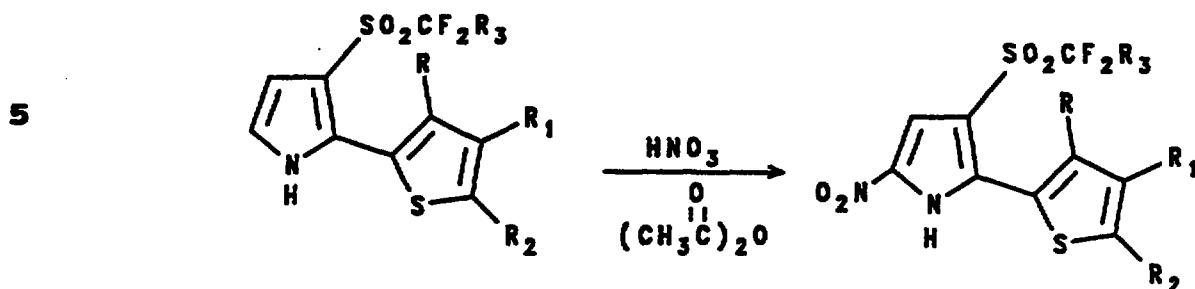
FLOW DIAGRAM XLI

2-(Thienyl and furyl)-3-nitro-5-(haloalkylthio)pyrrole compounds and 5-(thienyl and furyl)-3-nitro-2-(haloalkylthio)pyrrole compounds may be prepared by reacting a 2-(thienyl or furyl)-5-(haloalkylthio)pyrrole compound with fuming nitric acid in the presence of acetic anhydride as shown in Flow Diagram XLII.

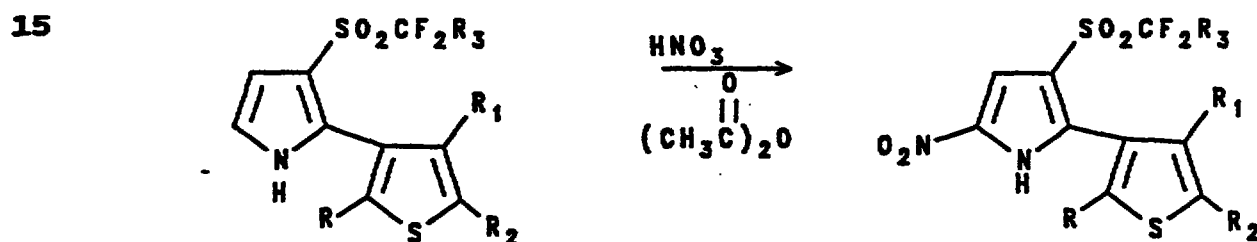
FLOW DIAGRAM XLII

wherein A and R_3 are as described above for formula I and R, R_1 and R_2 are halogen.

Similarly, 2-(2-thienyl)-5-nitro-3-(haloalkylsulfonyl)pyrrole compounds and 2-(3-thienyl)-5-nitro-3-(haloalkylsulfonyl)pyrrole compounds may be prepared as shown in Flow Diagrams XLIII and XLIV, respectively.

FLOW DIAGRAM XLIII

wherein A and R_3 are as described above for formula I and R, R_1 and R_2 are as described in Flow Diagram XI.

FLOW DIAGRAM XLIV

wherein A and R_3 are as described above for formula I and R, R_1 and R_2 are as described in Flow Diagram XII.

Methods for preparing 2-(2-thienyl)-3-(haloalkylthio)pyrrole compounds and 2-(3-thienyl)-3-(haloalkylthio)pyrrole compounds are shown in Flow Diagrams XLV and XLVI, respectively.

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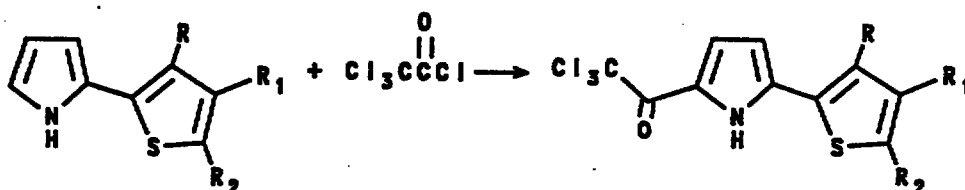
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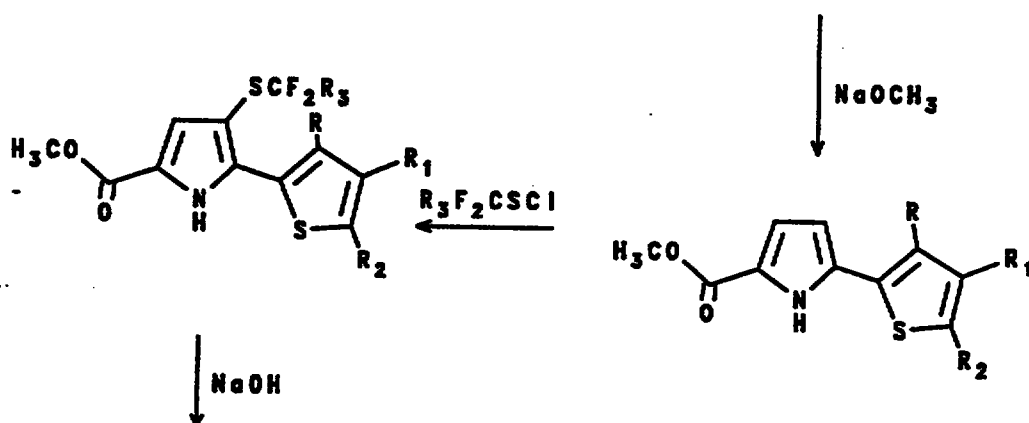
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FLOW DIAGRAM XLV

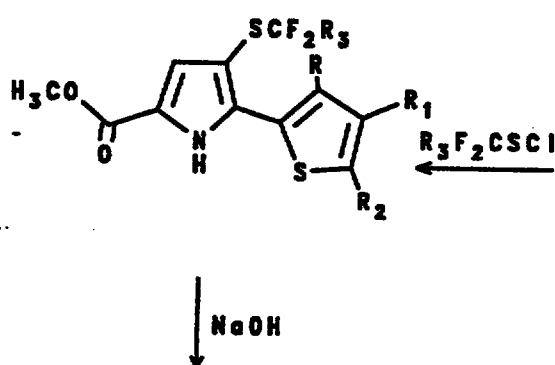
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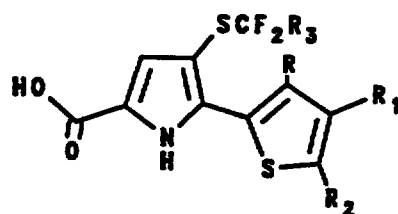
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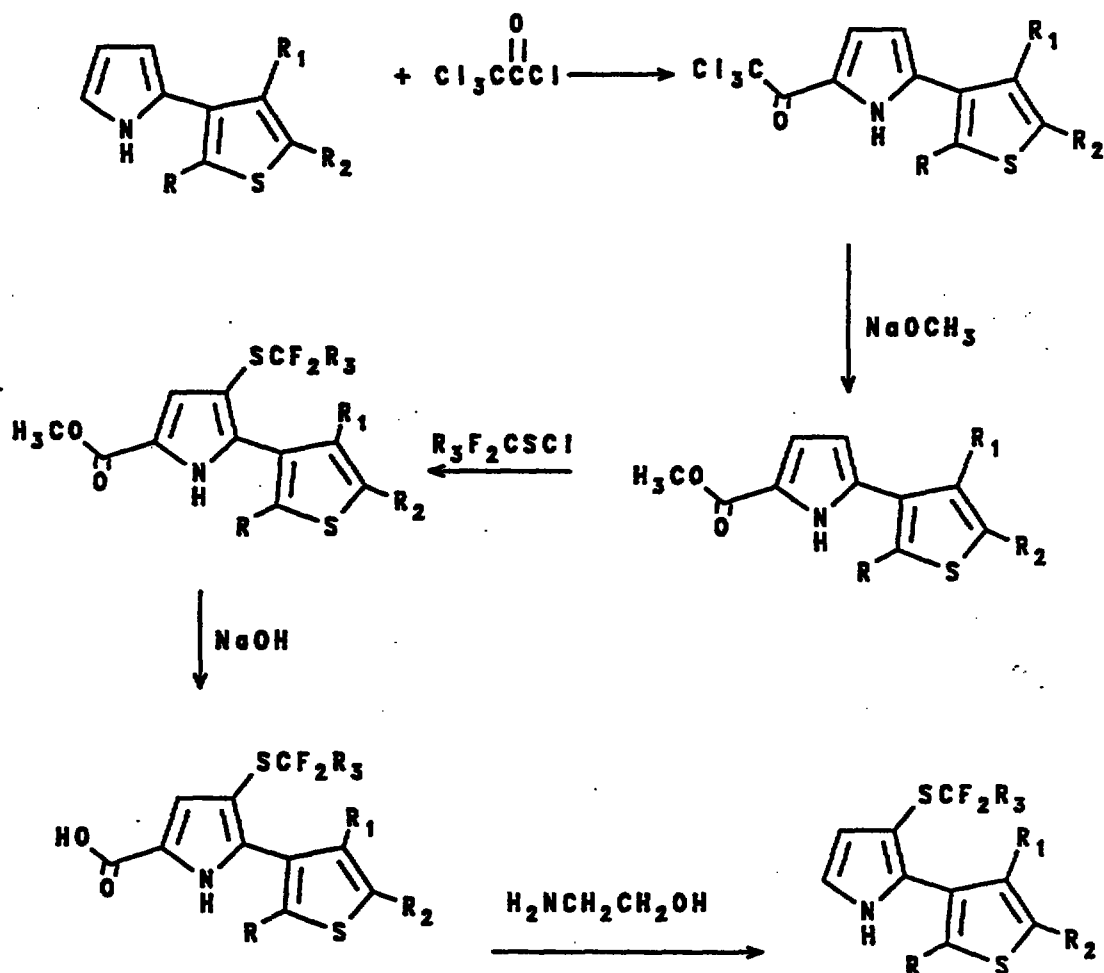


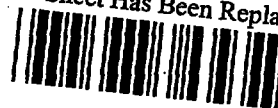
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wherein R , R_1 and R_2 are as described in Flow Diagram XI.

FLOW DIAGRAM XLVI





wherein R, R₁ and R₂ are as described in Flow Diagram XII.

3-Bromo-5-(thienyl or furyl)-2-(haloalkyl-sulfinyl and -sulfonyl-4-(haloalkylsulfonyl)pyrrole compounds may be prepared as shown in Flow Diagrams XLVII and XLVIII.

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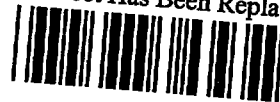
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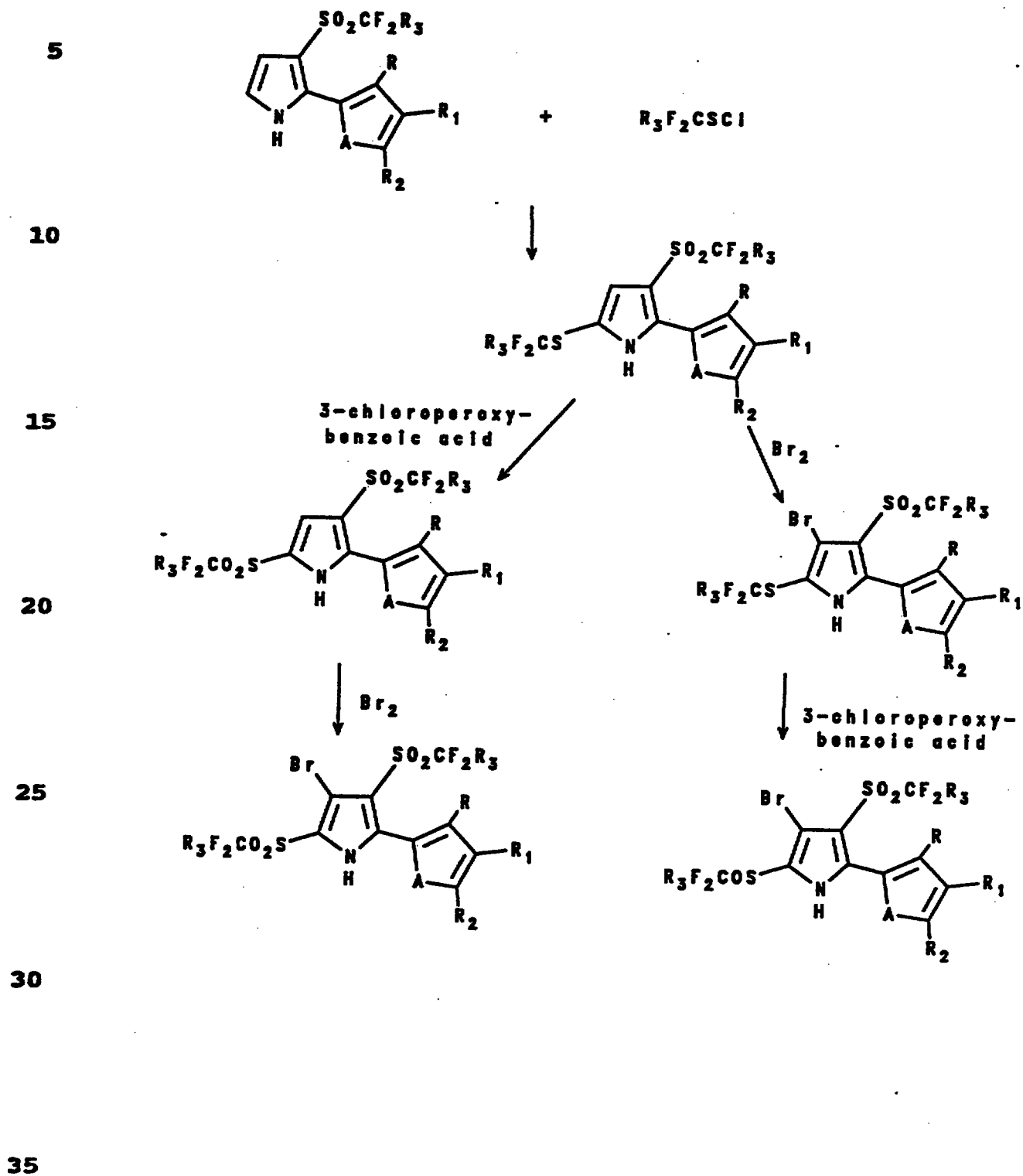
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FLOW DIAGRAM XLVII





wherein A and R₃ are as described above for formula I and R, R₁ and R₂ are as described in Flow Diagram XI.

FLOW DIAGRAM XLVIII

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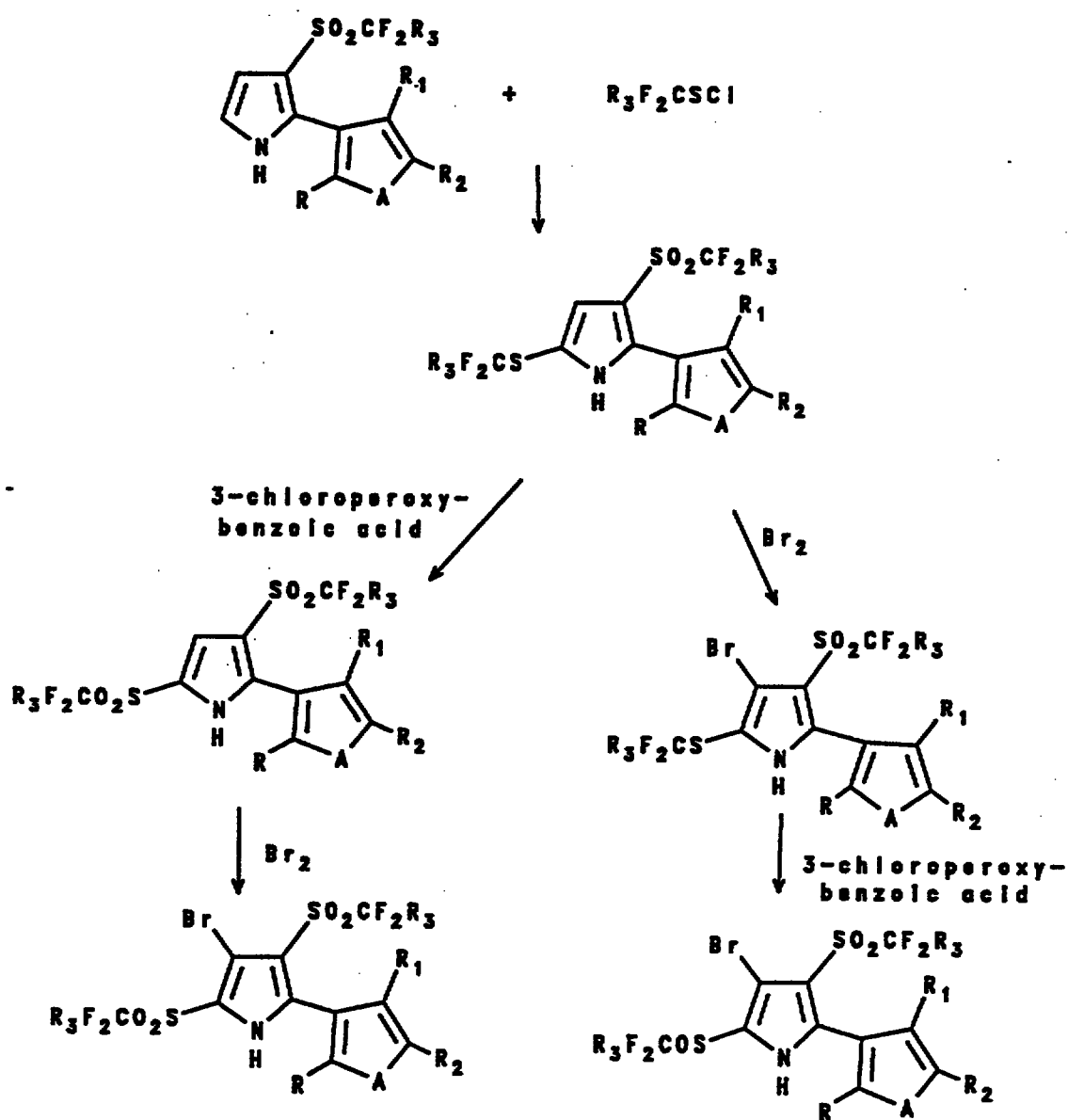
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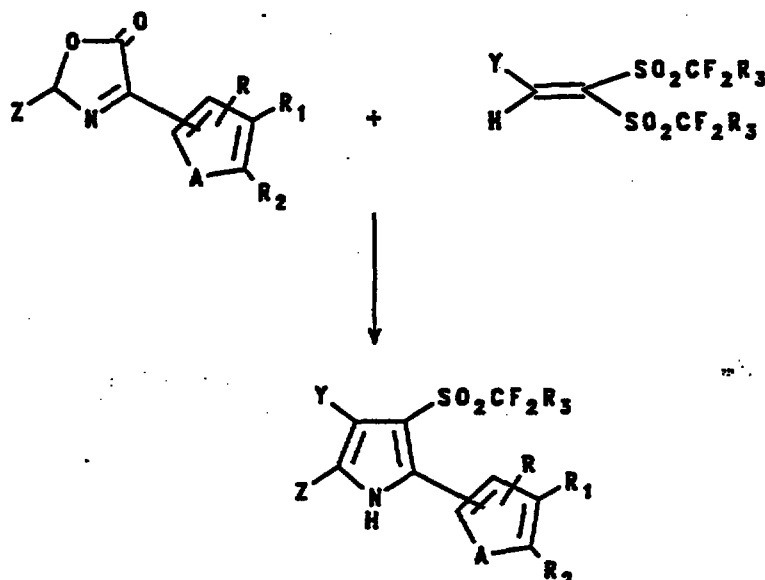


- 74 -

wherein A and R₃ are as described above for formula I and R, R₁ and R₂ are as described in Flow Diagram XII.

2-(Thienyl and furyl)-4-aryl-5-haloalkyl-3-(haloalkylsulfonyl)pyrrole compounds may be prepared as shown in Flow Diagram XLIX.

FLOW DIAGRAM XLIX

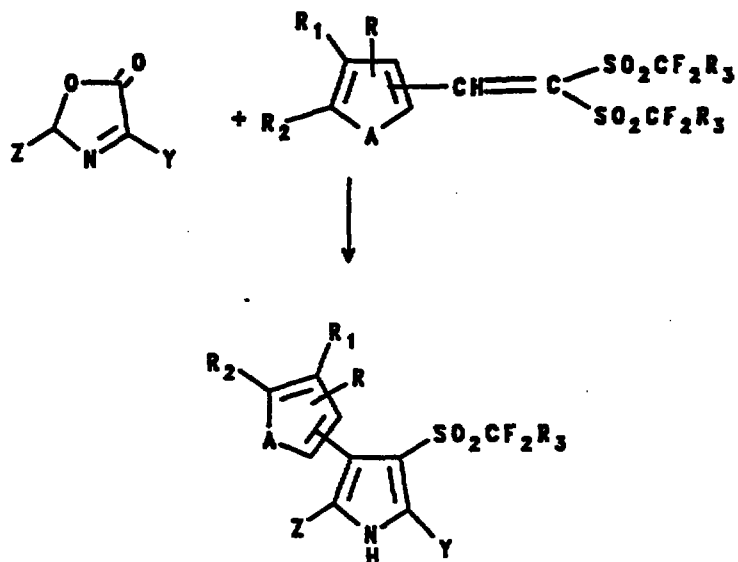


wherein A, R, R₁, R₂, Y and Z are as described in Flow Diagram XXI and R₃ is as described above for formula I.

Similarly, 2-aryl-4-(thienyl and furyl)-5-haloalkyl-3-(haloalkylsulfonyl)pyrrole compounds may be prepared as shown in Flow Diagram L.



- 75 -

FLOW DIAGRAM L

wherein A, R, R₁, R₂, Y and Z are as described in Flow Diagram XXI and R₃ is as described above for formula I.

2-(Thienyl and furyl)-5-(haloalkylsulfonyl)-pyrrole-3-carbonitrile compounds may be prepared as shown in Flow Diagram LI.

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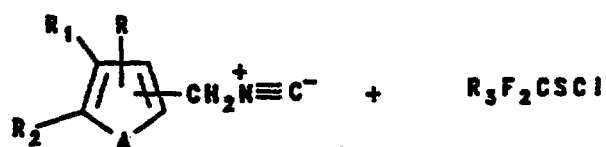
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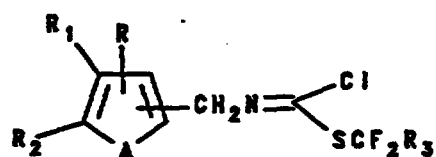
- 76 -

FLOW DIAGRAM L1

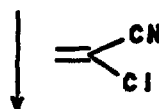
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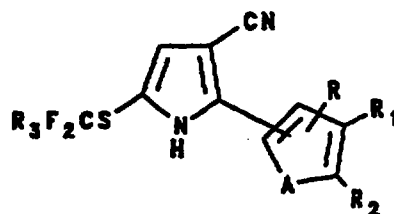
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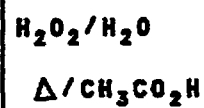
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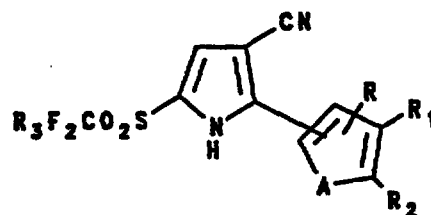
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Conversion of formula I compounds wherein Y and/or Z are hydrogen to the corresponding formula I compounds wherein Y and/or Z are halogen is readily achieved by reaction of the formula I hydrogen substituted pyrrole with at least about 1 or 2 equivalents of a halogenating agent such as a sulfuryl halide, bromine or chlorine in the presence of a solvent such as dioxane, tetrahydrofuran, acetic acid or a chlorinated hydrocarbon solvent. In addition, formula I compounds wherein R, R₁ and/or R₂ are hydrogen may be converted to the corresponding formula I compounds wherein R, R₁ and/or R₂ are halogen by reaction of the formula I compound wherein R, R₁ and/or R₂ are hydrogen with a halogenating agent in the presence of a solvent. Halogenating agents that may be employed include bromine, sulfuryl chloride, sulfuryl bromide, sodium hypochlorite, t-butylhypochlorite, N-bromosuccinimide, N-iodosuccinimide and the like. Several halogenation reaction schemes are shown in Flow Diagram LII.



FLOW DIAGRAM LII

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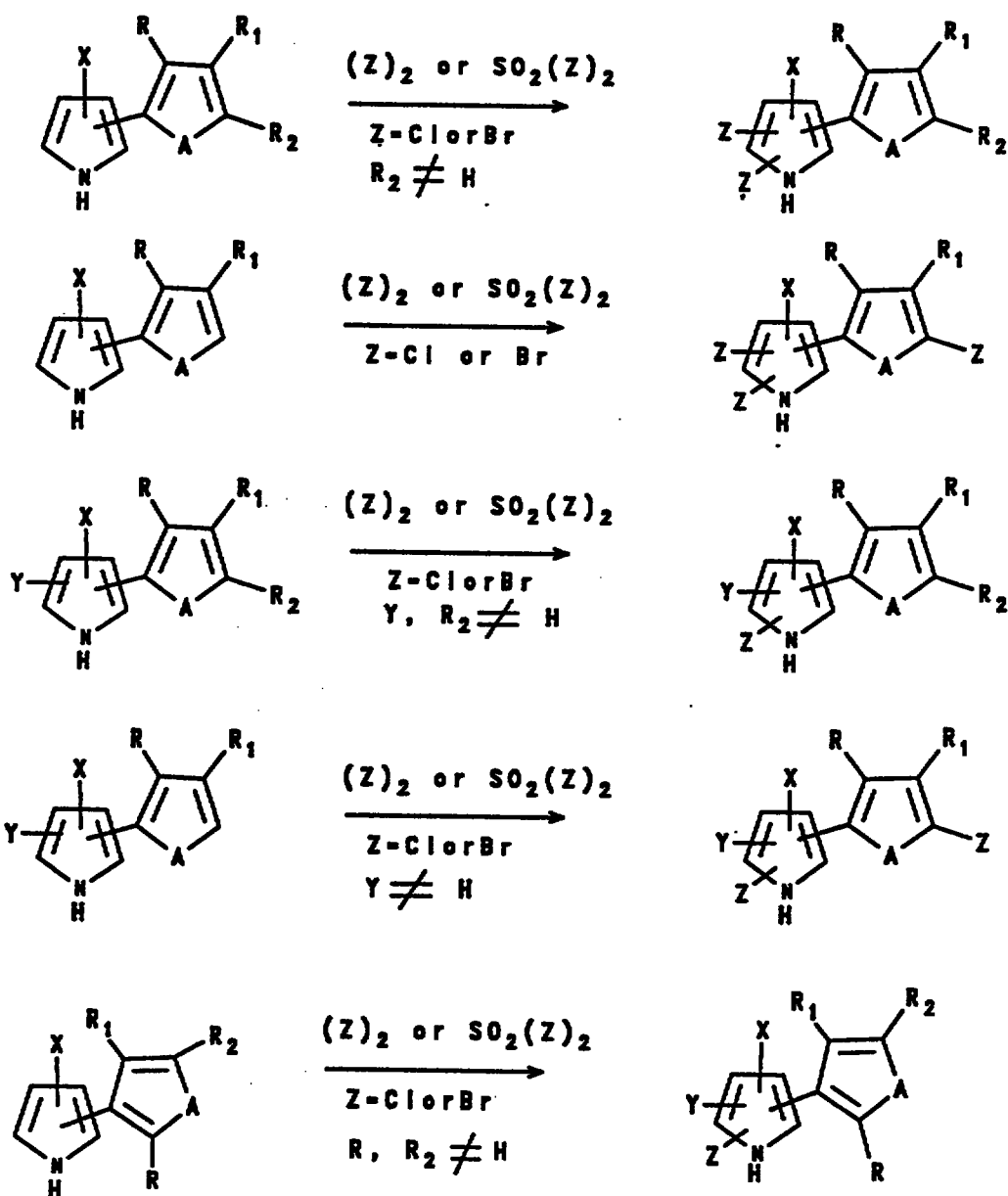
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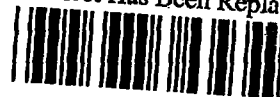
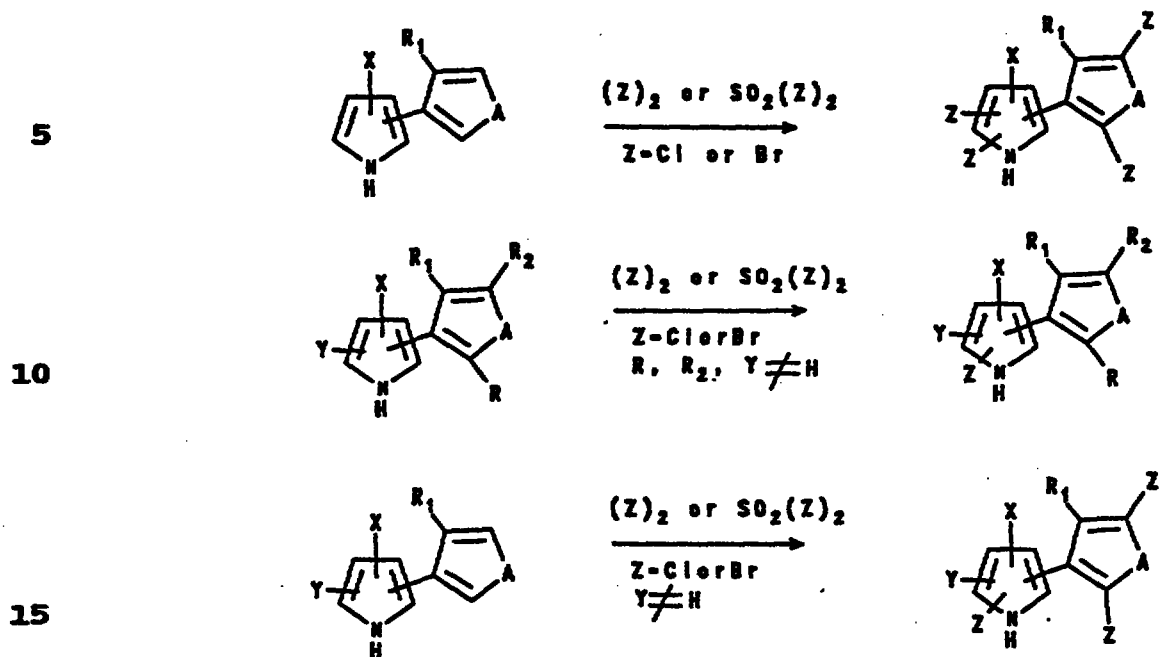
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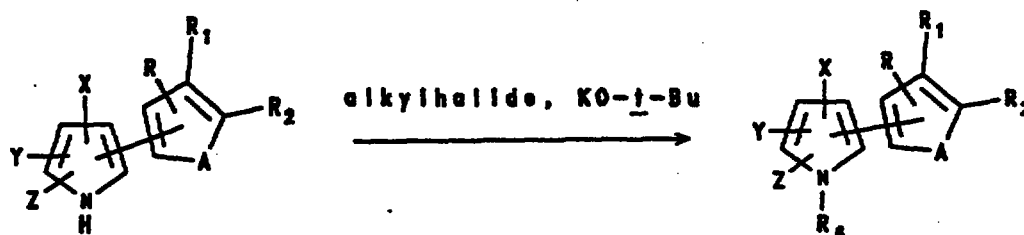


FLOW DIAGRAM LII (cont.)

Preparation of 1-substituted formula I compounds can be achieved by reaction of the appropriately substituted formula I compound having B as hydrogen with an alkylating or acylating agent in the presence of an alkali metal alkoxide or hydride. For example, a formula I compound wherein B is hydrogen and R, R₁, R₂, A, X, Y and Z are as described for formula I above, is reacted with an appropriate alkylating agent such as a C₁-C₆ alkylhalide in which the alkyl group is straight or branched and is optionally substituted with from one to three halogen atoms, one hydroxy, one cyano, one C₁-C₄ alkoxy, one C₁-C₄ alkylthio, one phenyl group optionally substituted with from one to three halogen atoms, or one benzyloxy group optionally substituted with from one to three halogen atoms, and an alkali metal alkoxide such as sodium or potassium t-butoxide. This reaction provides a thienyl- or furylpyrrole having the same substituents as the starting material, but in addition is substituted on



the nitrogen with a C_1-C_6 alkyl group optionally substituted as described above. This reaction scheme may be illustrated as follows:

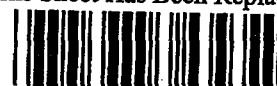


wherein R , R_1 , R_2 , A , X , Y and Z are as described for formula I above and R_6 is C_1-C_6 alkyl optionally substituted as described above. In a similar reaction cyanogen bromide is substituted for the alkylhalide and yields a formula I thienyl- or furylpyrrole having a carbonitrile, rather than an alkyl group on the 1-position.

Advantageously, the above-described alkylation procedure may also be applied to the preparation of formula I thienyl- and furylpyrroles having an $N-C_3-C_6$ alkenyl or $N-C_3-C_6$ alkynyl substituent. This substitution is obtained by simply substituting a C_3-C_6 alkenyl hal-

ide or C_3-C_6 alkynyl halide for the C_1-C_6 alkyl halide in the above-described reaction.

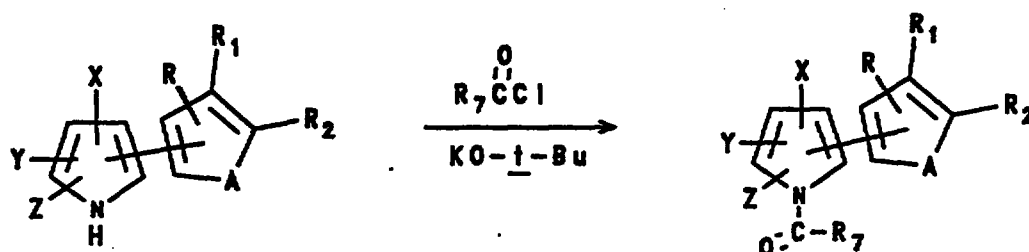
In a similar manner, preparation of 1-acylated thienyl- and furylpyrroles may be achieved by the reaction of an appropriately substituted formula I thienyl- or furylpyrrole wherein B is hydrogen with an acylating agent in the presence of an alkali metal alkoxide. Acylating agents such as C_1-C_6 alkyl or C_2-C_6 alkenyl acid chlorides, substituted C_1-C_6 alkyl or C_2-C_6 alkenyl acid chlorides, benzoyl chloride, substituted benzoyl chlorides, phenylchloroformate, substituted phenylchloroformates, C_1-C_6 alkyl or C_2-C_6 alk-



enylchloroformates, substituted C_1 - C_6 alkyl or C_2 - C_6 alkenylchloroformates, N-substituted carbamoyl chlorides and the like may be employed. the reaction may be illustrated as follows:

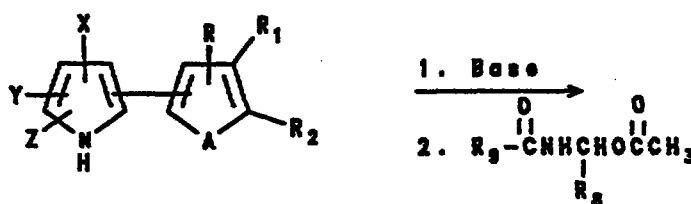
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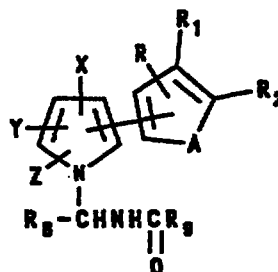


Formula I thienyl- and furylpyrroles wherein R_6 is CH_2SQ may be prepared by reaction of the appropriately substituted formula I thienyl- or furylpyrrole having R_6 as chloromethyl with an alkali metal salt of an SQ compound in the presence of a base. And formula I thienyl- and furylpyrrole compounds wherein R_6 is $CHR_8NHC(O)R_9$ may be prepared as shown below.

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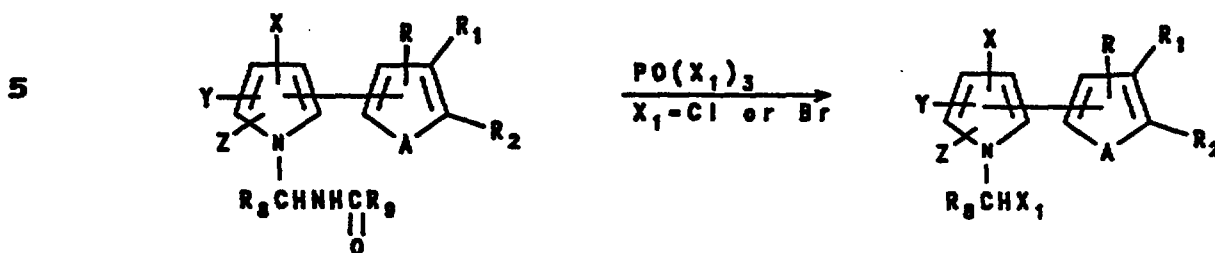
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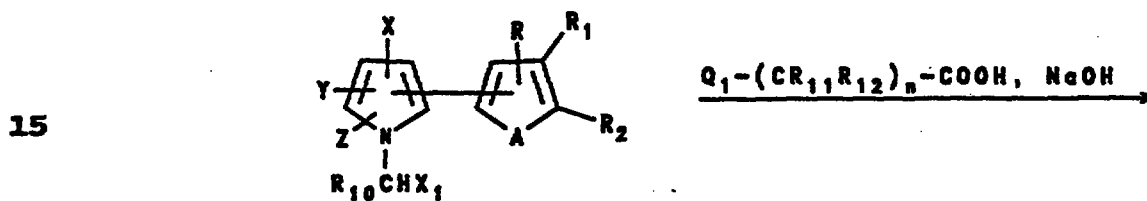
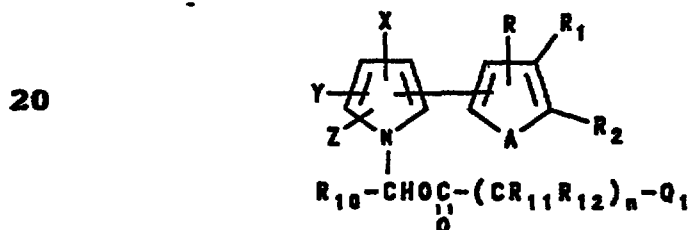
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Advantageously, 1-halomethyl thienyl- and furylpyrroles may be prepared as shown below.



10 Formula I compounds wherein R_6 is $R_{10}\text{CHOC(O)}-(\text{CR}_{11}\text{R}_{12})_n\text{Q}_1$ may be prepared as shown below.



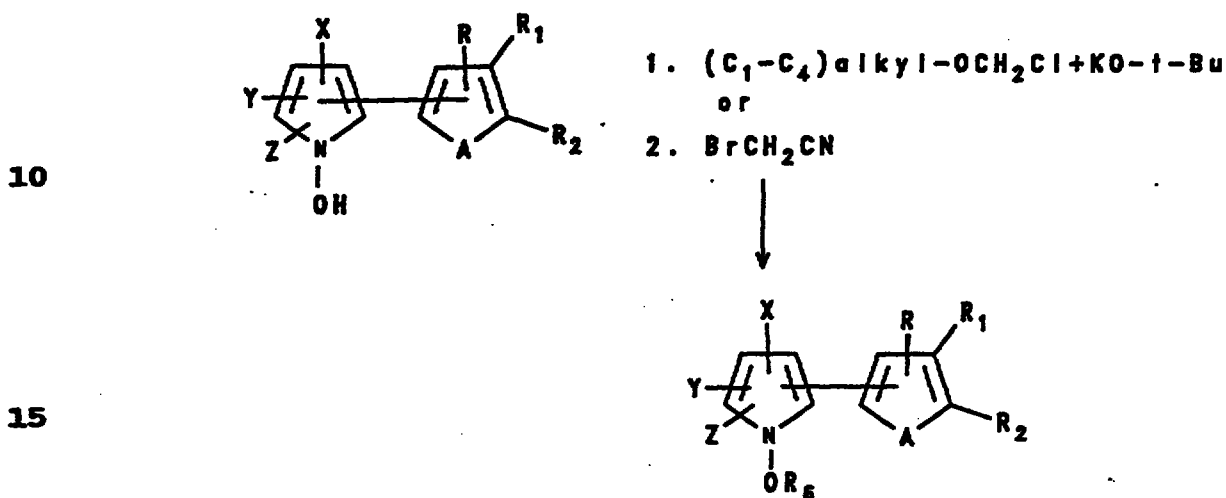
25 Formula I compounds wherein B is OR_6 may be prepared by reacting an appropriately substituted formula I thienyl- or furylpyrrole compound, wherein B is OH, and R, R_1 , R_2 , A, X, Y and Z are as described for formula I above, with an appropriate alkylating agent and a suitable base, for example, a chloromethyl $\text{C}_1\text{-C}_4$ alkyl ether and potassium t-butoxide. This reaction provides a thienyl- or furylpyrrole having the same substituents as the starting material, but in addition is substituted on the oxygen with $\text{C}_1\text{-C}_4$

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alkoxymethyl. In a similar reaction bromoacetonitrile is substituted for the chloromethyl C_1 - C_4 alkyl ether and gives a formula I thienyl- or furylpyrrole with an acetonitrile substituent on the oxygen. The reactions may be illustrated as follows:



wherein R , R_1 , R_2 , A , X , Y and Z are as described for formula I above and R_6 is (1) C_1 - C_4 alkoxymethyl or (2) CH_2CN .

Similarly, formula I compounds wherein B is C(O)R_7 may be prepared by reacting an appropriately substituted formula I thienyl- or furylpyrrole compound, wherein B is OH , and R , R_1 , R_2 , A , X , Y and Z are as described for formula I above, with an appropriate acylating agent and a suitable base, for example, a C_1 - C_6 acid chloride and potassium *t*-butoxide. This reaction provides a thienyl- or furylpyrrole compound having the same substituents as the starting material, but in addition is substituted on the oxygen with C_1 - C_6 alkanoyl. The reaction may be illustrated as follows:



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5 The thienyl- and furylpyrrole compounds of this invention are also effective for controlling insects and acarina, when applied to the foliage of plants and/or to the soil or water in which said plants are growing in sufficient amount to provide a rate of from about 0.1 kg/ha to 4.0 kg/ha of active ingredient.

10 While the compounds of this invention are effective for controlling insects and acarina when employed alone, they may also be used in combination with other biological chemicals, including other insecticides and acaricides. For example, the formula I compounds of this invention may be used effectively in conjunction or combination with pyrethroids, phosphates, carbamates, cyclodienes, endotoxin of bacillus thuringiensis (Bt), formamidines, phenol tin compounds, chlorinated hydrocarbons, benzoylphenyl ureas and the like.

20 The compounds of this invention may be formulated as emulsifiable concentrates, flowable concentrates or wettable powders with are diluted with water or other suitable polar solvent, generally in situ, and then applied as a dilute spray. Said compounds may also be formulated in dry compacted granules, granular formulations, dusts, dust concentrates, suspension concentrates, microemulsions and the like all of which

25 lend themselves to seed, soil, water and/or foilage applications to provide the requisite plant protection. Such formulations include the compounds of the invention admixed with inert, solid or liquid diluents.

30 For example , wettable powders, dusts and dust concentrate formulations can be prepared by grinding and blending together about 25% to about 85% by weight of a formula I compound and about 73% to about 13% by weight of a solid diluent such as bentonite, diatomaceous earth, kaolin, attapulgite, or the

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like, about 1% to 5% by weight of a dispersing agent such as sodium lignosulfonate and about 1% to 5% by weight of a nonionic surfactant, such as octylphenoxy polyethoxy ethanol, nonylphenoxy polyethoxy ethanol or the like.

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A typical emulsifiable concentrate can be prepared by dissolving about 15% to about 70% by weight of a formula I compound in about 84% to about 29% by weight of a solvent such as isophorone, toluene, butyl cellosolve, methyl acetate, propylene glycol monomethyl ether or the like and dispersing therein about 1% to 5% by weight of a nonionic surfactant such as an alkylphenoxy polyethoxy alcohol.

10

In order to facilitate a further understanding of the invention, the following examples are presented primarily for the purpose of illustrating more specific details thereof. The examples generally utilize the above reaction schemes and also provide further means for preparing even more compounds of the present invention which are not specifically described above. The invention should not be deemed limited by the examples as the full scope of the invention is defined in the claims.

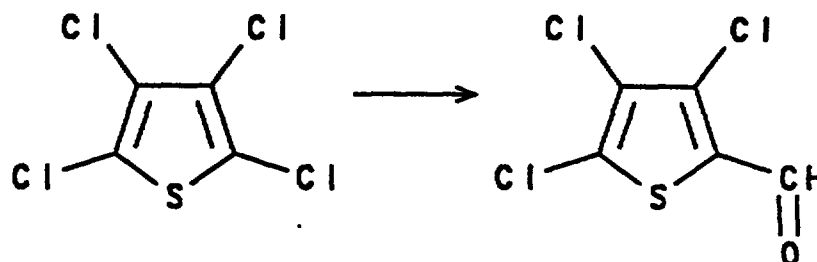
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**EXAMPLE 1****Preparation of 3,4,5-Trichloro-2-thiophenecarboxaldehyde**

Butyllithium (2.5 molar in tetrahydrofuran, 3.96 mL, 9.9 mmol) is added to a solution of tetrachlorothiophene (2.00 g, 9.01 mmol) in tetrahydrofuran at 0°C. The reaction mixture is stirred at 0°C for 30 minutes, warmed to room temperature over 45 minutes, treated with N,N-dimethylformamide (0.79 g, 10.8 mmol), stirred for three hours, poured into one molar hydrochloric acid at 4°C and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over MgSO₄ and concentrated in vacuo to obtain a brown solid. Flash chromatography of the solid using silica gel and a 5% ethyl acetate in hexane solution gives a beige solid which is recrystallized from ethyl acetate and hexane to obtain the title product as beige needles (1.63 g, 84%, mp 81°-82°C).

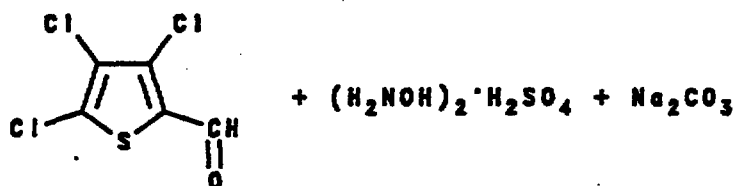
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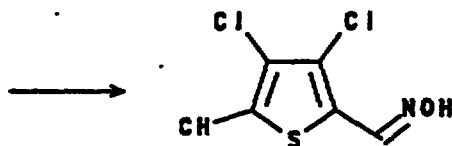
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EXAMPLE 2**Preparation of the Oxime of 3,4,5-trichloro-2-thiophenecarboxaldehyde**

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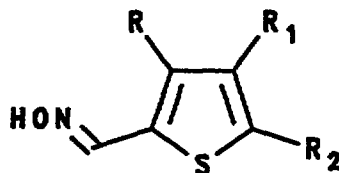
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A solution of sodium carbonate (10.91 g, 99.2 mmol) in water is added to a slurry of 3,4,5-trichloro-2-thiophenecarboxaldehyde (10.69 g, 49.6 mmol) and hydroxylamine sulfate (8.14 g, 49.6 mmol) in water. After stirring at room temperature for 18 hours, the solids are filtered out of the reaction mixture and dried under high vacuum overnight to give the title product as a white solid (10.24 g, 92%).

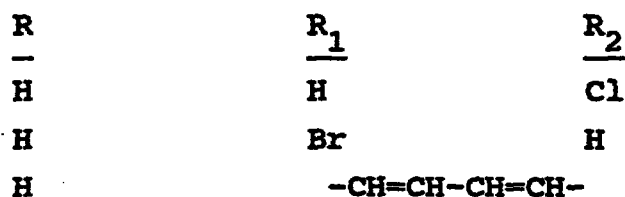
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Using essentially the same procedure, and employing the appropriately substituted thiophene-carboxaldehyde, the following compounds are obtained.

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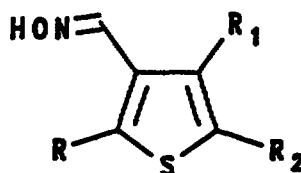
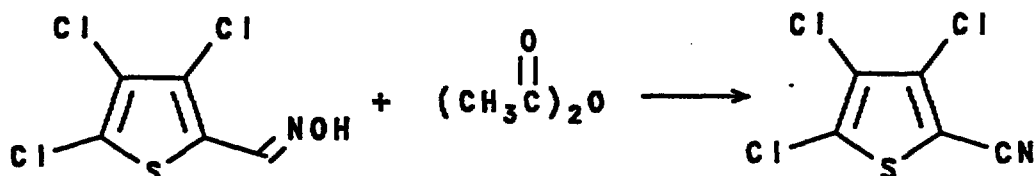
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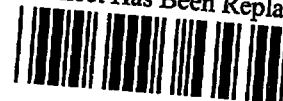


- 89 -

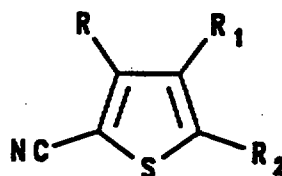
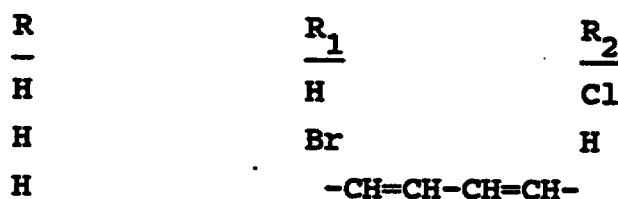
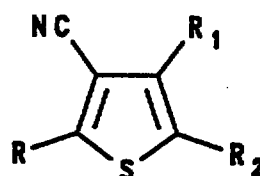
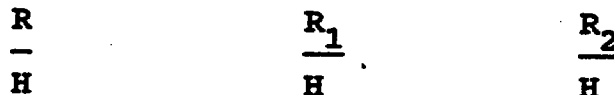
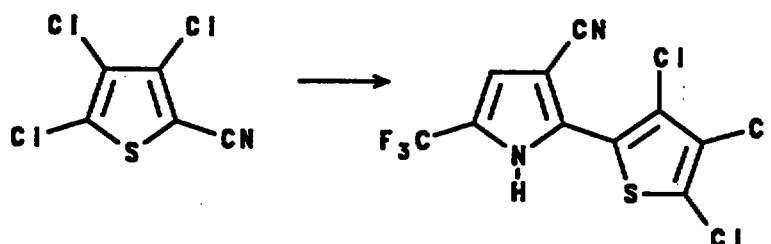

$$\begin{array}{c} R \\ - \\ H \end{array}$$
$$\begin{array}{c} R_1 \\ - \\ H \end{array}$$
$$\begin{array}{c} R_2 \\ - \\ H \end{array}$$
EXAMPLE 3**Preparation of 3,4,5-Trichloro-2-thiophenecarbonitrile**

A solution of the oxime of 3,4,5-trichloro-2-thiophenecarboxaldehyde (10.075 g, 43.7 mmol) in acetic anhydride is refluxed for two hours and concentrated in vacuo to obtain a brown oil. The oil is diluted with ether and the organic solution is washed sequentially with water and brine, dried over MgSO_4 and concentrated in vacuo to give a brown oil. Flash chromatography of the oil using silica gel and a 5% ethyl acetate in hexane solution gives a beige solid which is recrystallized from ethyl acetate and hexane to obtain the title product as beige needles (8.23 g, 89%, mp $63^\circ\text{--}64^\circ\text{C}$).

Using essentially the same procedure, and employing the appropriately substituted oxime, the following compounds are obtained:



- 90 -

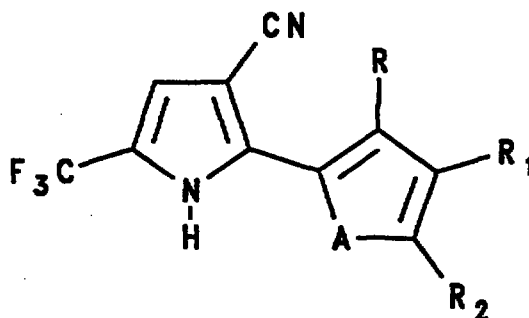
**EXAMPLE 4****Preparation of 2-(3,4,5-Trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile**

Acetonitrile (0.97 g, 23.7 mmol) is added dropwise to a solution of lithium diisopropylamide (two molar in hydrocarbons, 10.9 mL, 21.8 mmol) in tetrahydrofuran at -78°C . The reaction mixture is stirred at -78°C for 30 minutes, treated with a solution of 3,4,5-trichloro-2-thiophenecarbonitrile (3.87 g, 18.2 mmol) in tetrahydrofuran, stirred for 30 minutes at -78°C , warmed to room temperature over 45 minutes,

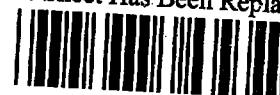
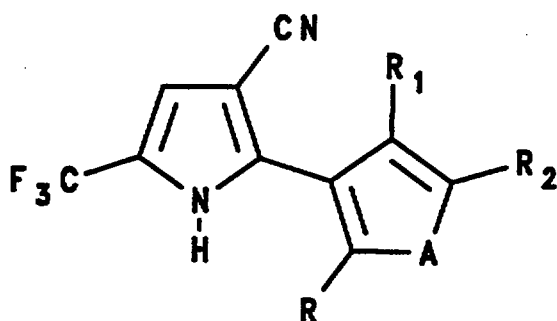


quenched with saturated ammonium chloride solution and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over MgSO_4 and concentrated in vacuo to obtain a red solid. A mixture of the red solid and 1-bromo-3,3,3-trifluoroacetone (1.95 mL, 18.7 mmol) in acetic acid is refluxed for three hours and 30 minutes, diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over MgSO_4 and concentrated in vacuo to obtain a red solid. Flash chromatography of the solid using silica gel and a 15% ethyl acetate in hexane solution gives the title product as a white solid (0.49 g, 7.8%, mp $220^\circ\text{--}221^\circ\text{C}$).

Using essentially the same procedure, and employing the appropriately substituted cyanofuran or cyanothiophene, the following compounds are obtained:



A	R	R ₁	R ₂	mp ^o C
S	H	H	H	210
S	H	H	Br	230 - 231
S	H	H	Cl	232 - 233
S	H	Br	H	>230
O	H	H	H	196 - 197
S	H	-CH=CH-CH=CH-		>230
S	Cl	-CH=CH-CH=CH-		193 - 195



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$\frac{A}{S}$

$\frac{R}{H}$

$\frac{R_1}{H}$

$\frac{R_2}{H}$

$\frac{mp^{\circ}C}{229 - 231}$

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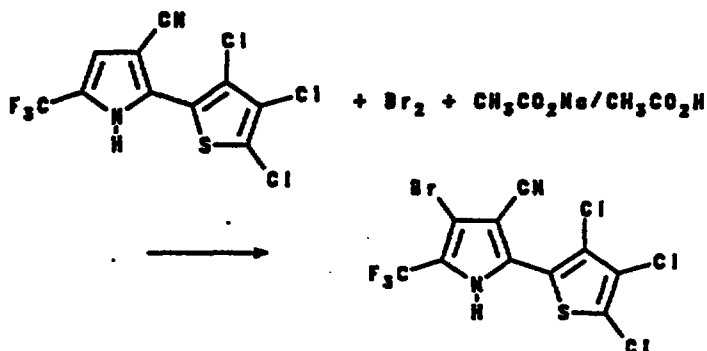
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**EXAMPLE 5****Preparation of 4-Bromo-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile**

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Bromine (0.208 g, 1.31 mmol) is added to a solution of 2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (0.38 g, 1.09 mmol) and sodium acetate (0.11 g, 1.31 mmol) in acetic acid at 50°C. After stirring at 50°C for 30 minutes, additional sodium acetate (0.11 g, 1.31 mmol) and bromine (0.208 g, 1.31 mmol) are added to the reaction mixture. The reaction mixture is stirred for 15 minutes, cooled to room temperature and poured into a 1% sodium bisulfite solution. The solids are filtered out of the aqueous mixture and dried overnight under high vacuum to give a white solid. The solid is recrystallized from ethyl acetate and hexane to obtain the title product as white crystals (0.45 g, 96%, mp 221°C-224°C).

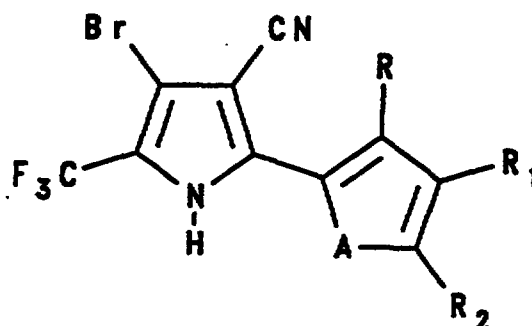
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Using essentially the same procedure, and employing the appropriately substituted 2-(thienyl or furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile, the following compounds are obtained:

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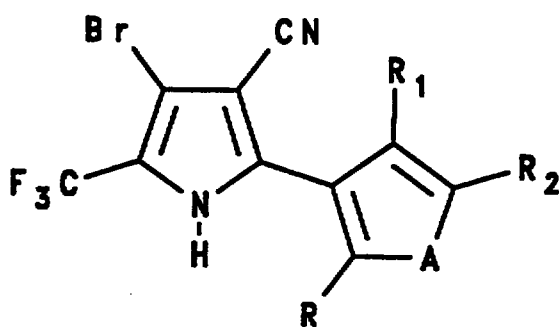
10	A	R	<u>R₁</u>	<u>R₂</u>	<u>mp°C</u>
	S	H	H	Br	254 (dec.)
	S	H	H	Cl	>230
	S	H	Br	Br	>230
	O	H	H	Br	>230
15	S	Br	-CH=CH-CH=CH-		201 - 203
	S	Cl	-CH=CH-CH=CH-		205 - 206

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$\frac{A}{S}$

$\frac{R}{Br}$

$\frac{R_1}{H}$

$\frac{R_2}{H}$

$\frac{mp^{\circ}C}{183 - 185}$

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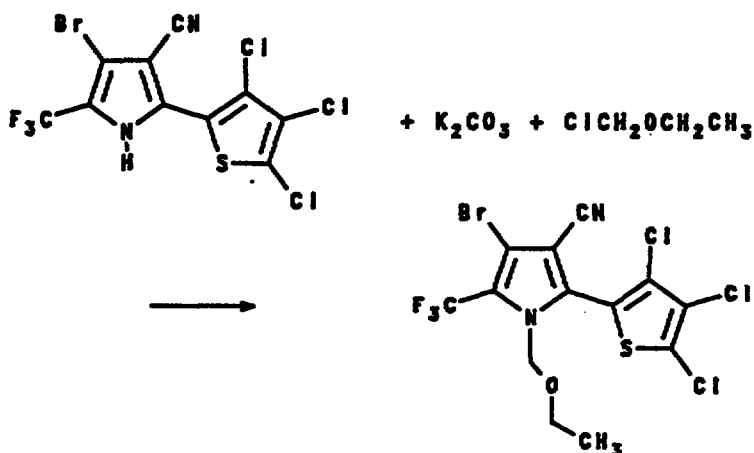
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**EXAMPLE 6****Preparation of 4-Bromo-1-(ethoxymethyl)-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile**

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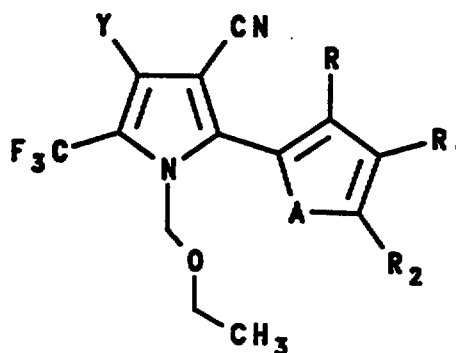
Chloromethyl ethyl ether (0.20 g, 2.13 mmol) is added to a mixture of 4-bromo-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (0.30 g, 0.71 mmol) and potassium carbonate (0.29 g, 2.13 mmol) in N,N-dimethylformamide. The reaction mixture is stirred at room temperature for 30 minutes, diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over $MgSO_4$ and concentrated in vacuo to obtain a clear oil. Flash chromatography of the oil using silica gel and a 15% ethyl acetate in hexane solution gives the title product as white crystals (0.24 g, 71%, mp $85^{\circ}-87^{\circ}C$).

Using essentially the same procedure, and employing the appropriately substituted 4-halo-2-(thienyl or furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile, the following compounds are obtained:

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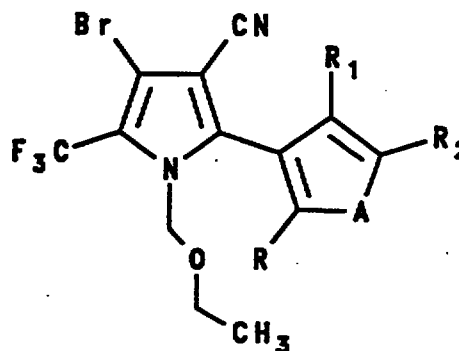
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<u>Y</u>	<u>A</u>	<u>R</u>	<u>R₁</u>	<u>R₂</u>	<u>mp °C</u>
Cl	S	H	H	H	82 - 83
Br	S	H	H	Br	81 - 83
Br	S	H	H	Cl	81 - 83
Br	O	H	H	Br	80 - 81
Br	S	Br	-CH=CH-CH=CH-		111 - 113
Br	S	Cl	-CH=CH-CH=CH-		113 - 115

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<u>A</u>	<u>R</u>	<u>R₁</u>	<u>R₂</u>	<u>mp °C</u>
S	Br	H	H	109 - 110

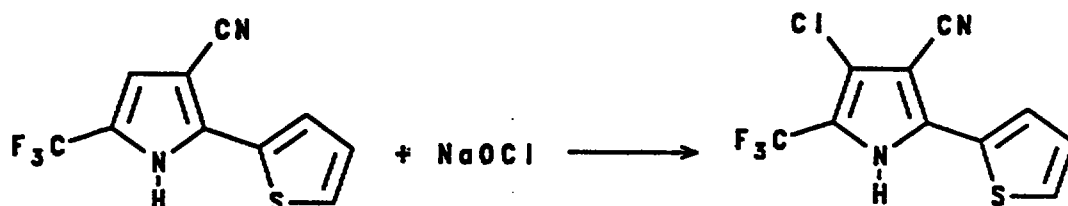
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**EXAMPLE 7****Preparation of 4-Chloro-2-(2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile**

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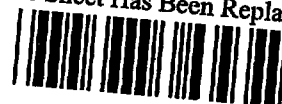
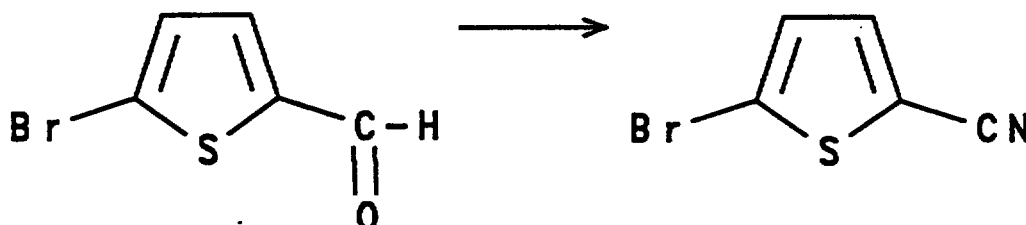
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Sodium hypochlorite (12 mL of a 5.25% solution, 17 mmol) is added dropwise to a solution of 2-(2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (2.00 g, 8.26 mmol) in tetrahydrofuran. The reaction mixture is stirred for 2 hours and 15 minutes, quenched with a 1% sodium bisulfite solution and diluted with ether. The layers are separated and the organic layer is washed sequentially with water and brine, dried over MgSO₄ and concentrated in vacuo to obtain a yellow solid. Flash chromatography of the solid using silica gel and a 15% ethyl acetate in hexane solution gives a solid which is recrystallized from ethyl acetate and hexane to obtain the title product as a yellow solid (0.35 g, 15%, mp 221°-223°C).

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**EXAMPLE 8****Preparation of 5-Bromo-2-thiophenecarbonitrile**

10 Hydroxylamine-O-sulfonic acid (17.58 g, 157 mmol) is added to a solution of 5-bromo-2-thiophenecarboxaldehyde (15.0 g, 78.5 mmol) in water and acetonitrile. The reaction mixture is stirred for 17 hours, poured into water and extracted with ether and ethyl acetate. The combined organic extracts are washed

15 sequentially with water and brine, dried over MgSO_4 and concentrated in vacuo to give a brown, oily solid. A solution of the oily solid in acetic anhydride is refluxed for five hours, concentrated in vacuo, poured into water and extracted with ether. The combined

20 organic extracts are washed sequentially with water, half-saturated sodium hydrogen carbonate solution and brine, dried over MgSO_4 and concentrated in vacuo to obtain a brown oil. Flash chromatography of the oil using silica gel and a 15% ethyl acetate in hexane

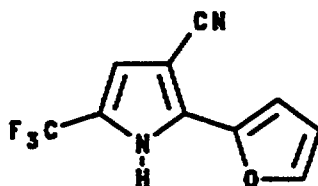
25 solution gives the title product as a yellow oil (3.6 g, 24%).

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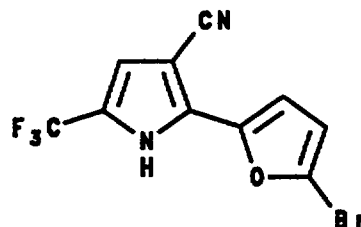
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**EXAMPLE 9****Preparation of 2-(5-Bromo-2-furyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile**

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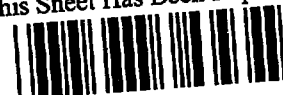
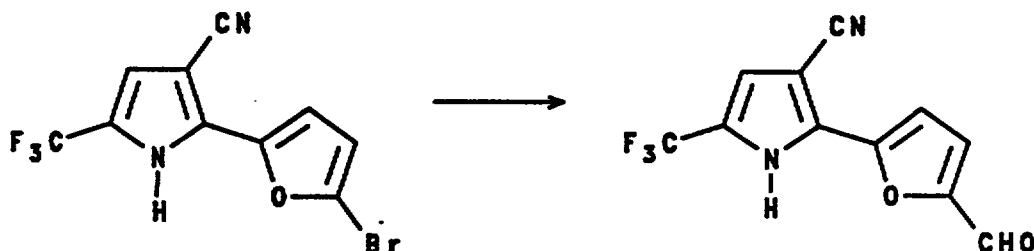
Bromine (0.71 g, 4.42 mmol) is added to a solution of 2-(2-furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (1.00 g, 4.42 mmol) and sodium acetate (0.36 g, 4.42 mmol) in acetic acid. The reaction mixture is stirred for 15 minutes and poured into a 1% sodium bisulfite solution. The solids are filtered from the aqueous mixture, dried overnight under high vacuum and recrystallized from ethyl acetate and hexane to obtain the title product as red crystals (1.21 g, 90%, mp 224^o-226^oC.

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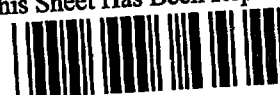
Using essentially the same procedure, but substituting 2-(2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile for 2-(2-furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile, 2-(2-bromo-3-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile is obtained as a solid, mp 170^oC.

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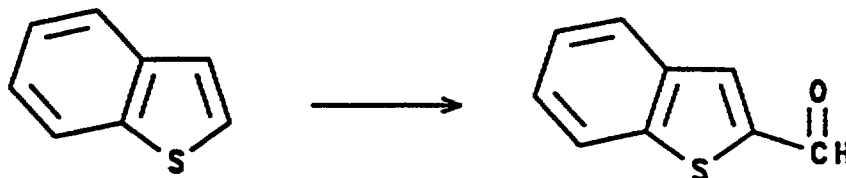
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**EXAMPLE 10****Preparation of 2-(5-Formyl-2-furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile**

Butyllithium (3.45 mL, 7.78 mmol) is added dropwise to a solution of 2-(5-bromo-2-furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (1.13 g, 3.70 mmol) in tetrahydrofuran at -78°C . The reaction mixture is stirred at -78°C for 30 minutes, warmed to room temperature, treated with N,N-dimethylformamide (1.35 g, 18.5 mmol), poured into one molar hydrochloric acid and extracted with ether and ethyl acetate. The combined organic extracts are washed sequentially with water and brine, dried over Na_2SO_4 and concentrated in vacuo to obtain an orange solid. Flash chromatography of the solid using silica gel and 20% to 50% ethyl acetate in hexane solutions give an orange solid which is recrystallized from ethyl acetate to obtain the title product as orange crystals (0.66 g, 70%, mp 224°C - 225°C).

**EXAMPLE 11****Preparation of Benzo[b]thiophene-2-carboxaldehyde**

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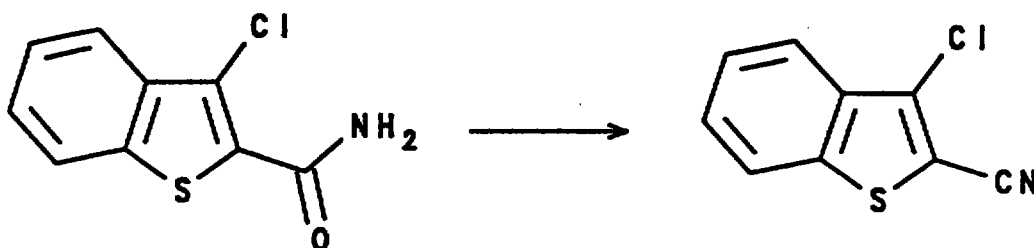
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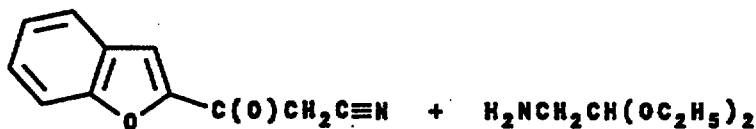
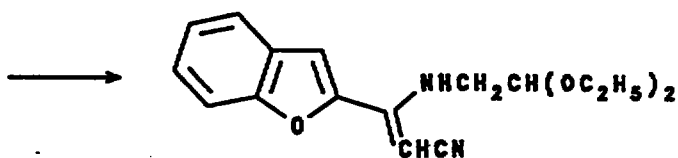
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Butyllithium (54 mL, 134 mmol) is added dropwise to a solution of N,N,N',N'-tetramethylethylenediamine (15.57 g, 134 mmol) in tetrahydrofuran under nitrogen at 0°C. The reaction mixture is treated dropwise with a solution of benzothiophene (15.00 g, 112 mmol) in tetrahydrofuran, warmed to room temperature, treated with additional N,N,N',N'-tetramethylethylenediamine (15.57 g, 134 mmol) and butyllithium (54 mL, 134 mmol), stirred at room temperature for 13 hours, cooled to 0°C, treated with N,N-dimethylformamide (24.40 g, 336 mmol), warmed to room temperature, stirred for five hours, poured into one molar hydrochloric acid and extracted with ether. The combined organic extracts are washed sequentially with water and brine, dried over Na₂SO₄ and concentrated in vacuo to obtain an orange oil. Flash chromatography of the oil using silica gel and a 15% ethyl acetate in hexane solution gives the title product as an orange oil (12.51 g, 69%).

**EXAMPLE 12****Preparation of 3-Chlorobenzo[b]thiophene-2-carbonitrile**

15 Trifluoroacetic anhydride (11.90 g, 56.6 mmol) is added dropwise to a mixture of pyridine (5.23 g, 66.1 mmol) and 3-chlorobenzo[b]thiophene-2-carboxamide (10.0 g, 47.2 mmol) in methylene chloride at 0°C. The reaction mixture is warmed to room temperature over one hour, diluted with water and extracted with ether. The combined organic extracts are washed sequentially with water, one molar hydrochloric acid and brine, dried over MgSO₄ and concentrated in vacuo to obtain a yellow solid. The solid is recrystallized from ethyl acetate and hexane to give the title product as off-white needles (8.80 g, 96%).

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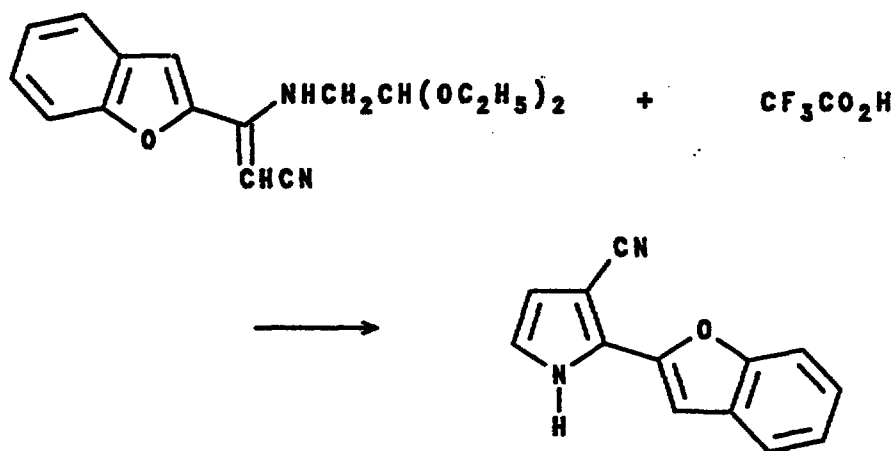
EXAMPLE 13**Preparation of β -[(Formylmethyl)amino-2-benzofuran-
acrylonitrile, diethyl acetal**



A mixture of 2-*o*-cyanoacetobenzofuran (18.52 g, 100.0 mmol) and aminoacetaldehyde diethyl acetal (14.50 mL, 13.28 g, 99.7 mmol) in toluene is refluxed overnight with removal of water (Dean-Stark trap) and concentrated in vacuo to obtain a black oil. Dry column chromatography of the oil using silica gel and methylene chloride gives a reddish-black oil. The oil is mixed with a methylene chloride/hexane solution. The mixture is filtered and the filtrate is concentrated in vacuo to obtain the title product as a reddish-black oil, 10.20 g.

EXAMPLE 14

Preparation of 2-(2-Benzofurananyl)pyrrole-3-carbonitrile



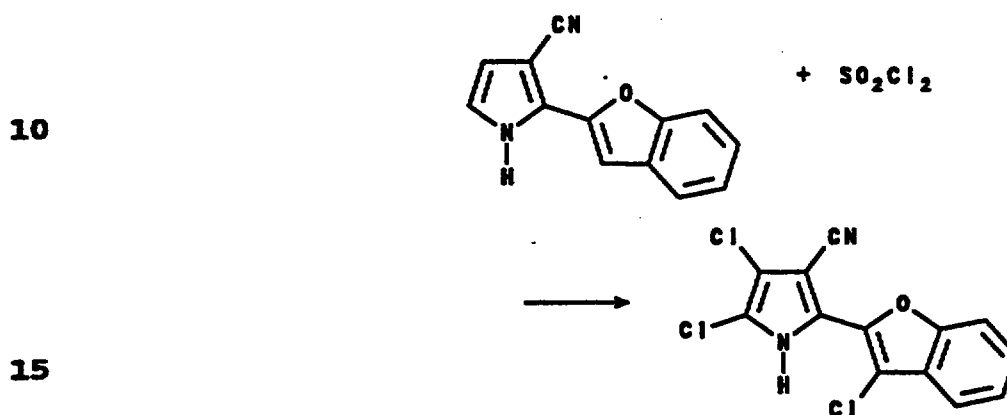
β -[(Formylmethyl)amino]-2-benzofuranacrylonitrile (1.00 g, 3.33 mmol) is added dropwise to trifluoroacetic acid (5 mL). The reaction mixture is stirred at room temperature for one hour, diluted with water and extracted with ethyl acetate. The organic extract is washed sequentially with saturated sodium hydrogen carbonate solution and brine, dried over MgSO_4 , decolorized with charcoal and concentrated in vacuo to obtain an orange solid. Dry column chromatography of the solid using silica gel and methylene



chloride gives the title product as a brown-white solid (0.32 g, 46%, mp 157°-160.5°C).

EXAMPLE 15

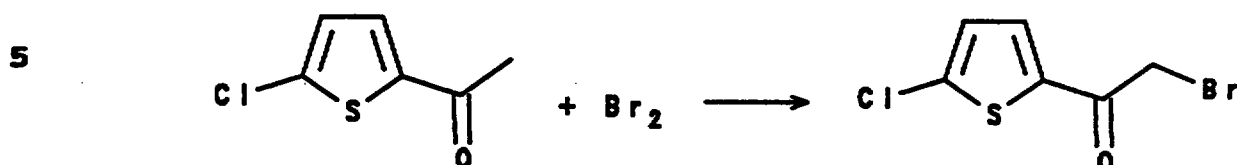
5 Preparation of 4,5-Dichloro-2-(3-chloro-2-benzofuranyl)pyrrole-3-carbonitrile



15 Sulfuryl chloride (1.20 mL, 2.02 g, 14.9 mmol) is added dropwise to a solution of 2-(2-benzofuranyl)pyrrole-3-carbonitrile (1.00 g, 4.8 mmol) in acetic acid. The reaction mixture is stirred at room temperature for 45 minutes and filtered to collect solids. The solids are washed with cold acetic acid and dried overnight to obtain a gray powder. A solution of the gray powder and tetrahydrofuran is dried over MgSO₄, decolorized with charcoal and concentrated in vacuo to give a yellow-white solid. A slurry of the yellow-white solid and methylene chloride is stirred for 90 minutes and filtered to obtain the title product as an off-white solid (0.74 g, mp 258°-260.5°C).

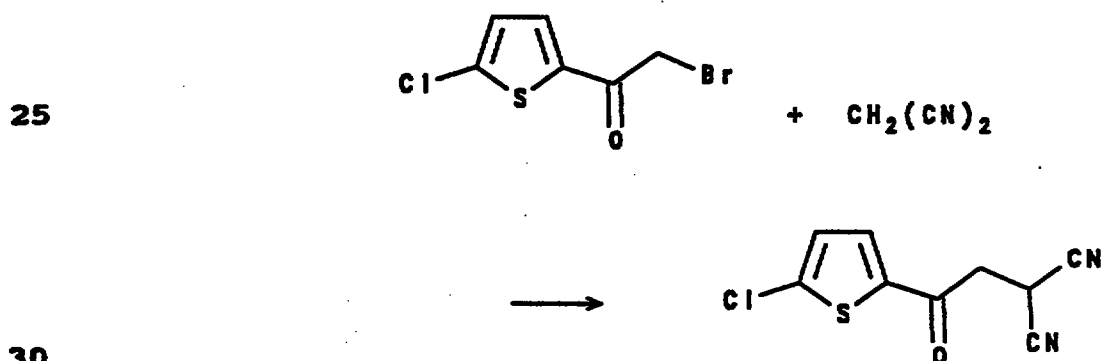
30 Using essentially the same procedure, but employing two equivalents of sulfuryl chloride, 5-chloro-2-(3-chloro-2-benzofuranyl)pyrrole-3-carbonitrile is obtained as a white solid, mp 223.5°-225.5°C.

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**EXAMPLE 16****Preparation of 2-Bromo-1-(5-chloro-2-thienyl)ethanone**

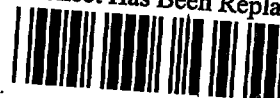
10 A solution of bromine (18.90 g, 118 mmol) in chloroform is added to a solution of 2-acetyl-5-chlorothiophene (19.00 g, 118 mmol) in chloroform at 40°-45°C. The reaction mixture is stirred at room temperature for two hours and diluted with water. The organic layer is separated, dried over MgSO₄ and concentrated

15 in vacuo to give a solid. The solid is slurried in an ether/hexane solution, filtered and dried to give the title product as a solid (12.20 g, mp 68°-70°C).

EXAMPLE 17**Preparation of [(5-Chloro-2-thienoyl)methyl]malononitrile**

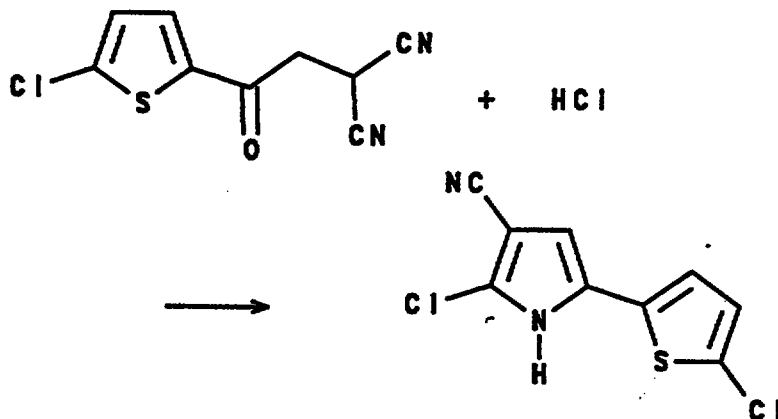
A solution of 2-bromo-1-(5-chloro-2-thienyl)ethanone (11.50 g, 48 mmol) in tetrahydrofuran is added to a solution of malononitrile (3.17 g, 48 mmol) and potassium tert-butoxide (5.70 g, 51 mmol) in tetrahydrofuran at 0°C. The reaction mixture is stirred for

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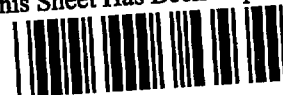


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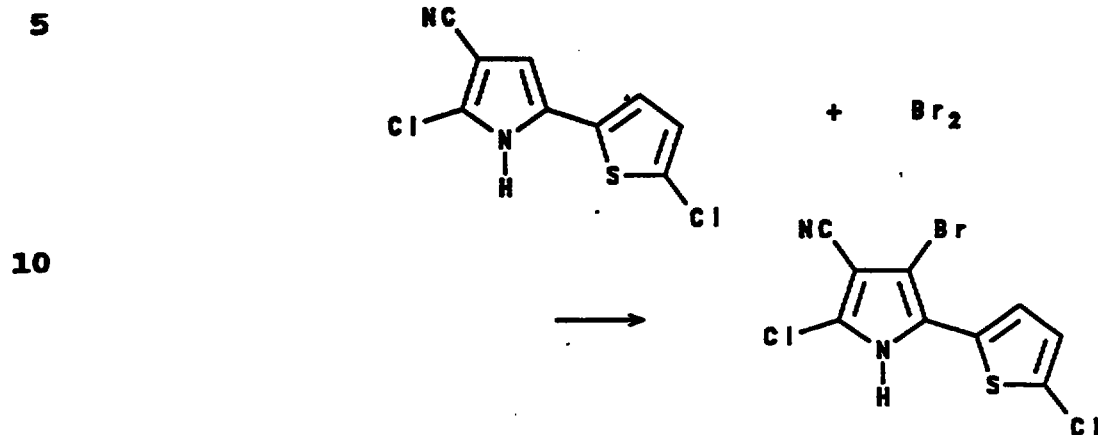
several minutes, concentrated in vacuo, diluted with water and filtered to collect solids. Flash chromatography of the solids using silica gel and a (4:1) hexane/ethyl acetate solution gives the title compound as a yellow solid, mp 155°-158°C.

EXAMPLE 18**Preparation of 2-Chloro-5-(5-chloro-2-thienyl)pyrrole-3-carbonitrile**

Hydrogen chloride gas is bubbled through a mixture of [(5-chloro-2-thienoyl)methyl]malononitrile (4.60 g, 20.5 mmol), ether and chloroform at a moderate rate for 20 minutes. The reaction mixture is poured into an ice-water mixture and extracted with ether. The combined organic extracts are dried over MgSO_4 and concentrated in vacuo to give a brown solid. The solid is mixed with a hexane/ether solution and filtered to obtain the title product as a brown solid, mp $>200^\circ\text{C}$.



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EXAMPLE 19**Preparation of 4-Bromo-2-chloro-5-(5-chloro-2-thienyl)-pyrrole-3-carbonitrile**

15 A solution of bromine (0.70 g, 4.3 mmol) in p-dioxane is added dropwise to a solution of 2-chloro-5-(5-chloro-2-thienyl)pyrrole-3-carbonitrile (1.0 g, 4.1 mmol) in p-dioxane. The reaction mixture is stirred overnight at room temperature and concentrated

20 in vacuo to obtain a residue. Flash chromatography of the residue using silica gel and a (6:1) hexane/ethyl acetate solution gives the title product as a yellow solid, mp >200°C.

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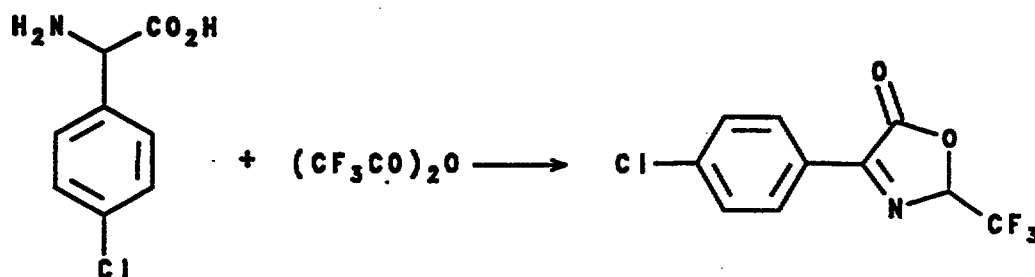
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**EXAMPLE 20****Preparation of 4-(p-Chlorophenyl)-2-(trifluoromethyl)-3-oxazolin-5-one**

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A solution of (p-chlorophenyl)glycine (5.05 g, 27.3 mmol) and trifluoroacetic anhydride (22.90 g, 109.2 mmol) in toluene is refluxed for five minutes and concentrated in vacuo to obtain the title product as a clear orange oil which is identified by high performance liquid chromatography analysis.

20

Using essentially the same procedure, but substituting α -amino-2-thiopheneacetic acid for (p-chlorophenyl)glycine, 4-(2-thienyl)-2-(trifluoromethyl)-3-oxazolin-5-one is obtained as a brown oil.

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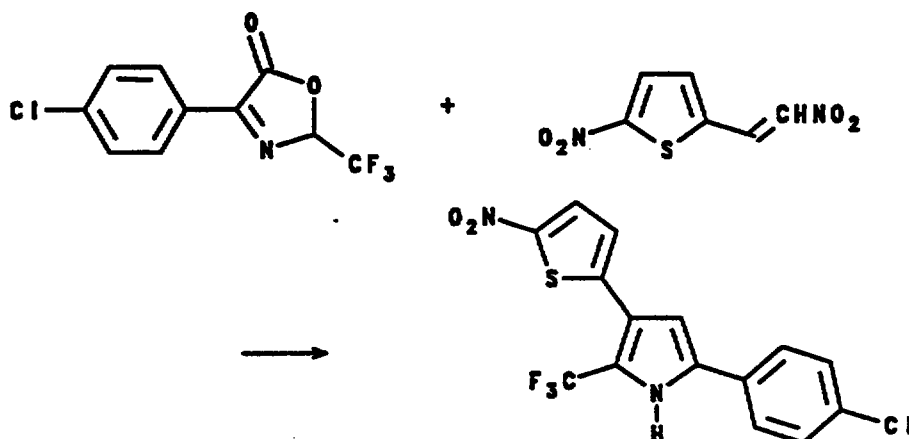
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**EXAMPLE 21****Preparation of 5-(p-Chlorophenyl)-3-(5-nitro-2-thienyl)-2-(trifluoromethyl)pyrrole**

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Triethylamine (1.16 g, 11.3 mmol) is added to a solution of 4-(p-chlorophenyl)-2-(trifluoromethyl)-3-oxazolin-5-one (2.97 g, 11.3 mmol) and 2-nitro-5-(2-nitrovinyl)thiophene (2.26 g, 11.3 mmol) in acetonitrile near reflux. The reaction mixture is refluxed for one hour, stirred overnight at room temperature and concentrated in vacuo to obtain a red oil. Chromatography of the oil gives the title product as a tan solid, mp 166°-169°C.

25

Using essentially the same procedure, but substituting 2-(2-nitrovinyl)furan for 2-nitro-5-(2-nitrovinyl)thiophene, 5-(p-chlorophenyl)-3-(2-furyl)-2-trifluoromethylpyrrole is obtained as a tan solid, mp 65°-66°C.

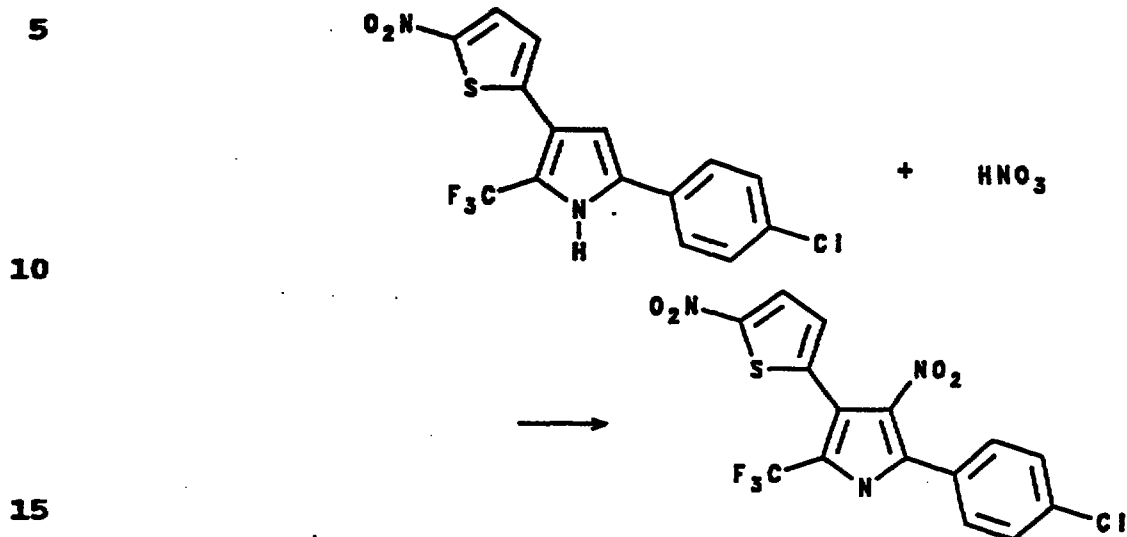
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And using essentially the same procedure, but substituting 4-(2-thienyl)-2-(trifluoromethyl)-3-oxazolin-5-one for 4-(p-chlorophenyl)-2-(trifluoromethyl)-3-oxazolin-5-one and 2-chloroacrylonitrile for 2-nitro-5-(2-nitrovinyl)thiophene, 2-(2-thienyl)-5-trifluoromethylpyrrole-3-carbonitrile is obtained as a tan solid, mp 210°C.

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EXAMPLE 22**Preparation of 2-(p-Chlorophenyl)-3-nitro-4-(5-nitro-2-thienyl)-5-(trifluoromethyl)pyrrole**

A 90% nitric acid solution (0.02 g, 0.28 mmol) is added to a solution of 5-(p-chlorophenyl)-3-(5-nitro-2-thienyl)-2-(trifluoromethyl)pyrrole (0.13 g, 0.34 mmol) in acetic anhydride. The reaction mixture is stirred at room temperature for ten minutes, treated with additional 90% nitric acid solution (0.02 g, 0.28 mmol), stirred at room temperature for 15 minutes, poured into water, stirred at room temperature overnight and extracted with ether. The combined organic extracts are dried over MgSO₄ and concentrated in vacuo to obtain the title product as a tan solid which is identified by ¹HNMR spectral analysis.

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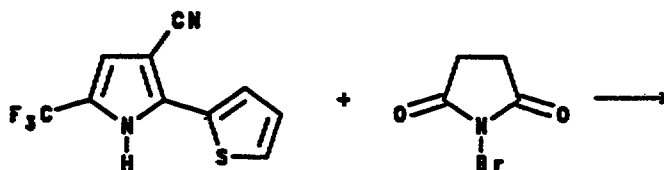
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**EXAMPLE 23**

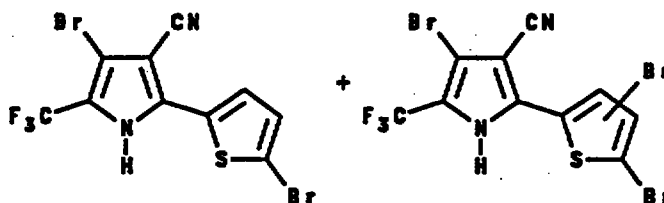
Preparation of 4-Bromo-2-(5-bromo-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile and 4-Bromo-2-[3(or 4),5-dibromo-2-thienyl]-5-(trifluoromethyl)pyrrole-3-carbonitrile

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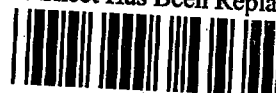
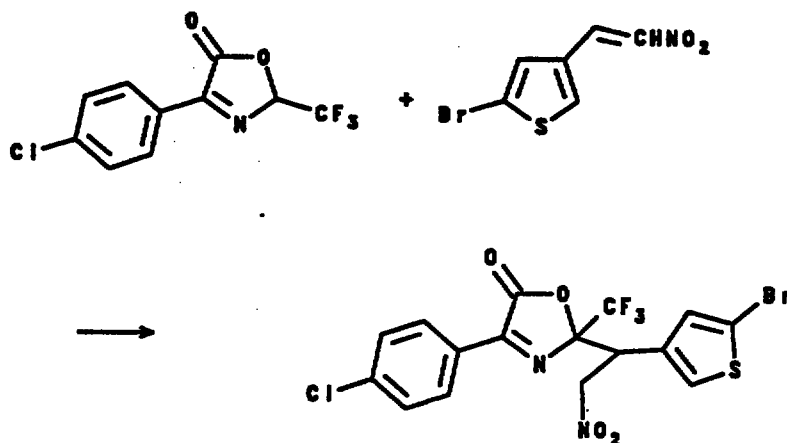
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A solution of N-bromosuccinimide (0.84 g, 4.63 mmol) and 2-(2-thienyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile (1.02 g, 4.21 mmol) in tetrahydrofuran is stirred at room temperature for 20 minutes, treated with additional N-bromosuccinimide (0.84 g, 4.63 mmol), stirred at room temperature for 20 minutes, stirred at reflux for two hours and poured into water. The aqueous mixture is filtered to obtain solids and filtrate. A mixture of the solids in toluene is heated, filtered and dried to give 4-bromo-2-(5-bromo-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile as a solid, mp 254°C (dec.). The filtrate obtained from the aqueous mixture is concentrated in vacuo and chromatographed using silica gel and a (4:1) hexane/ethyl acetate solution to obtain 4-bromo-2-[3(or 4),5-dibromo-2-thienyl]-5-(trifluoromethyl)pyrrole-3-carbonitrile as a solid, mp 203°C.

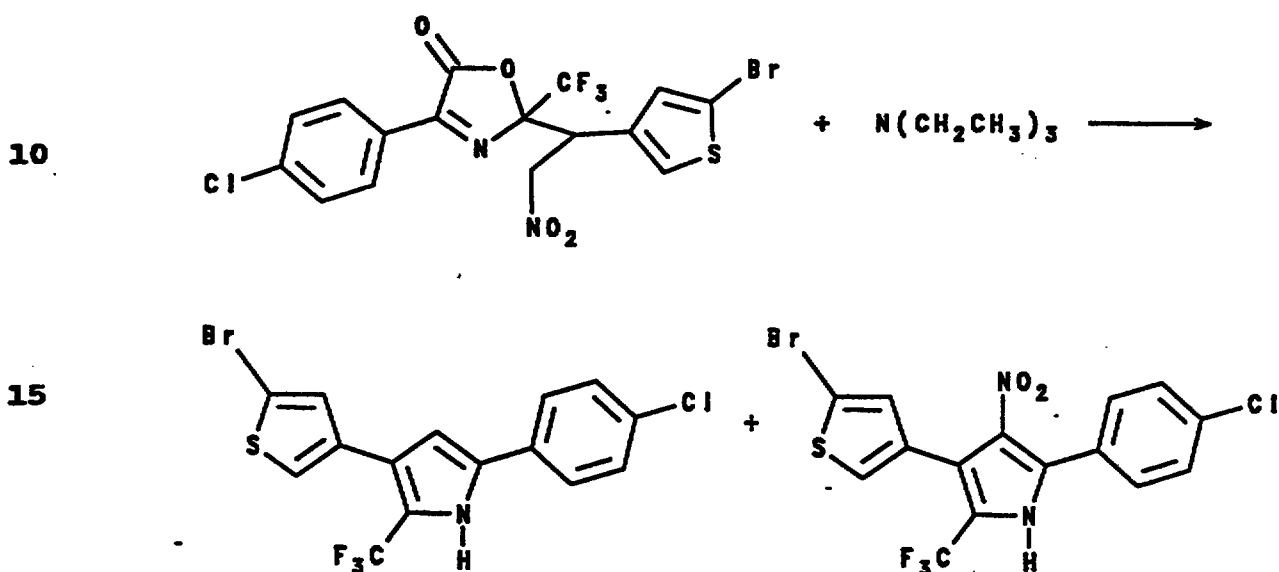
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**EXAMPLE 24****Preparation of 2-[1-(5-Bromo-3-thienyl)-2-nitroethyl]-4-(p-chlorophenyl)-2-(trifluoromethyl)-3-oxazolin-5-one**

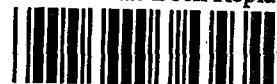
A solution of triethylamine (0.30 g, 3 mmol) in toluene is added to a solution of 4-(p-chlorophenyl)-2-(trifluoromethyl)-3-oxazolin-5-one (10.00 g, 38 mmol) and 2-bromo-4-(2-nitrovinyl)thiophene (8.98 g, 32 mmol) in toluene at 0°C. The reaction mixture is warmed to room temperature and diluted with dilute hydrochloric acid and ether. The organic layer is separated, dried over MgSO_4 , concentrated in vacuo, diluted with hexane, stirred at reflux, cooled to room temperature and decanted to obtain a clear solution. The solution is concentrated in vacuo and chromatographed to give the title product.

**EXAMPLE 25**

Preparation of 3-(5-Bromo-3-thienyl)-5-(p-chloro-phenyl)-2-(trifluoromethyl)pyrrole and 3-(5-Bromo-3-thienyl)-5-(p-chlorophenyl)-4-nitro-2-(trifluoromethyl)pyrrole)



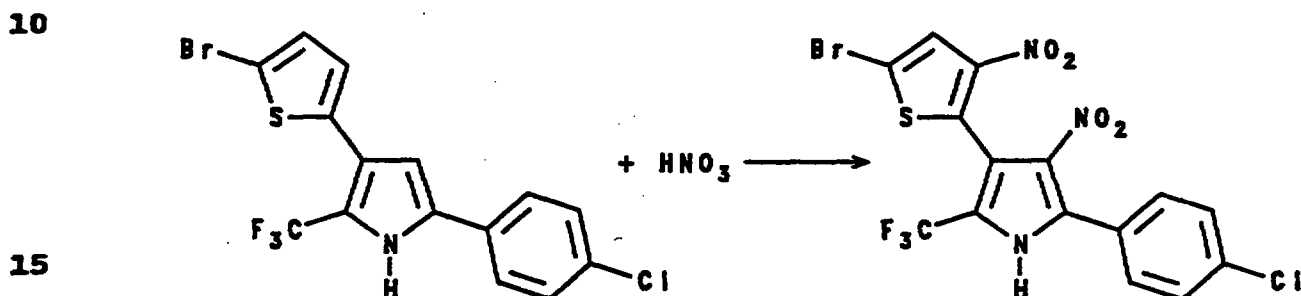
A solution of triethylamine (3.24 g, 32.1 mmol) in acetonitrile is added slowly to a solution of 2-[1-(5-bromo-3-thienyl)-2-nitroethyl]-4-(p-chlorophenyl)-2-(trifluoromethyl)-3-oxazolin-5-one (13.30 g, 26.8 mmol) in acetonitrile. The reaction mixture is stirred at room temperature for several minutes and diluted with dilute hydrochloric acid. The organic layer is separated, dried over MgSO_4 and concentrated in vacuo to obtain a black residue. Column chromatography of the residue using silica gel and a (9:1) hexane/ethyl acetate solution gives several solids. One of the solids is stirred in cold 1,2-dichloroethane, filtered and dried to give 3-(5-bromo-3-thienyl)-5-(p-chlorophenyl)-2-(trifluoromethyl)pyrrole as a light tan solid, mp $112^\circ\text{--}115^\circ\text{C}$. Another solid is diluted with hexane and the mixture is refluxed, cooled



to room temperature and filtered to obtain 3-(5-bromo-3-thienyl)-5-(p-chlorophenyl)-4-nitro-2-(trifluoromethyl)pyrrole as a yellow solid, mp 174°-176°C.

EXAMPLE 26

Preparation of 3-(5-Bromo-4-nitro-3-thienyl)-5-(p-chlorophenyl)-4-nitro-2-(trifluoromethyl)pyrrole



20 A solution of 3-(5-bromo-3-thienyl)-5-(p-chlorophenyl)-2-(trifluoromethyl)pyrrole (0.70 g, 1.7 mmol) and 90% nitric acid (0.145 g, 0.1 mL, 2.1 mmol) in acetic anhydride is stirred at room temperature for 20 minutes, treated with additional 90% nitric acid (several drops) and diluted with water. The solids are collected by filtration and dried overnight at 60°C in a vacuum oven to give the title product as a solid, mp 186°-190°C.

25

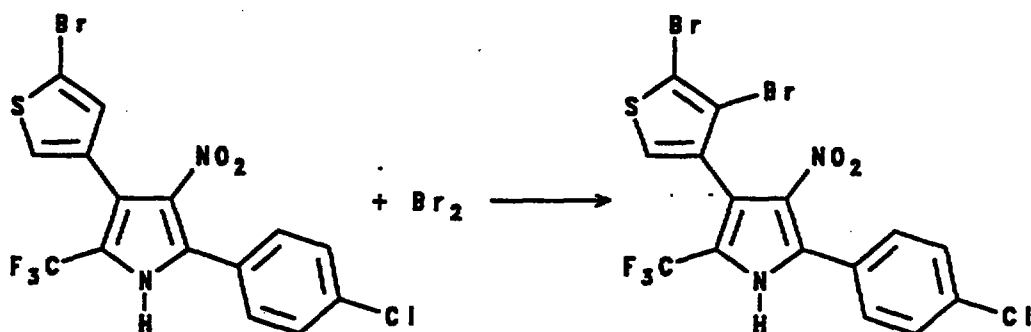
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**EXAMPLE 27****Preparation of 2-(p-Chlorophenyl)-4-(4,5-dibromo-3-thienyl)-3-nitro-5-(trifluoromethyl)pyrrole**

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A solution of 3-(5-bromo-3-thienyl)-5-(p-chlorophenyl)-4-nitro-2-(trifluoromethyl)pyrrole (0.50 g, 1.1 mmol), bromine (0.20 g, 1.3 mmol) and sodium acetate (0.11 g, 1.3 mmol) in acetic acid (10 mL) is heated overnight at 50°C and poured into water. The solids are collected and recrystallized from 1,2-dichloroethane to give the title product as a yellow solid, mp 241°C - 242°C .

EXAMPLE 28

25

Insecticide and acaricide evaluations

30

The following tests show the efficacy of the compounds as insecticides and acaricides. The evaluations are conducted with solutions of test compounds dissolved or dispersed in 50/50 acetone/water mixtures. The test compound is technical material dissolved or dispersed in said acetone/water mixtures in sufficient amounts to provide the concentrations set forth in Table I below.

35

All concentrations reported herein are in terms of active ingredient. All tests are conducted in



a laboratory maintained at about 27°C. The rating system employed is as follows:

Rating System

5	0 = no effect	5 = 56-65% kill
	1 = 10-25% kill	6 = 66-75% kill
	2 = 26-35% kill	7 = 76-85% kill
	3 = 36-45% kill	8 = 86-99% kill
	4 = 46-55% kill	9 = 100% kill
10		- = no evaluation

The test species of insects and acarina used in the present evaluations along with specific test procedures are described below.

15

Spodoptera eridania third instar larvae, southern armyworm

20

A sieva lima bean expanded to 7 to 8 cm in length is dipped in the test suspension with agitation for three seconds and placed in a hood to dry. The leaf is then placed in a 100x10 mm petri dish containing a damp filter paper on the bottom and ten third instar caterpillars. The dish is maintained for five days before observations are made of mortality, reduced feeding or any interference with normal moulting.

25

Spodoptera eridania, seven-day residual

30

The plants treated in the above test are maintained under high intensity lamps in the greenhouse for seven days. These lamps duplicate the effects of a bright sunny day and are kept on for 14 hour day length. After seven days, the foliage is sampled and assayed as in the above-said test.

35



Tetranychus urticae (OP-resistant strain), two-spotted spider mite

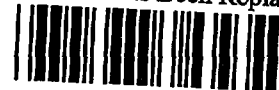
5 Sieva lima bean plants with primary leaves expanded to 7 to 8 cm are selected and cut back to one plant per pot. A small piece is cut from a leaf taken from the main colony and placed on each leaf of the test plants. This is done about two hours before treatment to allow the mites to move over to the test plant and to lay eggs. The size of the cut piece is varied to obtain about 100 mites per leaf. At the time of the treatment, the piece of leaf used to transfer the mites is removed and discarded. The mite-infested plants are dipped in the test formulation for three seconds with agitation and set in the hood to dry. 10 Plants are kept for two days before estimates of adult kill are made. 15

Heliothis virescens, third instar tobacco budworm

20 Cotton cotyledons are dipped in the test formulation and allowed to dry in a hood. When dry, each is cut into quarters and ten sections placed individually in 30 mL plastic medicine cups containing a 5 to 7 mm long piece of damp dental wick. One third instar caterpillar is added to each cup and a cardboard lid placed on the cup. Treatments are maintained for 25 three days before mortality counts and estimates of reduction in feeding damage are made.

30 Diabrotica undecimpunctata howardi, third instar southern corn rootworm

One cc of fine talc is placed in a 30 mL wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 mg of active ingredient per jar. 35 The jars are set under a gentle air flow until the



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5 acetone is evaporated. The dried talc is loosened, 1
cc of millet seed is added to serve as food for the
insects and 25 mL of moist soil is added to each jar.
The jars are capped and the contents thoroughly mixed
on a Vortex Mixer. Following this, ten third instar
rootworms are added to each jar and the jars are
loosely capped to allow air exchange for the larvae.
The treatments are held for six days before mortality
counts are made. Missing larvae are presumed dead,
10 since they decompose rapidly and can not be found. The
concentration used in this test corresponds to approxi-
mately 50 ppm.

15 Compounds employed in the above described
insecticide and acaricide evaluations are given a
compound number and identified by name. Data in Table
I are reported by compound number.

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COMPOUNDS EVALUATED AS INSECTICIDAL AND
ACARICIDAL AGENTS

5	Compound <u>No.</u>	
	1	2-(p-Chlorophenyl)-4-(4,5-dibromo-3-thienyl)-3-nitro-5-(trifluoromethyl)pyrrole
10	2	3-(5-Bromo-3-thienyl)-5-(p-chlorophenyl)-4-nitro-2-(trifluoromethyl)pyrrole
	3	5-(p-Chlorophenyl)-3-(2-furyl)-2-(trifluoromethyl)pyrrole
15	4	3-(5-Bromo-3-thienyl)-5-(p-chlorophenyl)-2-(trifluoromethyl)pyrrole
	5	2-(2-benzofuranyl)pyrrole-3-carbonitrile
20	6	3-Chloro-1-(ethoxymethyl)-2-(2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
	7	2-(2-Thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
25	8	4-Chloro-2-(2-thienyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
	9	2-(5-Bromo-2-thienyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
30	10	4-Bromo-2-(5-bromo-2-thienyl)-1-ethoxy-methyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
35		



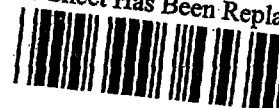
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Compound	
<u>No.</u>	
5	11 2-(5-Chloro-2-thienyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
	12 4-Bromo-2-(5-chloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
10	13 4-Bromo-2-(5-chloro-2-thienyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
15	14 2-(4-Bromo-2-thienyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
	15 2-(3,4,5-Trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
20	16 4-Bromo-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
25	17 4-Bromo-1-(ethoxymethyl)-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
	18 2-(2-Bromo-3-thienyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
30	19 4-Bromo-2-(2-bromo-3-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
35	20 2-(2-Furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile



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Compound		
<u>No.</u>		
5	21	1-(Ethoxymethyl)-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
	22	2-(5-Formyl-2-furyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
10	23	4-Bromo-2-(5-bromo-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
15	24	2-Chloro-5-(5-chloro-2-thienyl)pyrrole-3-carbonitrile
	25	4-Bromo-2-(5-bromo-2-furyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
20	26	4-Bromo-2-(5-bromo-2-furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
25	27	2-(5-Bromo-2-furyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
	28	4-Bromo-2-(4,5-dibromo-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
30	29	4,5-Dichloro-2-(3-chloro-2-benzofuranyl)-pyrrole-3-carbonitrile
35	30	5-Chloro-2-(3-chloro-2-benzofuranyl)pyrrole-3-carbonitrile



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Compound		
	<u>No.</u>	
5	31	4-Bromo-2-(3-chloro-2-benzo[b]thienyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
	32	4-Bromo-2-(3-chloro-2-benzo[b]thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
10	33	2-Benzo[b]thien-2-yl-5-(trifluoromethyl)-pyrrole-3-carbonitrile
15	34	4-Bromo-2-(3-bromobenzo[b]thien-2-yl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
	35	4-Bromo-2-(3-bromobenzo[b]thien-2-yl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
20	36	2-(p-Chlorophenyl)-3-nitro-4-(5-nitro-2-thienyl)-5-(trifluoromethyl)pyrrole
25	37	4-Bromo-2-chloro-5-(5-chloro-2-thienyl)-pyrrole-3-carbonitrile
	38	2-(3-Thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
30	39	4-Bromo-2-(2-bromo-3-thienyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile
35	40	2-(3-Chloro-2-benzo[b]thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile

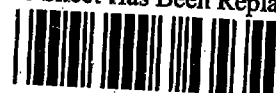


TABLE I

Insecticide And Acaricide Evaluations

Compound No.	Southern Armyworm			OP. Res. Mites		Tobacco Budworm		Southern Corn Rootworm	
	(ppm) 1000	(ppm) 300	7-Day Residual (ppm) 1000	(ppm) 300	(ppm) 300	(ppm) 300	(ppm) 100	(ppm) 50	
1	9	-	-	0	-	9		8	
2	9	-	-	0	-	0		0	
3	0	-	-	0	-	-		0	
4	0	-	-	0	-	-		0	
5	8	-	-	0	-	-		0	
6	-	0	-	4	0	0	0	9	
7	9	-	0	0	-	-		0	
8	9	8	-	7	9	6	9	9	
9	9	9	-	0	9	8	8	6	
10	-	0	-	9	9	8	8	9	

TABLE I (Continued)

Insecticide And Acaricide Evaluations

Compound No.	Southern Armyworm			OP. Res. Mites		Tobacco Budworm		Southern Corn Rootworm	
	(ppm) 1000	(ppm) 300	7-Day Residual (ppm) 1000	(ppm) 300	(ppm) 300	(ppm) 300	(ppm) 100	(ppm) 50	
11	9	9	-	9	0	9	9	7	
12	9	9	-	9	0	9	7	9	
13	9	9	-	9	9	3	-	9	
14	-	-	-	9	0	9	8	8	
15	9	-	-	9	8	9	9	8	
16	9	9	-	9	9	9	9	9	
17	9	9	-	9	9	9	9	9	
18	2	-	-	-	0	-	-	0	
19	9	9	-	9	8	9	6	9	
20	-	0	-	0	0	0	0	9	





TABLE I (Continued)

Insecticide And Acaricide Evaluations

Compound No.	Southern Armyworm		7-Day Residual		OP. Res. Mites		Tobacco Budworm		Southern Corn Rootworm	
	(ppm) 1000	(ppm) 300	(ppm) 1000	(ppm) 300	(ppm) 300	(ppm) 300	(ppm) 300	(ppm) 100	(ppm) 50	
21	9	-	-	9	9	9	9	9	9	
22	0	-	-	-	0	-	-	-	0	
23	9	-	9	-	0	-	-	0	9	
24	9	-	9	-	0	-	-	0	0	
25	-	0	-	9	9	9	9	9	9	
26	9	9	-	9	0	9	9	9	9	
27	9	9	-	9	4	4	4	0	8	
28	-	9	-	9	7	9	9	9	9	
29	9	-	9	-	0	-	-	-	7	
30	9	-	-	-	0	-	-	-	0	

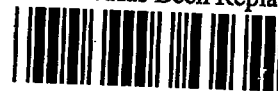
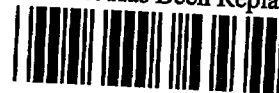


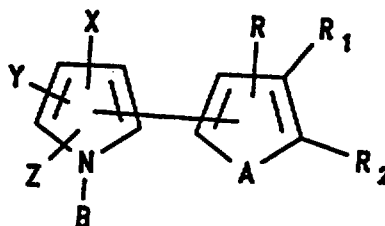
TABLE I (Continued)
Insecticide And Acaricide Evaluations

Compound No.	Southern Armyworm			OP. Res. Mites		Tobacco Budworm		Southern Corn Rootworm	
	(ppm) 1000	(ppm) 300	7-Day Residual (ppm) 1000	(ppm) 300	(ppm) 300	(ppm) 300	(ppm) 100	(ppm) 50	
31	-	-	9	-	0	-	-	9	
32	-	-	9	-	0	-	-	9	
33	-	-	7	0	0	-	-	0	
34	-	-	9	8	0	9	8	6	
35	-	-	9	9	0	5	0	8	
36	9	-	0	-	-	-	9	9	
37	9	-	9	-	0	-	9	0	
38	0	-	-	-	0	-	-	0	
39	9	2	-	3	0	2	0	9	
40	-	-	9	-	0	-	-	7	

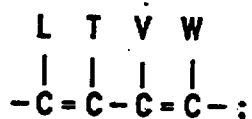


WHAT IS CLAIMED IS:

1. A compound having the structural formula



R, R₁ and R₂ are each independently hydrogen, halogen, NO₂ or CHO, and when R₁ and R₂ are taken together with the carbon atoms to which they are attached, they may form a ring in which R₁R₂ is represented by the structure:



L, T, V and W are each independently hydrogen, halogen, CN or NO₂;

A is O or S;

X is CN, NO₂, C₁-C₆ haloalkyl, S(O)_mCF₂R₃ or C(S)NR₄R₅;
R₃ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

m is an integer of 0, 1 or 2;

R₄ and R₅ are each independently hydrogen,

C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted



with one or more halogen atoms;
Y is hydrogen, halogen, C_1-C_6 haloalkyl, $S(O)_mCF_2R_3$,
CN or
phenyl optionally substituted with one or more
halogen atoms,
 NO_2 groups,
CN groups,
 C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;
Z is hydrogen, halogen or C_1-C_6 haloalkyl;
B is R_6 , OR_6 or CN;
 R_6 is hydrogen, $C(O)R_7$, $CHR_8NHC(O)R_9$, CH_2SQ ,
 $CHR_{10}OC(O)(CR_{11}R_{12})_nQ_1$,
 C_1-C_6 alkyl optionally substituted with one to
three halogen atoms,
one tri(C_1-C_4 alkyl)silyl,
one hydroxy,
one cyano,
one or two C_1-C_4 alkoxy groups optionally
substituted with one to three halogen
atoms,
one C_1-C_4 alkylthio,
one phenyl optionally substituted with one to
three halogen atoms, one to three C_1-C_4
alkyl groups or one to three C_1-C_4
alkoxy groups,
one phenoxy group optionally substituted
with one to three halogen atoms, one to
three C_1-C_4 alkyl groups or one to three
 C_1-C_4 alkoxy groups,
one benzyloxy group optionally substituted on
the phenyl ring with one to three
halogen atoms, one to three C_1-C_4 alkyl



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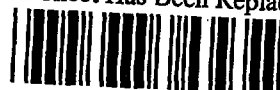


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groups or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkoxy carbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or
one benzylcarbonyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
 C_3-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group, or
 C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group;
 R_7 is C_1-C_6 alkyl or C_3-C_6 cycloalkyl each optionally substituted with one to three halogen atoms,
one hydroxy,
one cyano,
one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms,
one C_1-C_4 alkylthio,
one phenyl group optionally substituted with



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- one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkoxy carbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or
- one benzyloxy carbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- C_2-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl groups,
- C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group,



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phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, phenoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,

phenoxy optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,

1- or 2-naphthyl,

2-, 3-, or 4-pyridyl optionally substituted with one to three halogen atoms,

C_1-C_6 alkoxy optionally substituted with one to three halogen atoms, or

C_2-C_6 alkenyloxy optionally substituted with one to three halogen atoms;

R_8 is hydrogen or C_1-C_4 alkyl;

R_9 is C_1-C_6 alkyl optionally substituted with one to three halogen atoms,

phenyl optionally substituted with one to three halogen atoms, CN groups, NO_2 groups, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups or CF_3 groups,

2- or 3-thienyl, or

2- or 3-furyl;

Q is $\overset{\overset{A_1}{\parallel}}{C}-R_{13}$, $\overset{\overset{A_1}{\parallel}}{C}-OR_{14}$, $\overset{\overset{A_1}{\parallel}}{C}-NR_{15}R_{16}$, $\overset{\overset{A_1}{\parallel}}{P}-(OR_{17})_2$, $\overset{\overset{NR_{18}}{\parallel}}{C}-NR_{19}R_{20}$,
 $\overset{\overset{NR_{18}}{\parallel}}{C}-A_1R_{21}$,

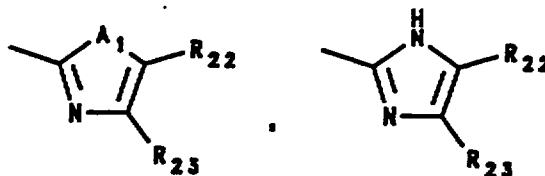


* C L M S *

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CN,

C_1-C_6 alkyl optionally substituted with one or more halogen atoms, CN groups or phenyl groups, or

phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups, CF_3 groups or $NR_{24}R_{25}$ groups;

A_1 is O or S;

R_{13} is C_1-C_6 alkyl or phenyl;

R_{14} is C_1-C_6 alkyl;

R_{15} and R_{16} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;

R_{17} is C_1-C_4 alkyl;

R_{18} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{19} or R_{21} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl;

R_{21} is C_1-C_4 alkyl or when taken together with R_{18} and the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

R_{22} and R_{23} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{22}R_{23}$ is represented by $-CH=CH-CH=CH-$;



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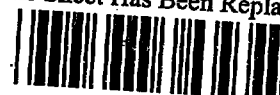
R_{24} and R_{25} are each independently hydrogen or C_1-C_4 alkyl;
 R_{10} is hydrogen or C_1-C_4 alkyl;
 R_{11} and R_{12} are each independently hydrogen, C_1-C_6 alkyl optionally substituted with one or more halogen atoms, C_1-C_6 alkoxy optionally substituted with one or more halogen atoms, C_1-C_6 alkylthio optionally substituted with one or more halogen atoms, or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms, or when R_{11} and R_{12} are taken together with the atom to which they are attached may form a C_3-C_6 cycloalkyl group optionally substituted with one to three C_1-C_4 alkyl groups, C_2-C_6 alkenyl groups or phenyl groups, or R_{11} or R_{12} may be taken together with R_{26} and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

n is an integer of 0, 1, 2, 3 or 4;

Q_1 is A_2R_{26} , $\overset{\text{O}}{\parallel}P-(OR_{27})_2$, $NR_{28}R_{29}$, $CR_{30}R_{31}C(O)R_{32}$, or C_3-C_6 cycloalkyl optionally substituted with one or more C_1-C_6 alkyl groups, C_2-C_6 alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms, NO_2 groups,



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CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

A₂ is O or S(O)_p;

p is an integer of 0, 1 or 2;

R₂₆ is hydrogen,

C₁-C₆ alkyl

C₂-C₆ alkenyl,

C₂-C₆ alkynyl,

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

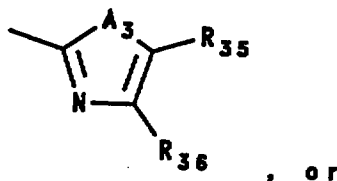
C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms,

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms,

C(O)R₃₃ provided p is 0,

C(O)R₃₄ provided p is 0,

(CH₂CH₂O)_qR₃₃, or



R₂₆ may be taken together with either R₁₁ or R₁₂ and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

A₃ is O or S;

R₃₃ is C₁-C₆ alkyl,

C₂-C₆ alkenyl,



* C L M S *

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C_2-C_6 alkynyl, or
phenyl optionally substituted with one or more
halogen atoms,
 NO_2 groups,
CN groups,
 C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;

q is an integer of 1, 2 or 3;

R_{34} is OR_{37} or $NR_{38}R_{39}$;

R_{37} is C_1-C_6 alkyl or
phenyl optionally substituted with one or more
halogen atoms,
 NO_2 groups,
CN groups,
 C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;

R_{38} and R_{39} are each independently hydrogen or C_1-C_4
alkyl;

R_{35} and R_{36} are each independently hydrogen or C_1-C_4
alkyl, or
when taken together may form a ring wherein
 $R_{35}R_{36}$ is represented by $-CH=CH-CH=CH-$;

R_{27} is C_1-C_4 alkyl;

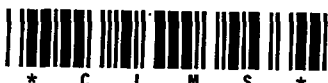
R_{28} is hydrogen,

C_1-C_6 alkyl,

C_2-C_6 alkenyl,

C_2-C_6 alkynyl, or

phenyl optionally substituted with one or more
halogen atoms,
 NO_2 groups,
CN groups,



C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms, or

R_{28} may be taken together with either R_{11} or R_{12}
and the atoms to which they are attached to form a
4- to 7-membered heterocyclic ring;

R_{29} is hydrogen,

C_1-C_6 alkyl,

C_2-C_6 alkenyl,

C_2-C_6 alkynyl,

phenyl optionally substituted with one or more
halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms,

$C(A_4)R_{40}$,

CN,

SO_2R_{41} , or

$C(O)CHR_{42}NHR_{43}$;

A_4 is O or S;

R_{40} is OR_{44} , CO_2R_{44} , $NR_{45}R_{46}$,

C_1-C_6 alkyl optionally substituted with one to
three halogen atoms,

C_2-C_6 alkenyl,

C_2-C_6 alkynyl, or

phenyl optionally substituted with one or more
halogen atoms,

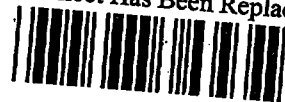
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or



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- C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;
- R_{44} is C_1-C_6 alkyl optionally substituted with one
phenyl group, or
phenyl optionally substituted with one or more
halogen atoms,
 NO_2 groups,
CN groups,
 C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;
- R_{45} and R_{46} are each independently hydrogen or C_1-C_4
alkyl;
- R_{41} is $NR_{47}R_{48}$,
 C_1-C_6 alkyl,
 C_2-C_6 alkenyl,
 C_2-C_6 alkynyl, or
phenyl optionally substituted with one or more
halogen atoms,
 NO_2 groups,
CN groups,
 C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;
- R_{47} and R_{48} are each independently hydrogen or C_1-C_4
alkyl;
- R_{42} is hydrogen,
 C_1-C_4 alkyl optionally substituted with
one hydroxy group,
one SR_{49} group,
one $C(O)NH_2$ group,
one NH_2 group,
one $NHC(=NH)NH_2$ group,



one CO_2H group,
one phenyl group optionally substituted with
one hydroxy group,
one 3-indolyl group or
one 4-imidazolyl group;

R_{49} is hydrogen or $\text{C}_1\text{-C}_4$ alkyl;

R_{43} is $\text{C}(\text{A}_4)\text{R}_{50}$;

R_{50} is $\text{C}_1\text{-C}_6$ alkyl optionally substituted with one or
more halogen atoms,

$\text{C}_1\text{-C}_6$ alkoxyalkyl,

$\text{C}_1\text{-C}_6$ alkylthio,

phenyl optionally substituted with one or more
halogen atoms,

NO_2 groups,

CN groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted
with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted
with one or more halogen atoms,

OR_{44} ,

CO_2R_{44} or

$\text{NR}_{45}\text{R}_{46}$;

R_{30} and R_{31} are each independently hydrogen,

$\text{C}_1\text{-C}_6$ alkyl optionally substituted with one
or more halogen atoms,

$\text{C}_1\text{-C}_6$ alkoxy optionally substituted with one
or more halogen atoms,

$\text{C}_1\text{-C}_6$ alkylthio optionally substituted with
one or more halogen atoms,

phenyl optionally substituted with one or more
halogen atoms,

CN groups,

NO_2 groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted
with one or more halogen atoms, or



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C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms, or when R_{30} and R_{31} are taken together with the atom to which they are attached may form a C_3-C_6 cycloalkyl group optionally substituted with one to three C_1-C_4 alkyl groups, C_2-C_6 alkenyl groups or phenyl groups;

R_{32} is OR_{51} , $NR_{47}R_{48}$, C_1-C_4 alkyl or phenyl optionally substituted with one or more halogen atoms, CN groups, NO_2 groups, C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms; and

R_{51} is C_1-C_4 alkyl or phenyl optionally substituted with one or more halogen atoms, CN groups, NO_2 groups, C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

provided that when A is S, X is $S(O)_mCF_2R_3$ and Z is hydrogen, then Y is hydrogen, halogen, C_1-C_6 haloalkyl, $S(O)_mCF_2R_3$ or CN; and further provided that when the pyrrole ring is substituted with hydrogen at each of the pyrrole carbon atoms adjacent to the ring nitrogen atom, then X cannot be CN or NO_2 .

2. The compound according to claim 1 wherein R , R_1 and R_2 are each independently hydrogen, halogen



or NO_2 , and when R_1 and R_2 are taken together with the carbon atoms to which they are attached, they may form a ring in which R_1R_2 is represented by the structure:



A is O or S;

X is CN or NO_2 ;

~~Y~~-Y is halogen, CF_3 or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

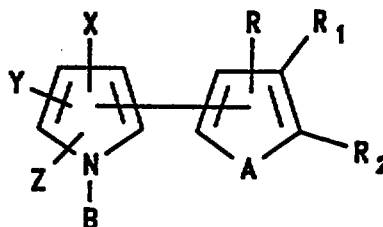
C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF_3 ; and

B is hydrogen or C_1 - C_6 alkyl substituted with one C_1 - C_4 alkoxy group.

3. A method for controlling insects and acarina which comprises contacting said insects and acarina, their breeding grounds, food supply or habitat with an insecticidally or acaricidally effective amount of a compound having the structural formula



wherein R, R_1 , R_2 , A, X, Y, Z and B are as described in claim 1.



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4. The method according to claim 3 wherein the compound is selected from the group consisting of
4-bromo-1-(ethoxymethyl)-2-(3,4,5-trichloro-2-thienyl)-
5-(trifluoromethyl)pyrrole-3-carbonitrile;
4-bromo-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoro-
methyl)pyrrole-3-carbonitrile;
4-bromo-2-(5-bromo-2-furyl)-1-(ethoxymethyl)-5-
(trifluoromethyl)pyrrole-3-carbonitrile;
4-bromo-2-(5-bromo-2-furyl)-5-(trifluoromethyl)-
pyrrole-3-carbonitrile;
1-(ethoxymethyl)-2-(3,4,5-trichloro-2-thienyl)-5-
(trifluoromethyl)pyrrole-3-carbonitrile;
2-(5-chloro-2-thienyl)-5-(trifluoromethyl)pyrrole-
3-carbonitrile;
2-(p-chlorophenyl)-4-(4,5-dibromo-3-thienyl)-3-nitro-
5-(trifluoromethyl)pyrrole;
2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)-
pyrrole-3-carbonitrile;
4-bromo-2-(4,5-dibromo-2-thienyl)-5-(trifluoro-
methyl)pyrrole-3-carbonitrile;
2-(p-chlorophenyl)-3-nitro-4-(5-nitro-2-thienyl)-
5-(trifluoromethyl)pyrrole; and
4-bromo-2-chloro-5-(5-chloro-2-thienyl)pyrrole-
3-carbonitrile.

5. The method according to claim 3 further comprising the simultaneous or sequential addition of an insecticidally or acaricidally effective amount of one or more other biological chemicals.

6. A method for protecting growing plants from attack by insects and acarina which comprises applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or

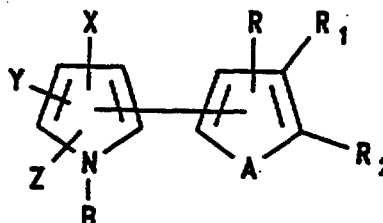


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acaricidally effective amount of a compound having the structural formula



wherein R, R₁, R₂, A, X, Y, Z and B are as described in claim 1.

7. The method according to claim 6 wherein the compound is selected from the group consisting of
4-bromo-1-(ethoxymethyl)-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile;
4-bromo-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile;
4-bromo-2-(5-bromo-2-furyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile;
4-bromo-2-(5-bromo-2-furyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile;
4-(ethoxymethyl)-2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile;
2-(5-chloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile;
2-(p-chlorophenyl)-4-(4,5-dibromo-3-thienyl)-3-nitro-5-(trifluoromethyl)pyrrole;
2-(3,4,5-trichloro-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile;
4-bromo-2-(4,5-dibromo-2-thienyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile;
2-(p-chlorophenyl)-3-nitro-4-(5-nitro-2-thienyl)-5-(trifluoromethyl)pyrrole; and
4-bromo-2-chloro-5-(5-chloro-2-thienyl)pyrrole-



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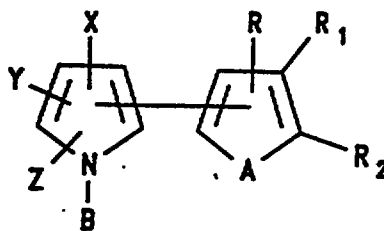


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3-carbonitrile.

8. The method according to claim 6 wherein the compound is applied to the plants or to the soil or water in which they are growing at a rate of about 0.1 kg/ha to 4.0 kg/ha.

9. A composition for controlling insects and acarina which comprises an inert liquid or solid carrier and an insecticidally or acaricidally effective amount of a compound having the structural formula



wherein R, R₁, R₂, A, X, Y, Z and B are as described in claim 1.

10. The composition according to claim 9, further comprising a pesticidally effective amount of one or more other pesticidal agents.