



US005389600A

United States Patent [19]
Selby

[11] **Patent Number:** **5,389,600**[45] **Date of Patent:** **Feb. 14, 1995**[54] **SUBSTITUTED FUSED HETEROCYCLIC HERBICIDES**[75] **Inventor:** **Thomas P. Selby, Wilmington, Del.**[73] **Assignee:** **E. I. du Pont de Nemours and Company, Wilmington, Del.**[21] **Appl. No.:** **50,475**[22] **PCT Filed:** **Nov. 14, 1991**[86] **PCT No.:** **PCT/US91/08266**§ 371 Date: **May 21, 1993**§ 102(e) Date: **May 21, 1993**[87] **PCT Pub. No.:** **WO92/09578****PCT Pub. Date:** **Nov. 6, 1992****Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 617,707, Nov. 26, 1990, Pat. No. 5,110,347.

[51] **Int. Cl.⁶** **A01N 43/54; C07D 239/72; C07D 239/80; C07D 239/88**[52] **U.S. Cl.** **504/240; 544/283; 544/285; 544/286; 544/287; 544/288; 544/289**[58] **Field of Search** **544/283, 285, 286, 287, 544/288, 289; 504/240**[56] **References Cited****U.S. PATENT DOCUMENTS**

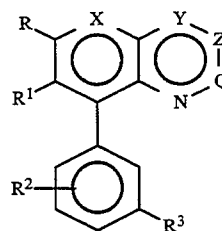
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FOREIGN PATENT DOCUMENTS

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OTHER PUBLICATIONSGogte et al., "Synthesis of Heterocyclic Compounds: Part XXII—Synthesis of 1,5-1,6- and 1,8-Naphthyridines", *Indian Journal of Chemistry*, 19B, 1011-1013, 1980.Baker et al, *J. Med. Chem.* 15 pp. 235-237 (1972).*Primary Examiner*—Emily Bernhardt[57] **ABSTRACT**

The invention relates to certain substituted fused compounds of Formula I



I

which are useful as herbicides, and their agriculturally suitable compositions, as well as methods for their use as general or selective preemergent or postemergent herbicides or as plant growth regulants.

12 Claims, No Drawings

SUBSTITUTED FUSED HETEROCYCLIC HERBICIDES

CROSS-REFERENCE TO RELATED APPLICATION

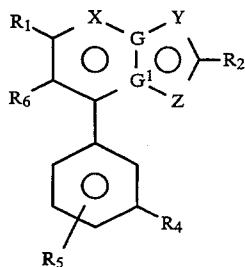
This application is a continuation-in-part of application Serial No. 07/617,707, filed Nov. 26, 1990, now U.S. Pat. No. 5,110,347, granted May 5, 1992.

BACKGROUND OF THE INVENTION

This invention relates to certain substituted fused heterocyclic compounds which are useful as herbicides and their agriculturally suitable compositions as well as methods for their use as general or selective preemergent or postemergent herbicides or as plant growth regulants.

New compounds effective for controlling the growth of undesired vegetation are in constant demand. In the most common situation, such compounds are sought to selectively control the growth of weeds in useful crops such as cotton, rice, corn, wheat and soybeans, to name a few. Unchecked weed growth in such crops can cause significant losses, reducing profit to the farmer and increasing costs to the consumer. In other situations, herbicides are desired which will control all plant growth. Examples of areas in which complete control of all vegetation is desired are areas around railroad tracks, storage tanks and industrial storage areas. There are many products commercially available for these purposes, but the search continues for products which are more effective, less costly and environmentally safe.

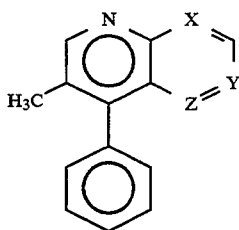
EP-A-353,902 discloses herbicidal compounds of the formula



wherein, inter alia

G and G¹ are N and C; and
X, Y and Z are independently CR⁷ or N.

Ind. J. Chem. 1980, 19 B, 1011-1013 discloses without teaching herbicidal utility compounds of the formula

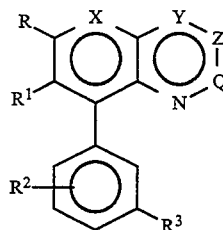


only one of X, Y, or Z can be N; otherwise CH.

SUMMARY OF THE INVENTION

This invention comprises compounds of Formula I, agriculturally suitable compositions containing them,

and their method-of-use as preemergence and/or post-emergence herbicides or plant growth regulants.



wherein

X is N or CH;

Y is N or CR⁸;

Z is N, CR⁴ or CR⁵;

Q is N, CR⁴ or CR⁵;

R is C₁-C₄ alkyl, C₂-C₄ alkoxyalkyl, C₂-C₄ alkenyl, C₂-C₄ alkynyl, C₁-C₄ alkoxy, C₁-C₄ alkylthio, C₁-C₃ alkylamino or N (C₁-C₃ alkyl) (C₁-C₃ alkyl);

R¹ is H, F, Cl or CH₃;

R² is H, halogen, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkoxy or C₁-C₃ haloalkoxy;

R³ is H, halogen, C₁-C₄ alkyl, C₂-C₄ alkenyl, C₂-C₄ alkynyl, C₁-C₄ haloalkyl, C₃-C₄ halocycloalkyl, C₂-C₄ haloalkenyl, C₂-C₄ haloalkynyl, OR⁶, S(O)_nR⁷ or CN;

R⁴ is H, CN, C₁-C₃ alkyl, C₁-C₃ alkoxy or halogen;

R⁵ is C₁-C₄ haloalkyl, C₃-C₅ halocycloalkyl, C₂-C₄ haloalkenyl, C₂-C₄ haloalkynyl, OR⁶, S(O)_nR⁷ or halogen;

R⁶ is C₁-C₄ alkyl, C₃-C₄ alkenyl, C₃-C₄ alkynyl, C₁-C₄ haloalkyl, C₂-C₄ haloalkenyl or C₂-C₄ haloalkynyl;

R⁷ is C₁-C₂ alkyl or C₁-C₂ haloalkyl;

R⁸ is H, CN, C₁-C₃ alkyl, C₁-C₃ alkoxy or halogen;

and

n is 0, 1 or 2.

and their mono N-oxides and their agriculturally suitable salts, provided that:

(a) when Z is N or CR⁴, then Q is CR⁵; and

(b) when Q is N or CR⁴, then Z is CR⁵.

In the above definitions, the term "alkyl" used either alone or in compound words such as "alkylthio" or "haloalkyl" includes straight chain or branched alkyl, e.g., methyl, ethyl, n-propyl, isopropyl or the different butyl isomers.

"Alkoxy", "alkenyl" and "alkynyl" analogously also includes straight chain or branched isomers.

"Halogen", either alone or in compound words such as "haloalkyl", means fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl" said alkyl may be partially or fully substituted with halogen atoms, which may be the same or different. Examples include CF₃, CH₂CF₃, CH₂CH₂F, CF₂CF₃ and CH₂CHFCl.

Preferred for reasons including ease of synthesis and/or greater herbicidal efficacy are:

1. Compounds of Formula I wherein

R¹ is H or F; and

R² is H or F.

2. Compounds of Preferred 1 wherein

R³ is F, Cl, Br, C₁-C₄ haloalkyl, OR⁶, S(O)_nR⁷ or CN;

n is 0;

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Y is N, CH or C—CN; and their mono N-oxides.

3. Compounds of Preferred 2 wherein

R is C₁–C₃ alkyl, C₂–C₃ alkoxyalkyl, C₂–C₃ alkenyl, C₂–C₃ alkynyl, C₁–C₂ alkoxy, C₁–C₂ alkylthio, C₁–C₂ alkylamino and N (C₁–C₂ alkyl) (C₁–C₂ alkyl);

R⁶ is C₁–C₃ alkyl, allyl, propargyl, C₁–C₃ haloalkyl, C₂–C₃ haloalkenyl.

4. Compounds of Preferred 3 wherein

Z is N, CH or C—CN.

Specifically Preferred for reasons of greatest ease of synthesis and/or greatest herbicidal efficacy are:

2-(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline;

7-methyl-3-(2,2,2-trifluoroethoxy)-5-[3-(trifluoromethyl)phenyl]-1,2,4-benzotriazine 1-oxide;

7-methyl-3-(2,2,2-trifluoroethoxy)-5-[3-(trifluoromethyl)phenyl]-1,2,4-benzotriazine; and

6-methyl-2-(trifluoromethyl)-8-[3-(trifluoromethyl)phenyl]quinoxaline.

DETAILED DESCRIPTION OF THE INVENTION

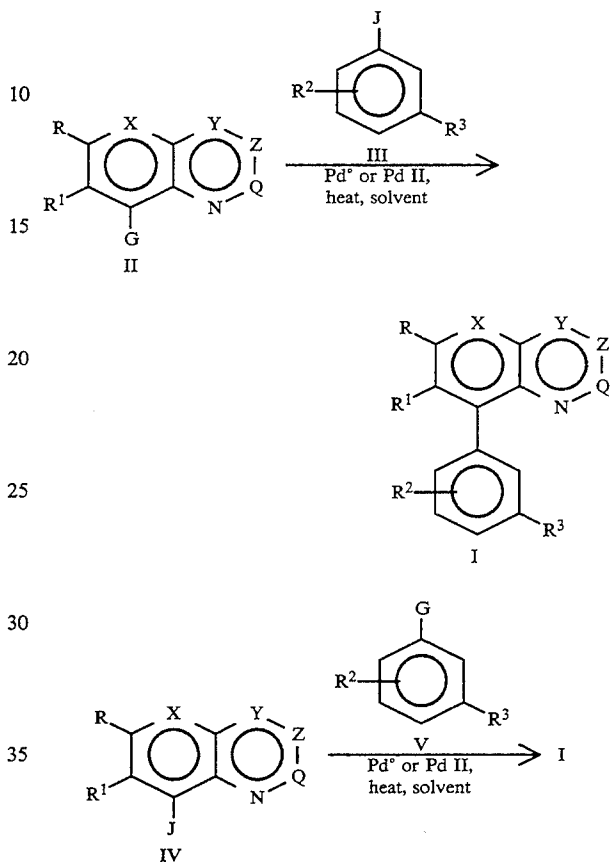
Compounds of General Formula I can be readily prepared by one skilled in the art by using the reactions and techniques described in Schemes 1–10 and Equations 1–5 of this section as well as by following the specific procedures given in Examples 1–7.

Scheme 1 illustrates the preparation of compounds of General Formula I (where R, R¹, R², R³, X, Y, Z, and Q are defined as above) whereby heterocycles of Formula II where G is bromine or iodine can be coupled with substituted aryl compounds of Formula III where J is a trialkyltin (e.g. Me₃Sn), trialkylsilyl (e.g. Me₃Si), or a boronic acid (e.g. B(OH)₂) moiety. The coupling is carried out using methods known in the art: Tsuji, *J. Organic Synthesis with Palladium Compounds*, Springer-Verlag, Berlin, 1980; Negishi, E., *Acc. Chem. Res.* 1982, 15, 340; Stille, J. K., *Angew. Chem.* 1986, 98, 504; Yamamoto, A., Yamagi, A., *Chem. Pharm. Bull.* 1982, 30, 1731 and 2003; Dondoni, A., Fogagnolo, M., Medici, A., Negrini, E., *Synthesis* 1987, 185; Dondoni, A., Fantin, G., Fogagnolo, M., Medici, A., Pedrini, P., *Synthesis* 1987, 693; Hoshino, Y., Miyaura, N., Suzuki, A., *Bull. Chem. Soc. Jpn.* 1988, 61, 3008; Sato, M., Miyaura, N., Suzuki, A., *Chem. Lett.* 1989, 1405; Miyaura, N., Yanagi, T., Suzuki, A., *Synthetic Commun.* 1981, 11, 513; Siddiqui, M. A., Snieckus, V., *Tetrahedron Lett.* 1988, 29, 5463; Sharp, M. J., Cheng, W., Snieckus, V., *Tetrahedron Lett.* 1987, 28, 5093; Hatanaka, Y., Fukushima, S., Hiyama, T., *Chem. Lett.* 1989, 1711; Bailey, T. R., *Tetrahedron Lett.* 1986, 27, 4407. The coupling of II and III is carried out by heating in the presence of a transition metal catalyst such as tetrakis(triphenylphosphine) palladium(0) or bis(triphenylphosphine) palladium(II) dichloride in a polar or nonpolar aprotic solvent such as acetonitrile or toluene. As shown in Scheme 1, compounds of General Formula I can also be prepared by coupling heterocyclic compounds of Formula IV where J is a trialkyltin (e.g. Me₃Sn), trialkylsilyl (e.g. Me₃Si), or boronic acid (e.g. B(OH)₂) moiety with aryl

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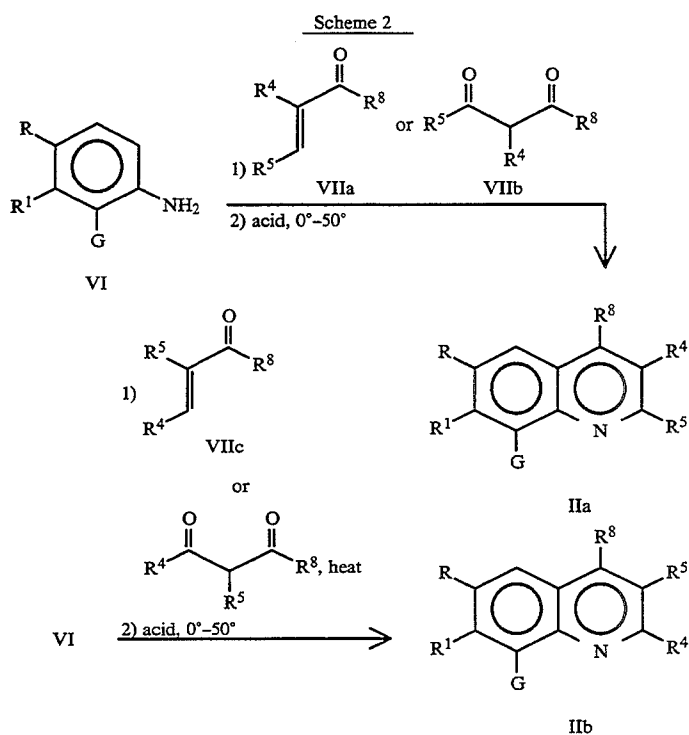
halides of Formula V where G is bromine or iodine using the same conditions as described above.

Scheme 1



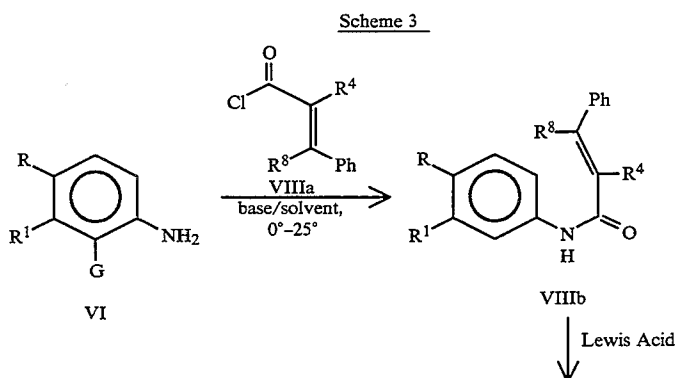
Heterocycles of Formula II can be prepared by the methods summarized in Schemes 2–10 and Equations 1–5. By methods also reported in the above cited art, treatment of heterocycles of Formula II where G is hydrogen, bromine, or iodine with base such as n-butyl lithium followed by quenching with a trialkyltin halide, trialkylsilyl halide, or trialkyl borate gives heterocyclic intermediates of Formula IV. Substituted aryl compounds of Formula III and V are either known or readily prepared by methods given in the above references.

As illustrated in Scheme 2, quinolines of Formula IIa and IIb can be prepared by reaction of anilines of Formula VI with substituted acroleins, vinyl ketones, and diketones of Formulas VIIa and VIId where R⁴ and R⁸ are hydrogen or alkyl, R⁵ is haloalkyl, haloalkenyl, haloalkynyl, or halocycloalkyl and R, R¹, and G are as previously defined. By the methods of Skrap (Chem. Ber. 1880, 13, 2086; 1882, 15, 987) and Combs (Compt. rend. 1887, 106, 142; Bull. Soc. Chim. France, 1888, 49, 90), anilines VI can be heated neat with compounds VIIa and VIId followed by treatment with a strong inorganic acid such as sulfuric acid to give IIa and IIb.

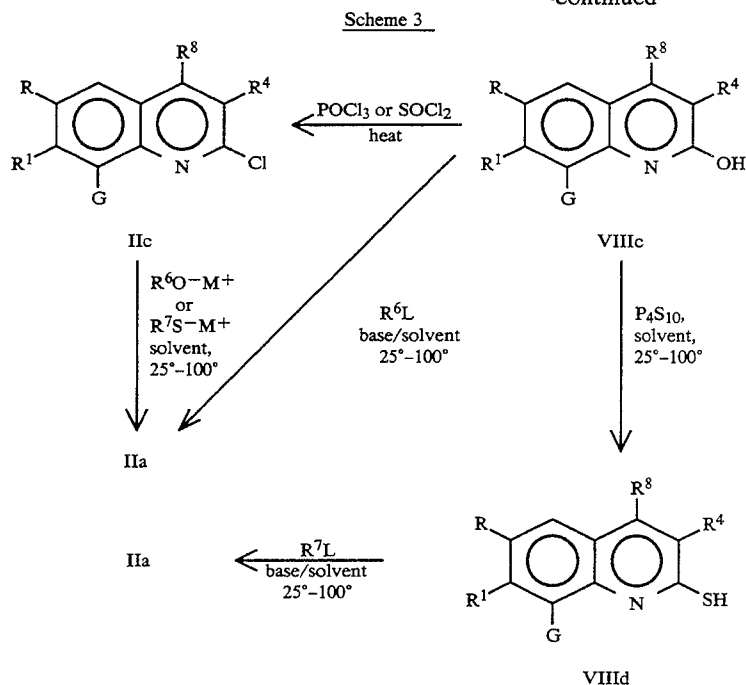


Scheme 3 illustrates the synthesis of quinolines IIa and IIc where R⁴ and R⁸ are hydrogen or alkyl, R⁵ is OR⁶, SR⁷ or chlorine, and R, R¹ and G are as defined above. Reaction of anilines of Formula VI with substituted cinnamoyl chlorides of Formula VIIa with a base such as pyridine with or without a solvent such as methylene chloride or tetrahydrofuran gives cinnamides of Formula VIIIb which can then be treated with an excess of a Lewis acid such as aluminum trichloride using the conditions of Johnston et al (*J. Chem. Soc. Perkin I* 1972, 1648) to give hydroxyquinolines of Formula VIIIc. Heating VIIIc in thionyl chloride or phosphorous oxychloride gives chloroquinolines IIc. Displacement of the chloro group with R⁶O⁻ M⁺ or R⁷S⁻ M⁺

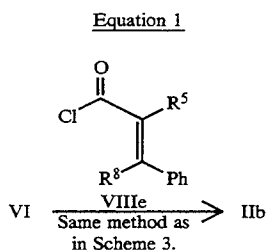
(where M is an alkali or alkaline metal such as sodium, potassium, or lithium and R⁶ and R⁷ are as previously defined) affords quinolines IIa where R⁵ is OR⁶ or SR⁷. Alkylation of VIIIc with R⁶L (where L is a leaving group such as halogen, e.g. bromine or chlorine) in the presence of a base such as triethylamine or sodium hydroxide can also give IIa where R⁵ is OR⁶. Reaction of VIIIc with phosphorous pentasulfide in a solvent such as pyridine affords mercaptopyridines of Formula VIIId which on alkylation with R⁷L (L is as described above) gives IIa where R⁵ is SR⁷. Oxidation of IIa where R⁵ is SR⁷ with an oxidizing agent such as meta-chloroperoxy-benzoic acid gives quinolines of Formula IIa where R⁵ is S(O)R⁷ or S(O)₂R⁷.



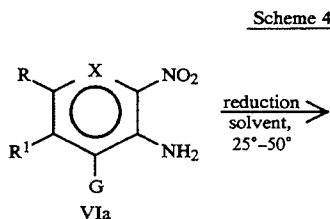
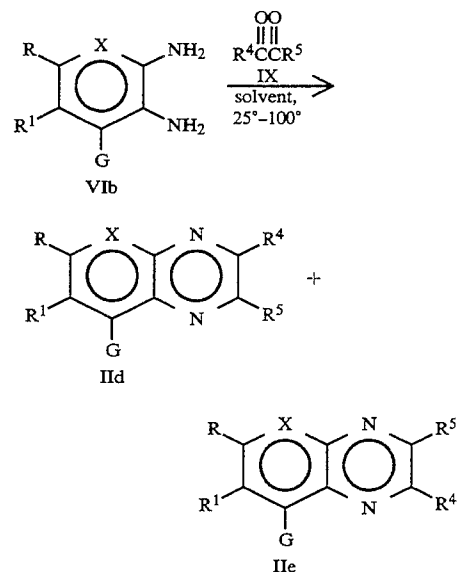
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Quinolines of Formula IIb where R^4 is alkoxy or halogen and R^5 is haloalkyl, haloalkenyl, haloalkynyl, or cyclohaloalkyl R^8 is hydrogen or alkyl and R, R^1 , and G are as defined above can be made from the starting materials VI and cinnamoyl chlorides of Formula VIIIe (Equation 1) using the same chemistry as shown in



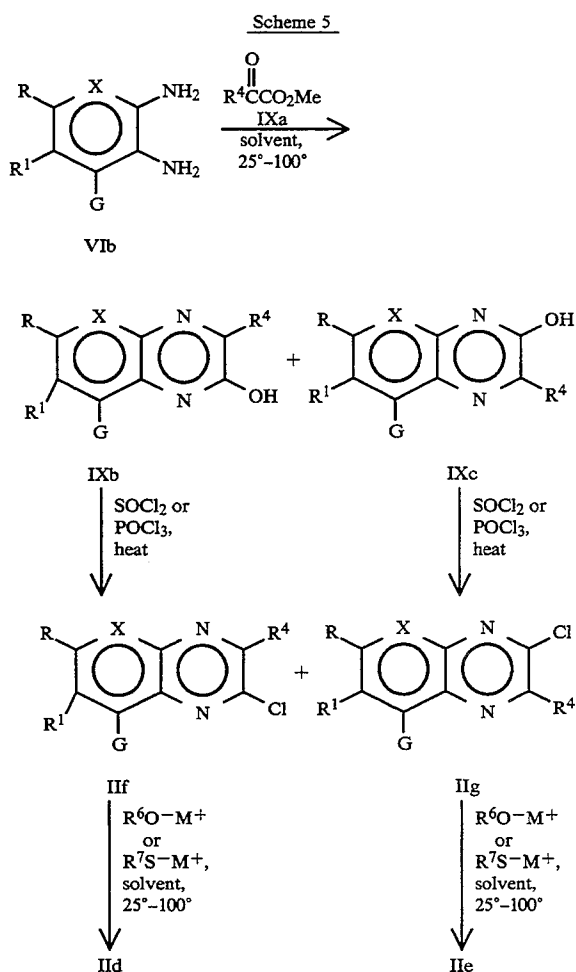
Quinoxalines and pyridopyrazines of Formula IId and IIe where X is CH or N, R^4 is hydrogen or alkyl, R^5 is haloalkyl, haloalkenyl, or haloalkynyl, and R, R^1 , and G are as previously defined can be made by the procedure shown in Scheme 4.

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Scheme 4

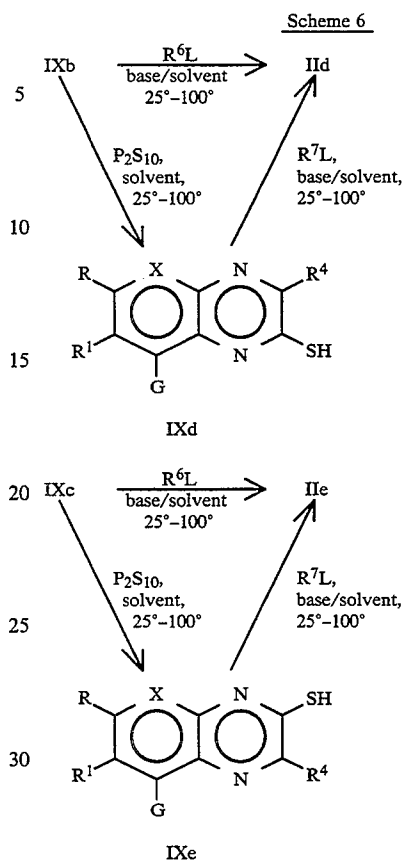
Reduction (e.g. catalytic hydrogenation with palladium on carbon in a solvent such as tetrahydrofuran or ethanol) of nitroanilines and nitropyridinyl amines of Formula VIa gives phenylenediamines and diaminopyridines of Formula rib. By the methods related to that of Jones et al (*Org. Syntheses* 1950, 30, 86), Gabriel et al (*Chem. Ber.* 1907, 40, 4850), and Bottcher (*Chem. Ber.* 1913, 46, 3084), condensation of VIb with α -diketones and α -ketoaldehydes of Formula IX in a nonpolar or polar protic or aprotic solvent such as ethanol, water, or tetrahydrofuran affords heterocycles IIc and IIe.

Schemes 5 and 6 illustrate the syntheses of quinoxalines and pyridopyrazines of Formula IIc and IIe where R^5 is halogen, OR^6 or SR^7 and X, R, R^1, R^4 , and G are

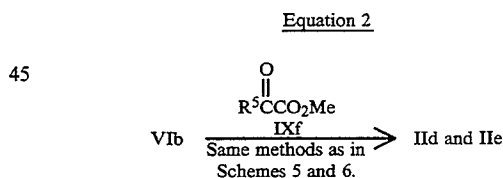
defined as above. Condensation of compounds of Formula VIb with α -aldo and α -ketoesters of Formula IXa (Scheme 5) by a method similar to that of Hinsberg (*Chem. Ber.* 1884, 18, 228) in a polar protic or aprotic solvent such as ethanol, water or tetrahydrofuran gives hydroxyheterocycles of Formula IXb and IXc. Ethyl ester analogs of IXa can also be readily used in this condensation. Treatment of these hydroxyheterocycles with thionyl chloride or phosphorous oxychloride gives the chloroheterocycles IIc and IIe. Displacement of the chloro substituent with $R^6O^-M^+$ or $R^7S^-M^+$ (where M is an alkali or alkaline metal such as sodium, potassium, or lithium) yields compounds IId and IIE (where R^5 is OR^6 or SR^7).



Scheme 6 demonstrates that hydroxyheterocycles IXb and IXc can also be converted to compounds IId and IIE using similar chemistry as that shown in Scheme 3. Preparation of compounds IId and IIE where R^5 is R^7S involve making intermediate mercaptoheterocycles IXd and IXe.

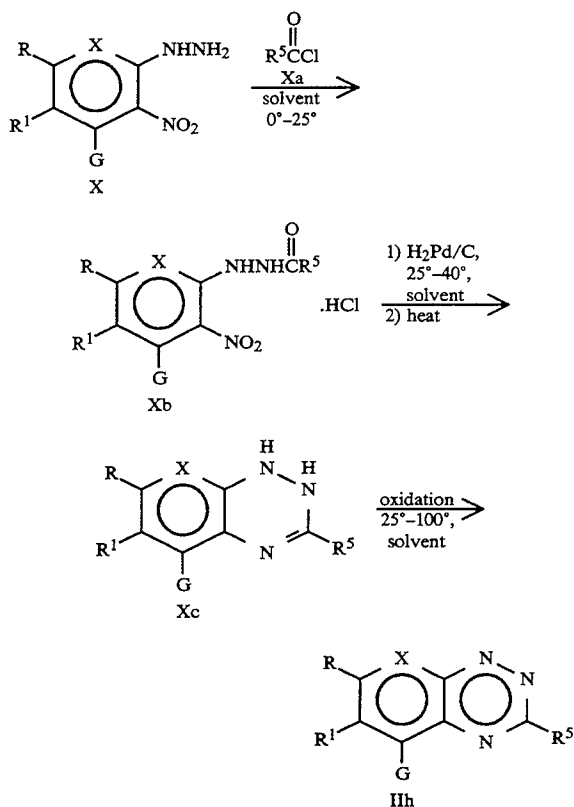


Equation 2 illustrates that compounds IId and IXe where R^4 is alkoxy and R^5 is haloalkyl, halocycloalkyl, haloalkenyl, or haloalkynyl and R, R^1 , X, and G are as defined above can be made from the starting materials VIb and the α -ketoesters IXf using the same chemistry as that in Schemes 5 and 6.



By a method similar to that reported by Reich et al (*J. Med. Chem.* 1989, 32, 2474), Scheme 7 summarizes the preparation of benzotriazines and pyridotriazines of Formula IIIh where R^5 is haloalkyl, halocycloalkyl, haloalkenyl, or haloalkynyl and R, R^1 , G, and X are as defined above. Reaction of nitrophenyl hydrazines and nitropyridinyl hydrazines of Formula X with an acid chloride of Formula Xa in a polar protic or aprotic solvent such as ethanol or acetonitrile gives hydrazide hydrochlorides of Formula Xb which can undergo catalytic hydrogenation using palladium on carbon or other suitable transition metal catalyst in a polar protic solvent such as ethanol followed by heating to give heterocycles of Formula Xc. Oxidation of Xc with an appropriate oxidizing agent in a suitable medium, e.g. manganese dioxide in aqueous sodium hydroxide or potassium ferricyanide in aqueous ammonium hydroxide, affords IIIh.

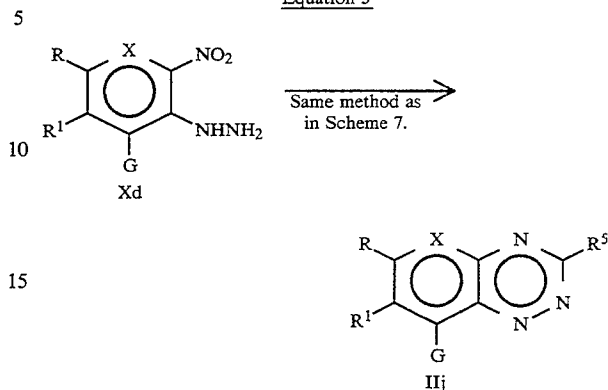
Scheme 7



By the same technique demonstrated in Scheme 7, nitrophenyl hydrazines and nitropyridinyl hydrazines of Formula Xd (Equation 3) can be converted to hetero-

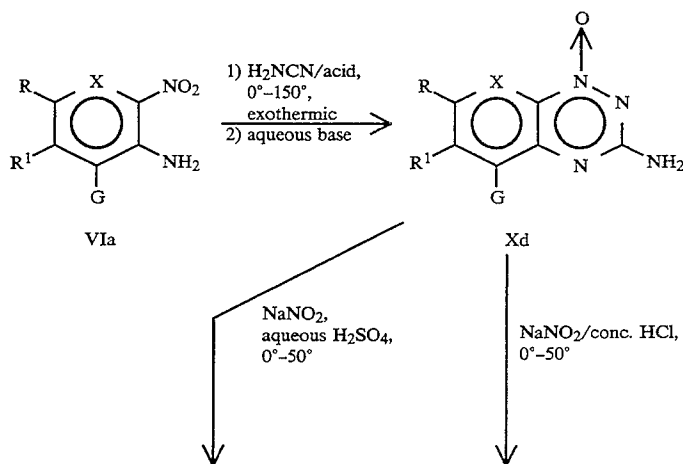
cycles of Formula IIj which are regioisomeric with IIIh.

Equation 3

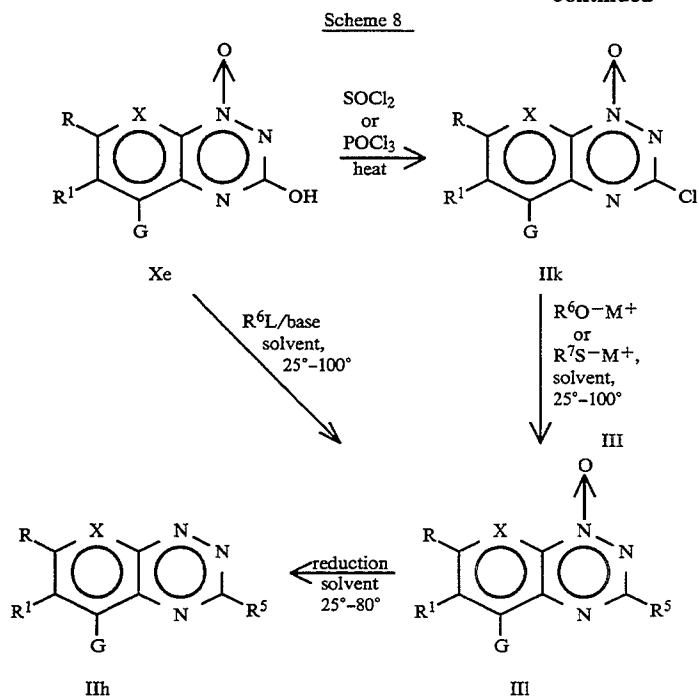


Scheme 8 illustrates the preparation of benzotriazines and pyridotriazines of Formula IIIh and their N-oxides IIIk and IIIl where R⁵ is halogen, OR⁶, or SR⁷ and R, R¹, X, and G are as previously defined. Using the conditions of Wolf et al (*J. Org. Chem.* 1954, 76, 3551), reaction of VIa with cyanamide in an acid medium such as a mixture of concentrated hydrochloric and acetic acid (extremely exothermic) followed by heating with aqueous base, e.g. sodium hydroxide, provides aminoheterocyclic N-oxides of Formula Xd. Diazotization with sodium nitrite in aqueous sulfuric acid gives hydroxyheterocycles Xe and diazotization in concentrated hydrochloric acid yields chloroheterocycles IIIk. By chemistry previously discussed in Scheme 3, IIIl can be obtained from both Xe and IIIk. Reduction of the N-oxides IIIl, e.g. catalytic hydrogenation over palladium, afford IIIh. N-oxides IIIl can also be coupled directly with III to give N-oxides of I.

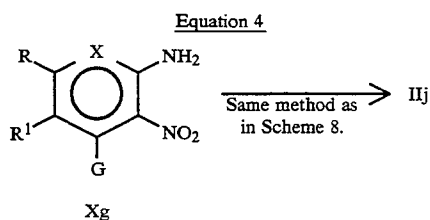
Scheme 8



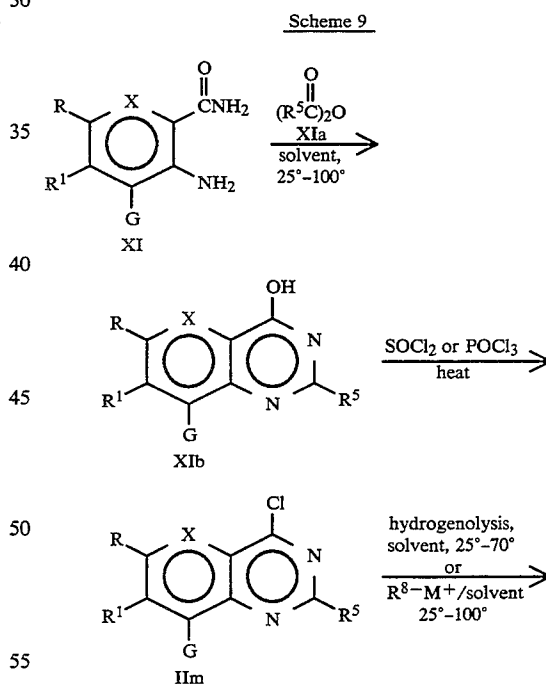
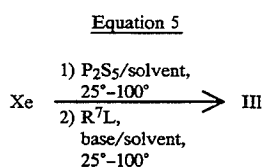
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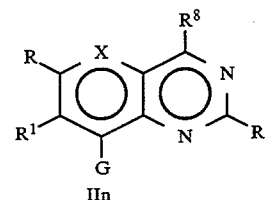
Regioisomeric benzotriazines and pyridotriazines of Formula IIj (Equation 4) and their N-oxides where R⁵ is halogen, OR⁶, or SR⁷ and R, R¹, G, and X are as defined previously, can be obtained by starting with nitroanilines and nitropyridinylamines of Formula Xg and applying the chemistry shown in Scheme 8.



By the methods illustrated in Scheme 3, compounds Xe (Scheme 8) can be converted to compounds of Formula III as shown in Equation 5.



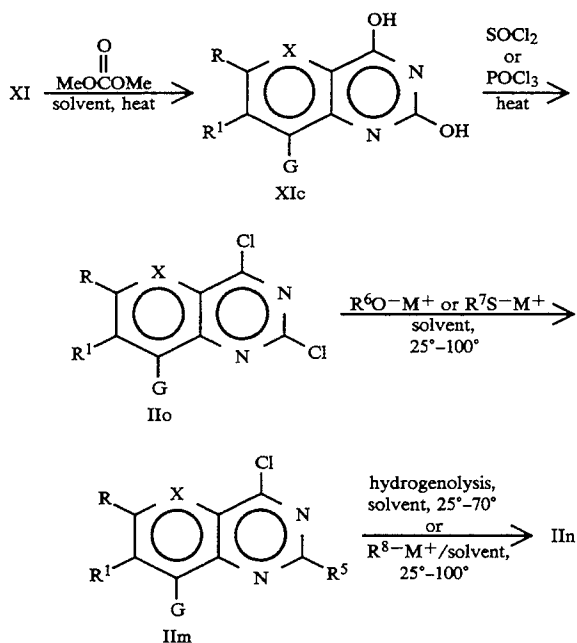
Scheme 9 demonstrates the synthesis of heterocycles of Formula IIm and IIn (where R⁵ is haloalkyl, halocycloalkyl, haloalkenyl, or haloalkynyl and other groups defined as indicated above) from amino compounds XI and anhydrides of Formula XIa. The chemistry is related to that described in previous schemes. Hydrogenolysis e.g. catalytic using palladium on carbon, or displacement with R⁸-M⁺ (where R⁸ is alkoxy, CN, or alkyl) of the chloro group of IIm affords IIn where R⁸ is hydrogen, alkoxy, CN, or alkyl.



Preparation of compounds of Formula IIo, IIm, and IIn where R⁵ is halogen, OR⁶ or SR⁷ and the remaining groups are as previously defined is shown in Scheme 10.

The chemistry in Scheme 10 is similar to that described in previous schemes.

Scheme 10



Cinnolines of Formula II where X is CH, Y is CR⁸, Z is CR⁵ and Q is N, (other substituents as previously defined) can be prepared by the methods reviewed by Elderfield (*Heterocyclic Compounds*, John Wiley & Sons, 1957, Volume 6, Chapter 5) and used in conjunction with procedures provided in the previous schemes.

N-oxides of compounds of Formula I can be made by treating compounds of Formula X with an oxidizing agent such as meta-peroxybenzoic acid in an appropriate solvent such as methylene chloride. Salts of Formula I can also be prepared by treating compounds of Formula I with a suitable acid such as hydrochloric acid.

EXAMPLE 1

Preparation of 3-(trifluoromethyl)phenyltrimethylstannane

To 20.0 g (88.9 mmol) of meta-bromobenzotrifluoride stirring in 200 ml of tetrahydrofuran at 78° C., 61.2 ml of 1.6M n-butyl lithium (97.9 mmol) in hexane was added dropwise. After stirring the reaction 10 minutes at -78° C., 19.5 g (97.8 mmol) of trimethyltin chloride dissolved in 30 ml of tetrahydrofuran was added dropwise and the mixture stirred for 10 minutes at -78° C. before allowing to warm to room temperature. The reaction mixture was quenched with excess saturated sodium bicarbonate and extracted with ethyl acetate (300 ml). The extract was washed with saturated sodium bicarbonate and brine, dried over magnesium sulfate, and evaporated in vacuo to give a crude yield of 20.2 g of the above product, isolated as a oily semi-solid. This aryl stannane was used directly as a crude material in the coupling reactions with heterocycles of Formula II.

EXAMPLE 2

Preparation of 6-Methyl-2-(2,2,2-trifluoroethoxy)-8-[3-(trifluoromethyl)phenyl]quinoline

To 25.0 g (134.4 mmol) of 2-bromo-4-methylaniline stirring in 100 ml of pyridine at 0° C., 29.1 g (174.7 mmol) of cinnamoyl chloride was added dropwise. The mixture was allowed to warm to room temperature and stirred as a thick suspension for 1 h. Methylene chloride (400 ml) and excess 5% hydrochloric acid was added. The organic layer was separated, washed with 5% hydrochloric acid (2 X), water and brine, dried over magnesium sulfate, and evaporated in vacuo. To the residue, n-butyl chloride was added and a solid filtered and dried to give a 33.8 g yield of N-2-bromo-4-methylphenyl cinnamide, m.p. 148-149° C. (ethyl acetate).

A mixture of 15.0 g (47.5 mmol) of the above prepared N-2-bromo-4-methylphenyl cinnamide and 18.9 g (142.1 mmol) of aluminum trichloride was heated as a melt at about 100° C. for 1.25 h. The viscous syrup was poured onto ice and the resulting aqueous mixture stirred 10 minutes and extracted with ethyl acetate (400 ml). The organic extract was washed with water, brine, dried over magnesium sulfate, and evaporated in vacuo. To the residue was added n-butyl chloride and 5.5 g of a crude solid (8-bromo-2-hydroxy-6-methylquinoline) was filtered, dried, and taken on directly to the next step without characterization.

A 5.0 g sample of the above solid and 35 ml of phosphorous oxychloride was heated at reflux for 30 minutes. The hot mixture was poured onto excess ice and the resulting aqueous mixture extracted with 300 ml of diethyl ether. The ether extract was separated and washed with water, brine, dried over magnesium sulfate, and evaporated in vacuo to give a dark oil. Silica gel column chromatography (5:1 followed by 3:1 hexane/ethyl acetate) afforded 1.8 g of 8-bromo-2-chloro-6-methylquinoline isolated as a solid, m.p. 107-108° C. A second lower R_f material (1.1g) was also isolated on chromatography and identified as 2-chloro-6-methylquinoline, m.p. 109-111° C.

To 0.8 g of 60% sodium hydride (oil dispersion) stirring in 20 ml of tetrahydrofuran at room temperature, 2.5 ml (34.3 mmol) of 2,2,2-trifluoroethanol was added dropwise. An exotherm occurred and to the resulting solution 1.7 g (6.7 mmol) of 8-bromo-2-chloro-6-methylquinoline was added followed by heating at reflux for 7 h. Ethyl acetate (200 ml) and excess water was added and the organic layer separated and washed with water and brine, dried over magnesium sulfate, and evaporated in vacuo to give an oil. Silica gel column chromatography (20:1 followed by 10:1 hexane/ethyl acetate) afforded 1.9 g of 8-bromo-6-methyl-2-(2,2,2-trifluoroethoxy) quinoline, m.p. 61-62° C.

A mixture of 1.5 g (6.2 mmol) of 8-bromo-6-methyl-2-(2,2,2-trifluoroethoxy) quinoline, 2.3 g of crude 3-(trifluoromethyl) phenyltrimethylstannane (Example 1), and 0.2 g of tetrakis (triphenylphosphine)palladium(O) was heated in 30 ml of toluene at reflux with stirring for 3 hours. Ethyl acetate (200 ml) and excess water was added. The organic layer was separated, washed with water and brine, dried over magnesium sulfate, and evaporated in vacuo to give an oil. Silica gel column chromatography (20:1 followed by 10:1 hexane/ethyl acetate) afforded 0.7 g of product, isolated as an oil.

NMR(CDC₃): ppm 2.55 (s, 3H), 4.71 (q, 2H), 7.15 (d, 1), 7.5–8.15 (m, 7H).

EXAMPLE 3

Preparation of

6-Methyl-2-(2,2,2-trifluoroethoxy)-8-[3-(trifluoromethyl)phenyl]quinoxaline and

6-Methyl-3-(2,2,2-trifluoroethoxy)-8-[3-(trifluoromethyl)phenyl]quinoxaline

A mixture of 22.0 g (92.2 mmol) of 2-bromo-4-methyl-6-nitroaniline and catalytic amount of 10% palladium on carbon in 120 ml of tetrahydrofuran was placed on a Paar hydrogenator for 6 h at room temperature at 50–40 psi. The reaction mixture was filtered through celite and to the filtrate was added dropwise 50.0 ml of 50% glyoxylic acid. The resulting suspension was stirred at room temperature overnight, the insoluble material filtered, washed with water and ethyl acetate, and oven dried to yield 8.5 g of a mixture of 8-bromo-2-hydroxy-6-methylquinoxaline and 8-bromo-3-hydroxy-6-methylquinoxaline.

A 5.0 g (20.9 mmol) sample of the above mixture of 2- and 3-hydroxyquinoxalines was heated in 30 ml of thionyl chloride containing a few drops of dimethylformamide. The reaction was heated at reflux for 1.5 h and the resulting solution, which gradually formed on heating, was poured carefully onto ice. The aqueous mixture was extracted with ethyl acetate (250 ml) and the separated organic layer washed with water (2X) and brine, dried over magnesium sulfate, and evaporated in vacuo (not to dryness) to give a wet yellow solid residue. Hexane was added and the mixture stirred several minutes before filtering to give 2.1 g of only 8-bromo-3-chloro-6-methyl-quinoxaline. Evaporating the hexane filtrate to dryness gave another 3.2 g of a crude solid which was roughly a 1:1 mixture of 8-bromo-2-chloro-6-methyl-quinoxaline and 8-bromo-3-chloro-6-methyl-quinoxaline.

To 0.46 g of 60% sodium hydride (oil dispersion) stirring in 20 ml of tetrahydrofuran, was added dropwise 1.54 ml of 2,2,2-trifluoroethanol followed by the addition of 1.8 g of the above crude mixture of quinoxalines. The reaction mixture was heated at reflux 45 minutes. Glacial acetic acid (2.0 ml) and excess water was added and the aqueous mixture extracted with ethyl acetate. The separated organic layer was washed with water, saturated sodium bicarbonate and brine, dried over magnesium sulfate, and evaporated in vacuo to give 2.4 g of an oily solid residue which was taken on directly to the next step.

A stirred mixture of 2.4 g of the above oily solid residue, 4.5 g of crude 3-(trifluoromethyl)-phenyltrimethylstannane (Example 1), and 0.2 g of tetrakis(triphenylphosphine)palladium(O) was heated in 30 ml of toluene for 4 h. The reaction mixture was concentrated to dryness in vacuo and the residue flash chromatographed on silica gel (40:1 hexane/ethyl acetate) to give 0.7 g of 6-methyl-3-(2,2,2-trifluoroethoxy)-8-[3-(trifluoromethyl)phenyl]quinoxaline (first to elute, m.p. 114°–117° C.) and 0.8 g of 6-methyl-2-(2,2,2-trifluoroethoxy)-8-[3-(trifluoromethyl)phenyl]quinoxaline (m.p. 46°–48° C.).

EXAMPLE 4

Preparation of

2-Methoxy-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline and

3-Methoxy-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline

To 2.3 g of a crude sample mixture of 8-bromo-2-chloro-6-methylquinoxaline and 8-bromo-3-chloro-6-methylquinoxaline (prepared as in Example 3) stirring in 20 ml of methanol, 6.3 ml of a 25 weight % of sodium methoxide in methanol was added and the mixture heated at reflux for 1 h. Glacial acetic acid (3.0 ml), 200 ml of ethyl acetate, and excess water was added. The separated organic layer was washed with saturated sodium bicarbonate, brine; dried over magnesium sulfate, and evaporated in vacuo to give 2.0 g of an oily solid residue which was taken on directly to the next step.

A stirred mixture of the above oily solid residue, 3.2 g of crude 3-(trifluoromethyl)phenyltrimethylstannane (Example 1), and 0.2 g of tetrakis(triphenylphosphine)palladium(O) were heated in 35 ml of toluene at reflux for 8 h. In vacuo, the reaction mixture was evaporated to dryness and the residue flash chromatographed on silica gel (1:1 hexane/n-butyl chloride followed by straight n-butyl chloride) to give 0.4 g of 3-methoxy-5-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline (first product isomer to elute, m.p. 141°–142° C.) and 0.5 g of 2-methoxy-5-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline (m.p. 119°–121° C.).

EXAMPLE 5

Preparation of

2-(Difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline and

3-(Difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline

To a suspension of 5.0 g (20.9 mmol) of the above isomer mixture of 8-bromo-2-hydroxy-6-methylquinoxaline and 8-bromo-3-hydroxy-6-methylquinoxaline (prepared as in Example 3) and 9.0 g (27.1 mmol) of tetra-n-butylammonium bromide stirring in 150 ml of dioxane, 20 g (250.0 mmol) of 50% aqueous sodium hydroxide were added. The reaction mixture was placed under an atmosphere of chlorodifluoromethane (Freon-22*) whereby slight pressure was maintained by having a balloon over the reaction flask. A slow exotherm occurred and the mixture stirred 4 h. Excess water and 300 ml of diethyl ether were added. The separated organic extract was washed with water, brine, dried over magnesium sulfate, and evaporated in vacuo to give an oil residue which quickly solidified. Hexane was added, the mixture stirred several minutes, and filtered to give 3.1 g of 8-bromo-3-difluoromethoxy-6-methylquinoxaline. Evaporating the filtrate gave 2.5 g of a crude isomer mixture of 8-bromo-2-difluoromethoxy-6-methylquinoxaline and 8-bromo-3-difluoromethoxy-6-methylquinoxaline.

A stirred mixture of 1.5 g (5.2 mmol) of the above 2- and 3-difluoromethoxyquinoxaline isomer mixture, 4.0 g of crude 3-(trifluoromethyl)phenyltrimethylstannane (Example 1), and 0.2 g of tetrakis(triphenylphosphine)palladium(O) was heated at reflux for 16 h. The reaction mixture was evaporated in vacuo and the residue flash chromatographed on silica gel (9:1 followed by 1:1 hexane/n-butyl chloride) to afford 0.51 g of 3-(di-

fluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)-phenyl]quinoxaline (first product isomer to elute, m.p. 105°–106° C.) and 0.4 g of 2-(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline (m.p. 103°–104° C.).

EXAMPLE 6

Preparation of

6-Methyl-2-(trifluoromethyl)-8-[3-(trifluoromethyl)-phenyl]quinoxaline and
6-Methyl-3-(trifluoromethyl)-8-[3-(trifluoromethyl)-phenyl]quinoxaline

A mixture of 20.0 g (86.6 mmol) of 2-bromo-4-methyl-6-nitroaniline and a catalytic amount of 10% palladium on carbon in 100 ml of tetrahydrofuran was placed on a Paar hydrogenator at room temperature at 50–40 psi for 6 h. The reaction mixture was filtered through celite which was then washed with ethyl acetate. A total of 300 ml of ethyl acetate was added to the filtrate which was washed with water, brine, dried over magnesium sulfate and evaporated in vacuo to give a dark oily semi-solid. Flash column silica gel chromatography (methylene chloride followed by 2:1 hexane/ethyl acetate) afforded 17.0 g of the main component: 3-bromo-5-methyl-ortho-phenylenediamine. The chromatographed product, which still contained some minor impurities, was used directly in the next step. It was initially a dark oil which solidified.

To 10.0 g (37.0 mmol) of 1,1-dibromo-3,3,3-trifluoroacetone stirring in 50 ml of water, 8.0 g (97.6 mmol) of anhydrous sodium acetate was added and the stirred mixture heated near reflux for 45 minutes followed by stirring at ambient temperature for 30 minutes. A 4.0 g (20.0 mmol) sample of the above phenylenediamine was added and the mixture stirred 2 h. Excess water and 250 ml of ethyl acetate was added and the separated organic extract washed with 5% hydrochloric acid, brine, dried over magnesium sulfate, and evaporated in vacuo to give dark oil. Flash column silica gel chromatography (40:1 followed by 30:1 hexane/ethyl acetate) afforded 4.3 g of a mixture (two close migrating spots) of 8-bromo-6-methyl-2-trifluoromethylquinoxaline and 8-bromo-6-methyl-3-trifluoromethylquinoxaline, isolated as a solid which melted at 69°–71° C.

A starred mixture of 2.0 g (6.9 mmol) of the above quinoxaline isomers, 4.2 g of crude 3-(trifluoromethyl)-phenyltrimethylstannane, and 0.2 g of tetrakis(triphenylphosphine)palladium(O) were heated in 30 ml of toluene for 6 h. Additional stannane (about 0.5 g) and palladium catalyst (0.1 g) were added and the reaction heated another 6 h. The reaction mixture was evaporated in vacuo to dryness and the residue flash chromatographed (4:1 followed by 1:1 hexane/n-butyl chloride followed in turn by 100% n-butyl chloride) to afford 0.2 g of 6-methyl-3-(trifluoromethyl)-8-[3-(trifluoromethyl)-phenyl]quinoxaline (first product isomer to elute, m.p. 93°–94° C.) and 1.08 g of 6-methyl-2-(trifluoro-methyl)-8-[3-(trifluoromethyl)phenyl]quinoxaline (m.p. 117°–118° C.).

EXAMPLE 7

7-Methyl-3-(2,2,2-trifluoroethoxy)-5-[3-(trifluoromethyl)phenyl]-1,2,4-benzotriazine-1-oxide and
7-Methyl-3-(2,2,2-trifluoroethoxy)-5-[3-(trifluoromethyl)phenyl]1,2,4-benzotriazine

To 13.0 g (56.3 mmol) of 2-bromo-4-methyl-6-nitroaniline stirring in a mixture of 25 ml glacial acetic

acid and 5 ml of concentrated hydrochloric acid at 80° C., 29.0 g (690.5 mmol) of cyanamide and 25 ml of concentrated hydrochloric acid were added simultaneously, separately, and very slowly. At one point during the addition, a vigorous exotherm occurred and the external heat immediately removed. After the addition, the reaction was heated at reflux for 15 minutes. On cooling to about 50° C., 100 ml of 25% aqueous sodium hydroxide were added dropwise and the mixture heated at reflux 15 minutes. The reaction was cooled to room temperature, the insoluble orange solid filtered and washed with water followed by ethyl acetate to afford 7.4 g of yellow 3-amino-5-bromo-7-methyl-1,2,4-benzotriazine-1-oxide after drying.

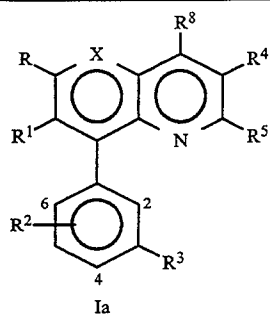
Sodium nitrite (7.0 g, 101.4 mmol) was added portionwise to a suspension of 7.0 g (27.5 mmol) of the above aminobenzotriazine-N-oxide stirring in 140 ml of concentrated hydrochloric acid at ambient temperature. The mixture was stirred overnight and heated at 60° C. for 2 h. Excess water and 400 ml of ethyl acetate were added and the separated organic layer washed with water, saturated sodium bicarbonate, brine, and dried over magnesium sulfate. Some insoluble starting aminoheterocycle was present during the extractive workup but was not attempted to be removed. Evaporating the organic extract to dryness in vacuo afforded a crude yellow solid residue which was flash chromatographed on silica gel (4:1 methylene chloride/hexane) to give 2.5 g of 5-bromo-3-chloro-7-methyl-1,2,4-benzotriazine-1-oxide, m.p. 207°–209° C.

To 0.5 g of 60% sodium hydride stirring in 30 ml of tetrahydrofuran, 3.0 ml of 2,2,2-trifluoroethanol was added dropwise at ambient temperature. A solution resulted and 2.0 g (7.29 mmol) of the above 5-bromo-3-chloro-7-methyl-1,2,4-benzotriazine-1-oxide was added and at ambient temperature and the mixture stirred 2 h. Ethyl acetate (200 ml) and excess water were added and the separated organic extract washed with water, brine, and dried over magnesium sulfate. The solvent was removed in vacuo, hexane added to the residue, and the suspended yellow solid filtered and dried to afford 1.7 g of 5-bromo-7-methyl-3-(2,2,2-trifluoroethoxy)-1,2,4-benzotriazine-1-oxide, m.p. 127°–128° C.

A stirred mixture of 1.3 g (3.84 mmol) of the above benzotriazine N-oxide, 1.4 g of crude 3-(trifluoromethyl)phenyltrimethylstannane, and 0.2 g of tetrakis(triphenylphosphine)palladium(O) were heated in 35 ml of toluene at reflux for 4 h. The reaction mixture was evaporated in vacuo to dryness and the residue flash chromatographed on silica gel (1:1 hexane/n-butyl chloride followed by 100% n-butyl chloride) to give 0.8 g of 7-methyl-3-(2,2,2-trifluoroethoxy)-5-[3-(trifluoromethyl)phenyl]-1,2,4-benzotriazine-1-oxide (m.p. 168°–169° C.) and 0.24 g of 7-methyl-3-(2,2,2-trifluoroethoxy)-5-[3-(trifluoromethyl)phenyl]-1,2,4-benzotriazine (m.p. 140°–141°).

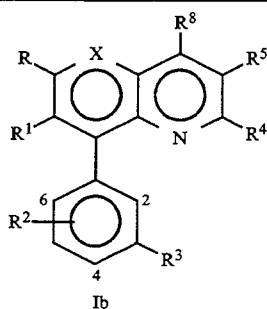
Using the procedures outlined in Schemes 1–10, Equations 1–5, and Examples 1–7, the compounds of Tables I–VIII and the Table of Compounds can readily be prepared by one skilled in the art.

TABLE I



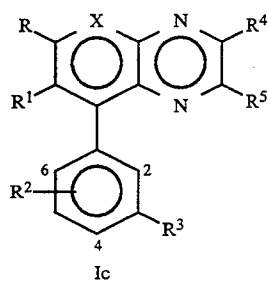
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CH	n-Pr	H	H	CF ₃	H	CF ₃	H
CH	Me	H	H	OCF ₃	H	CF ₃	H
CH	Et	H	H	OCF ₃	H	CF ₃	H
CH	n-Pr	H	H	OCF ₃	H	CF ₃	H
CH	Me	H	H	OCHF ₂	H	CF ₃	H
CH	Me	H	H	OCF ₃	H	OCHF ₂	H
CH	Me	H	H	CF ₃	H	OCHF ₂	H
CH	Me	F	H	CF ₃	H	CF ₃	H
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CH	Et	H	H	CN	H	CF ₃	H
CH	Me	H	H	SCF ₃	H	CF ₃	H
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TABLE II



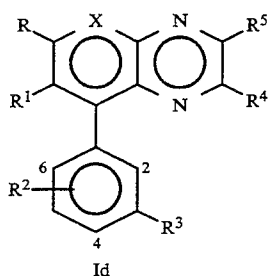
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TABLE III



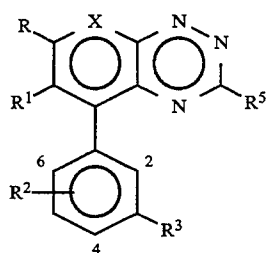
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CH	Me	H	H	CF ₃	H	CF ₃
CH	Et	H	H	CF ₃	H	CF ₃
CH	n-Pr	H	H	CF ₃	H	CF ₃
CH	Me	H	H	OCF ₃	H	CF ₃
CH	Et	H	H	OCF ₃	H	CF ₃
CH	n-Pr	H	H	OCF ₃	H	CF ₃
CH	Me	H	H	OCHF ₂	H	CF ₃
CH	Me	H	H	OCF ₃	H	OCHF ₂
CH	Me	H	H	CF ₃	H	OCHF ₂
CH	Me	F	H	CF ₃	H	CF ₃
CH	Me	H	6-F	CF ₃	H	CF ₃
CH	Me	H	4-F	CF ₃	H	CF ₃
CH	Me	H	2-OMe	CF ₃	H	CF ₃
CH	Me	H	2-CF ₃	H	H	CF ₃
CH	Me	H	H	Cl	H	CF ₃
CH	Et	H	H	CF ₃	H	OCHF ₂
CH	Me	H	H	Br	H	CF ₃
CH	Me	H	H	CN	H	CF ₃
CH	Et	H	H	CN	H	CF ₃
CH	Me	H	H	SCF ₃	H	CF ₃
CH	Me	H	H	H	H	CF ₃
CH	Me	H	H	CF ₃	H	OCH ₂ CF ₃
CH	Me	H	H	CF ₃	H	SCF ₃
CH	Me	H	H	CF ₃	H	OMe
CH	Et	H	H	CF ₃	H	OEt
CH	Me	H	H	CF ₃	H	OCHMe ₂
CH	Me	H	H	CF ₃	H	SMe
CH	Me	H	H	CF ₃	H	CHF ₂
CH	Et	H	H	CF ₃	H	CHF ₂
CH	Me	H	H	OCF ₃	H	CHF ₂
CH	Me	H	H	CF ₃	H	OCF ₂ CHF ₂
CH	Me	H	H	CF ₃	H	Cl
CH	MeCH=CH	H	H	CF ₃	H	CF ₃
CH	Me	H	H	CF ₃	H	CH=CHCF ₃
CH	Me	H	H	CF ₃	H	OCHF ₂
CH	Et	H	H	CF ₃	H	OCHF ₂
CH	MeOCH ₂	H	H	CF ₃	H	CF ₃
CH	Me ₂ N	H	H	CF ₃	H	CF ₃
CH	MeNH	H	H	CF ₃	H	CF ₃
CH	Me	H	H	OMe	H	CF ₃
CH	Me	H	H	CF ₃	H	SCHF ₂
CH	Me	H	H	CF ₃	H	SO ₂ CHF ₂
CH	MeO	H	H	CF ₃	H	CF ₃
CH	MeS	H	H	CF ₃	H	CF ₃
CH	Me	H	H	CF ₃	Me	CF ₃
CH	Me	H	H	CF ₃	CN	CF ₃
CH	Me	H	H	CF ₃	OMe	CF ₃
CH	Me	H	H	CF ₃	Cl	CF ₃
N	Me	H	H	CF ₃	H	CF ₃
N	Et	H	H	CF ₃	H	CF ₃
N	Me	H	H	CF ₃	H	OCHF ₂
N	Et	H	H	CF ₃	H	OCHF ₂
N	Me	H	H	OCF ₃	H	CF ₃
N	Me	H	H	OCHF ₂	H	CF ₃
N	Me	H	H	CN	H	CF ₃
N	Et	H	H	CN	H	CF ₃
N	Me	H	H	OCF ₃	H	OCHF ₂
N	Me	H	H	CF ₃	H	OMe
N	Me	H	H	SCF ₃	H	CF ₃

TABLE IV



X	R	R ¹	R ²	R ³	R ⁴	R ⁵
CH	Me	H	H	CF ₃	H	CF ₃
CH	Et	H	H	CF ₃	H	CF ₃
CH	n-Pr	H	H	CF ₃	H	CF ₃
CH	Me	H	H	OCF ₃	H	CF ₃
CH	Et	H	H	OCF ₃	H	CF ₃
CH	n-Pr	H	H	OCF ₃	H	CF ₃
CH	Me	H	H	OCHF ₂	H	CF ₃
CH	Me	H	H	OCF ₃	H	OCHF ₂
CH	Me	H	H	CF ₃	H	OCHF ₂
CH	Me	F	H	CF ₃	H	CF ₃
CH	Me	H	6-F	CF ₃	H	CF ₃
CH	Me	H	4-F	CF ₃	H	CF ₃
CH	Me	H	2-OMe	CF ₃	H	CF ₃
CH	Me	H	2-CF ₃	H	H	CF ₃
CH	Me	H	H	Cl	H	CF ₃
CH	Me	H	H	Br	H	CF ₃
CH	Et	H	H	CF ₃	H	OCHF ₂
CH	Me	H	H	CN	H	CF ₃
CH	Et	H	H	CN	H	CF ₃
CH	Me	H	H	SCF ₃	H	CF ₃
CH	Me	H	H	H	H	CF ₃
CH	Me	H	H	CF ₃	H	OCH ₂ CF ₃
CH	Me	H	H	CF ₃	H	SCF ₃
CH	Me	H	H	CF ₃	H	OMe
CH	Et	H	H	CF ₃	H	OEt
CH	Me	H	H	CF ₃	H	OCHMe ₂
CH	Me	H	H	CF ₃	H	SMe
CH	Me	H	H	CF ₃	H	CHF ₂
CH	Et	H	H	CF ₃	H	CHF ₂
CH	Me	H	H	OCF ₃	H	CHF ₂
CH	Me	H	H	CF ₃	H	OCF ₂ CHF ₂
CH	Me	H	H	CF ₃	H	Cl
CH	MECH=CH	H	H	CF ₃	H	CF ₃
CH	Me	H	H	CF ₃	H	CH=CHCF ₃
CH	Me	H	H	CF ₃	H	OCHF ₂
CH	Et	H	H	CF ₃	H	OCHF ₂
CH	MeOCH ₂	H	H	CF ₃	H	CF ₃
CH	Me ₂ N	H	H	CF ₃	H	CF ₃
CH	MeNH	H	H	CF ₃	H	CF ₃
CH	Me	H	H	OMe	H	CF ₃
CH	Me	H	H	CF ₃	H	SCHF ₂
CH	Me	H	H	CF ₃	H	SO ₂ CHF ₂
CH	MeO	H	H	CF ₃	H	CF ₃
CH	MeS	H	H	CF ₃	H	CF ₃
CH	Me	H	H	CF ₃	Me	CF ₃
CH	Me	H	H	CF ₃	CN	CF ₃
CH	Me	H	H	CF ₃	OMe	CF ₃
CH	Me	H	H	CF ₃	Cl	CF ₃
N	Me	H	H	CF ₃	H	CF ₃
N	Et	H	H	CF ₃	H	CF ₃
N	Me	H	H	CF ₃	H	OCHF ₂
N	Et	H	H	CF ₃	H	OCHF ₂
N	Me	H	H	OCF ₃	H	CF ₃
N	Me	H	H	OCHF ₂	H	CF ₃
N	Me	H	H	CN	H	CF ₃
N	Et	H	H	CN	H	CF ₃
N	Me	H	H	OCF ₃	H	OCHF ₂
N	Me	H	H	CF ₃	H	OMe
N	Me	H	H	SCF ₃	H	CF ₃

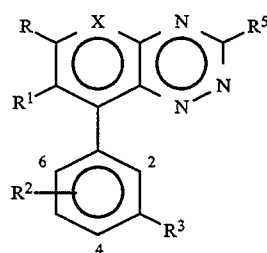
TABLE V



Ie

X	R	R ¹	R ²	R ³	R ⁵
CH	Me	H	H	CF ₃	CF ₃
CH	Et	H	H	CF ₃	CF ₃
CH	n-Pr	H	H	CF ₃	CF ₃
CH	Me	H	H	OCF ₃	CF ₃
CH	Et	H	H	OCF ₃	CF ₃
CH	n-Pr	H	H	OCF ₃	CF ₃
CH	Me	H	H	OCHF ₂	CF ₃
CH	Me	H	H	OCF ₃	OCHF ₂
CH	Me	H	H	CF ₃	OCHF ₂
CH	Me	F	H	CF ₃	CF ₃
CH	Me	H	6-F	CF ₃	CF ₃
CH	Me	H	4-F	CF ₃	CF ₃
CH	Me	H	2-OMe	CF ₃	CF ₃
CH	Me	H	2-CF ₃	H	CF ₃
CH	Me	H	H	Cl	CF ₃
CH	Et	H	H	CF ₃	OCHF ₂
CH	Me	H	H	Br	CF ₃
CH	Me	H	H	CN	CF ₃
CH	Et	H	H	CN	CF ₃
CH	Me	H	H	SCF ₃	CF ₃
CH	Me	H	H	H	CF ₃
CH	Me	H	H	CF ₃	OCH ₂ CF ₃
CH	Me	H	H	SCF ₃	SCF ₃
CH	Me	H	H	CF ₃	OMe
CH	Et	H	H	CF ₃	OEt
CH	Me	H	H	CF ₃	OCHMe ₂
CH	Me	H	H	CF ₃	SMe
CH	Me	H	H	CF ₃	CHF ₂
CH	Et	H	H	CF ₃	CHF ₂
CH	Me	H	H	OCF ₃	CHF ₂
CH	Me	H	H	CF ₃	OCF ₂ CHF ₂
CH	Me	H	H	CF ₃	Cl
CH	MeCH=CH	H	H	CF ₃	CF ₃
CH	Me	H	H	CF ₃	CH=CHCF ₃
CH	Me	H	H	CF ₃	OCHF ₂
CH	Et	H	H	CF ₃	OCHF ₂
CH	MeOCH ₂	H	H	CF ₃	CF ₃
CH	Me ₂ N	H	H	CF ₃	CF ₃
CH	MeNH	H	H	CF ₃	CF ₃
CH	Me	H	H	OMe	CF ₃
CH	Me	H	H	CF ₃	SCHF ₂
CH	Me	H	H	CF ₃	SO ₂ CHF ₂
CH	MeO	H	H	CF ₃	CF ₃
CH	MeS	H	H	CF ₃	CF ₃
N	Me	H	H	CF ₃	CF ₃
N	Et	H	H	CF ₃	CF ₃
N	Me	H	H	CF ₃	OCHF ₂
N	Et	H	H	CF ₃	OCHF ₂
N	Me	H	H	OCF ₃	CF ₃
N	Me	H	H	OCHF ₂	CF ₃
N	Me	H	H	CN	CF ₃
N	Et	H	H	CN	CF ₃
N	Me	H	H	OCF ₃	OCHF ₂
N	Me	H	H	CF ₃	OMe
N	Me	H	H	SCF ₃	CF ₃

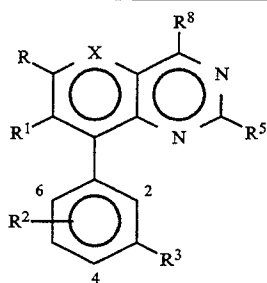
TABLE VI



If

5	X	R	R ¹	R ²	R ³	R ⁵
10	CH	Me	H	H	CF ₃	CF ₃
	CH	Et	H	H	CF ₃	CF ₃
	CH	n-Pr	H	H	CF ₃	CF ₃
	CH	Me	H	H	OCF ₃	CF ₃
20	CH	Et	H	H	OCF ₃	CF ₃
	CH	n-Pr	H	H	OCF ₃	CF ₃
	CH	Me	H	H	OCHF ₂	CF ₃
	CH	Me	H	H	OCF ₃	OCHF ₂
	CH	Me	H	H	CF ₃	OCHF ₂
25	CH	Me	F	H	CF ₃	CF ₃
	CH	Me	H	6-F	CF ₃	CF ₃
	CH	Me	H	4-F	CF ₃	CF ₃
	CH	Me	H	2-OMe	CF ₃	CF ₃
	CH	Me	H	2-CF ₃	H	CF ₃
	CH	Me	H	H	Cl	CF ₃
30	CH	Et	H	H	CF ₃	OCHF ₂
	CH	Me	H	H	Br	CF ₃
	CH	Me	H	H	CN	CF ₃
	CH	Et	H	H	CN	CF ₃
	CH	Me	H	H	SCF ₃	CF ₃
35	CH	Me	H	H	H	CF ₃
	CH	Me	H	H	CF ₃	OCH ₂ CF ₃
	CH	Me	H	H	CF ₃	SCF ₃
	CH	Me	H	H	CF ₃	OMe
	CH	Et	H	H	CF ₃	OEt
40	CH	Me	H	H	CF ₃	OCHMe ₂
	CH	Me	H	H	CF ₃	SMe
	CH	Me	H	H	CF ₃	CHF ₂
	CH	Et	H	H	CF ₃	CHF ₂
	CH	Me	H	H	OCF ₃	CHF ₂
	CH	Me	H	H	CF ₃	OCF ₂ CHF ₂
45	CH	Me	H	H	CF ₃	Cl
	CH	MeCH=CH	H	H	CF ₃	CF ₃
	CH	Me	H	H	CF ₃	CH=CHCF ₃
	CH	Me	H	H	CF ₃	OCHF ₂
	CH	Et	H	H	CF ₃	OCHF ₂
50	CH	MeOCH ₂	H	H	CF ₃	CF ₃
	CH	Me ₂ N	H	H	CF ₃	CF ₃
	CH	MeNH	H	H	CF ₃	CF ₃
	CH	Me	H	H	OMe	CF ₃
	CH	Me	H	H	CF ₃	SCHF ₂
55	CH	Me	H	H	CF ₃	SO ₂ CHF ₂
	CH	MeO	H	H	CF ₃	CF ₃
	CH	MeS	H	H	CF ₃	CF ₃
	N	Me	H	H	CF ₃	CF ₃
	N	Et	H	H	CF ₃	CF ₃
	N	Me	H	H	CF ₃	OCHF ₂
60	N	Et	H	H	CF ₃	OCHF ₂
	N	Me	H	H	OCF ₃	CF ₃
	N	Me	H	H	OCHF ₂	CF ₃
	N	Me	H	H	CN	CF ₃
	N	Et	H	H	CN	CF ₃
65	N	Me	H	H	OCF ₃	OCHF ₂
	N	Me	H	H	CF ₃	OMe
	N	Me	H	H	SCF ₃	CF ₃

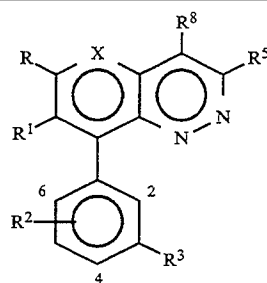
TABLE VII



Ig

X	R	R ¹	R ²	R ³	R ⁵	R ⁸
CH	Me	H	H	CF ₃	CF ₃	H
CH	Et	H	H	CF ₃	CF ₃	H
CH	n-Pr	H	H	CF ₃	CF ₃	H
CH	Me	H	H	OCF ₃	CF ₃	H
CH	Et	H	H	OCF ₃	CF ₃	H
CH	n-Pr	H	H	OCF ₃	CF ₃	H
CH	Me	H	H	OCHF ₂	CF ₃	H
CH	Me	H	H	OCF ₃	OCHF ₂	H
CH	Me	H	H	CF ₃	OCHF ₂	H
CH	Me	F	H	CF ₃	CF ₃	H
CH	Me	H	6-F	CF ₃	CF ₃	H
CH	Me	H	4-F	CF ₃	CF ₃	H
CH	Me	H	2-OMe	CF ₃	CF ₃	H
CH	Me	H	2-CF ₃	H	CF ₃	H
CH	Me	H	H	Cl	CF ₃	H
CH	Et	H	H	CF ₃	OCHF ₂	H
CH	Me	H	H	Br	CF ₃	H
CH	Me	H	H	CN	CF ₃	H
CH	Et	H	H	CN	CF ₃	H
CH	Me	H	H	SCF ₃	CF ₃	H
CH	Me	H	H	H	CF ₃	H
CH	Me	H	H	CF ₃	OCH ₂ CF ₃	H
CH	Me	H	H	CF ₃	SCF ₃	H
CH	Me	H	H	CF ₃	OMe	H
CH	Et	H	H	CF ₃	OEt	H
CH	Me	H	H	CF ₃	OCHMe ₂	H
CH	Me	H	H	CF ₃	SMe	H
CH	Me	H	H	CF ₃	CHF ₂	H
CH	Et	H	H	CF ₃	CHF ₂	H
CH	Me	H	H	OCF ₃	CHF ₂	H
CH	Me	H	H	CF ₃	OCF ₂ CHF ₂	H
CH	Me	H	H	CF ₃	Cl	H
CH	MeCH=CH	H	H	CF ₃	CF ₃	H
CH	Me	H	H	CF ₃	CH=CHCF ₃	H
CH	Me	H	H	CF ₃	OCHF ₂	H
CH	Et	H	H	CF ₃	OCHF ₂	H
CH	MeOCH ₂	H	H	CF ₃	CF ₃	H
CH	Me ₂ N	H	H	CF ₃	CF ₃	H
CH	MeNH	H	H	CF ₃	CF ₃	H
CH	Me	H	H	OMe	CF ₃	H
CH	Me	H	H	CF ₃	SCHF ₂	H
CH	Me	H	H	CF ₃	SO ₂ CHF ₂	H
CH	MeO	H	H	CF ₃	CF ₃	H
CH	MeS	H	H	CF ₃	CF ₃	H
CH	Me	H	H	CF ₃	CF ₃	Me
CH	Me	H	H	CF ₃	CF ₃	CN
CH	Me	H	H	CF ₃	CF ₃	OMe
CH	Me	H	H	CF ₃	Cl	Cl
N	Me	H	H	CF ₃	CF ₃	H
N	Et	H	H	CF ₃	CF ₃	H
N	Me	H	H	CF ₃	OCHF ₂	H
N	Et	H	H	CF ₃	OCHF ₂	H
N	Me	H	H	OCF ₃	CF ₃	H
N	Me	H	H	OCHF ₂	CF ₃	H
N	Me	H	H	CN	CF ₃	H
N	Et	H	H	CN	CF ₃	H
N	Me	H	H	OCF ₃	OCHF ₂	H
N	Me	H	H	CF ₃	OMe	H
N	Me	H	H	SCF ₃	CF ₃	H

TABLE VIII



Ih

X	R	R ¹	R ²	R ³	R ⁵	R ⁸
CH	Me	H	H	CF ₃	CF ₃	H
CH	Et	H	H	CF ₃	CF ₃	H
CH	n-Pr	H	H	CF ₃	CF ₃	H
CH	Me	H	H	OCF ₃	CF ₃	H
CH	Et	H	H	OCF ₃	CF ₃	H
CH	n-Pr	H	H	OCF ₃	CF ₃	H
CH	Me	H	H	OCHF ₂	CF ₃	H
CH	Me	H	H	OCF ₃	OCHF ₂	H
CH	Me	H	H	CF ₃	OCHF ₂	H
CH	Me	F	H	CF ₃	CF ₃	H
CH	Me	H	6-F	CF ₃	CF ₃	H
CH	Me	H	4-F	CF ₃	CF ₃	H
CH	Me	H	2-OMe	CF ₃	CF ₃	H
CH	Me	H	2-CF ₃	H	CF ₃	H
CH	Me	H	H	Cl	CF ₃	H
CH	Et	H	H	CF ₃	OCHF ₂	H
CH	Me	H	H	Br	CF ₃	H
CH	Me	H	H	CN	CF ₃	H
CH	Et	H	H	CN	CF ₃	H
CH	Me	H	H	SCF ₃	CF ₃	H
CH	Me	H	H	H	CF ₃	H
CH	Me	H	H	CF ₃	OCH ₂ CF ₃	H
CH	Me	H	H	CF ₃	SCF ₃	H
CH	Me	H	H	CF ₃	OMe	H
CH	Et	H	H	CF ₃	OEt	H
CH	Me	H	H	CF ₃	OCHMe ₂	H
CH	Me	H	H	CF ₃	SMe	H
CH	Me	H	H	CF ₃	CHF ₂	H
CH	Et	H	H	CF ₃	CHF ₂	H
CH	Me	H	H	OCF ₃	CHF ₂	H
CH	Me	H	H	CF ₃	OCF ₂ CHF ₂	H
CH	Me	H	H	CF ₃	Cl	H
CH	MeCH=CH	H	H	CF ₃	CF ₃	H
CH	Me	H	H	CF ₃	CH=CHCF ₃	H
CH	Me	H	H	CF ₃	OCHF ₂	H
CH	Et	H	H	CF ₃	OCHF ₂	H
CH	MeOCH ₂	H	H	CF ₃	CF ₃	H
CH	Me ₂ N	H	H	CF ₃	CF ₃	H
CH	MeNH	H	H	CF ₃	CF ₃	H
CH	Me	H	H	OMe	CF ₃	H
CH	Me	H	H	CF ₃	SCHF ₂	H
CH	Me	H	H	CF ₃	SO ₂ CHF ₂	H
CH	MeO	H	H	CF ₃	CF ₃	H
CH	MeS	H	H	CF ₃	CF ₃	H
CH	Me	H	H	CF ₃	CF ₃	Me
CH	Me	H	H	CF ₃	CF ₃	CN
CH	Me	H	H	CF ₃	CF ₃	OMe
CH	Me	H	H	CF ₃	Cl	Cl
N	Me	H	H	CF ₃	CF ₃	H
N	Et	H	H	CF ₃	CF ₃	H
N	Me	H	H	CF ₃	OCHF ₂	H
N	Et	H	H	CF ₃	OCHF ₂	H
N	Me	H	H	OCF ₃	CF ₃	H
N	Me	H	H	OCHF ₂	CF ₃	H
N	Me	H	H	CN	CF ₃	H
N	Et	H	H	CN	CF ₃	H
N	Me	H	H	OCF ₃	OCHF ₂	H
N	Me	H	H	CF ₃	OMe	H
N	Me	H	H	SCF ₃	CF ₃	H

Formulations

Useful formulations of the compounds of Formula I can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates and the like. Many of these may be applied directly. Sprayable formulations can be extended in suitable media and used at spray volumes of from a few liters to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations, broadly, contain about 0.1% to 99% by weight of active ingredient(s) and at least one of (a) about 0.1% to 20% surfactant(s) and (b) about 1% to 99.9% solid or liquid diluent(s). More specifically, they will contain these ingredients in the following approximate proportions:

	Weight Percent*		
	Active Ingredient	Diluent(s)	Surfactant(s)
Wettable Powders	20-90	0-74	1-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	3-50	40-95	0-15
Aqueous Suspension	10-50	40-84	1-20
Dusts	1-25	70-99	0-5
Granules and Pellets	0.1-95	5-99.9	0-15
High Strength Compositions	90-99	0-10	0-2

*Active ingredient plus at least one of a Surfactant or a Diluent equals 100 weight percent.

Lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surfactant to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

Typical solid diluents are described in Watkins, et al., "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed Dorland Books, Caldwell, N.J., but other solids, either mined or manufactured, may be used. The more absorptive diluents are preferred for wettable powders and the denser ones for dusts. Typical liquid diluents and solvents are described in Marsden, "Solvents Guide," 2nd Ed., Interscience, N.Y., 1950, Solubility under 0.1% is preferred for suspension concentrates; solution concentrates are preferably stable against phase separation at 0° C. "McCutcheon's Detergents and Emulsifiers Annual", MC Publishing Corp., Ridgewood, N.J., as well as Sisely and Wood, "Encyclopedia of Surface Active Agents", Chemical Publishing Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foaming, caking, corrosion, microbiological growth, etc.

The methods of making such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer or fluid energy mill. Suspensions are prepared by wet milling (see, for example, Littler, U.S. Pat. No. 3,060,084). Granules and pellets may be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See J. E. Browning, "Agglomeration", *Chemical Engineering*, Dec. 4, 1967, pp. 147ff. and

"Perry's Chemical Engineer's Handbook", 5th Ed., McGraw-Hill, New York, 1973, pp. 8-57ff.

For further information regarding the art of formulation, see for example:

H. M. Loux, U.S. Pat. No. 3,235,361, Feb. 15, 1966, Col. 6, line 16 through Col. 7, line 19 and Examples 10 through 41;

R. W. Luckenbaugh, U.S. Pat. No. 3,309,192, Mar. 14, 1967, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182;

H. Gysin and E. Knusli, U.S. Pat. No. 2,891,855, Jun. 23, 1959, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4;

G. C. Klingman, "Weed Control as a Science", John Wiley and Sons, Inc., New York, 1961, pp. 81-96; and

J. D. Fryer and S. A. Evans, "Weed Control Handbook", 5th Ed., Blackwell Scientific Publications, Oxford, 1968, pp. 101-103.

In the following examples, all parts are by weight unless otherwise indicated.

Example A

Wettable Powder	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	80%
sodium alkylnaphthalenesulfonate	2%
sodium ligninsulfonate	2%
synthetic amorphous silica	3%
kaolinite	13%

The ingredients are blended, hammer-milled until all the solids are essentially under 50 microns, reblended, and packaged.

Example B

Wettable, Powder	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	50%
sodium alkylnaphthalenesulfonate	2%
low viscosity methyl cellulose	2%
diatomaceous earth	46%

The ingredients are blended, coarsely hammer-milled and then air-milled to produce particles essentially all below 10 microns in diameter. The product is reblended before packaging.

Example C

Granule	
Wettable Powder of Example B	5%
attapulgite granules (U.S.S. 20-40 mesh; 0.84-0.42 mm)	95%

A slurry of wettable powder containing 25% solids is sprayed on the surface of attapulgite granules in a double-cone blender. The granules are dried and packaged.

Example D

Extruded Pellet	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	25%

-continued

Extruded Pellet	
anhydrous sodium sulfate	10%
crude calcium ligninsulfonate	5%
sodium alkyl naphthalenesulfonate	1%
calcium/magnesium bentonite	59%

The ingredients are blended, hammer-milled and then moistened with about 12% water. The mixture is extruded as cylinders about 3 mm diameter which are cut to produce pellets about 3 mm long. These may be used directly after drying, or the dried pellets may be crushed to pass a U.S.S. No. 20 sieve (0.84 mm openings). The granules held on a U.S.S. No. 40 sieve (0.42 mm openings) may be packaged for use and the fines recycled.

Example E

Low Strength Granule	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	1%
N,N-dimethylformamide	9%
attapulgite granules (U.S.S. 20 to 40 sieve)	90%

The active ingredient is dissolved in the solvent and the solution is sprayed upon dedusted granules in a double-cone blender. After spraying of the solution has been completed, the blender is allowed to run for a short period and then the granules are packaged.

Example F

Granule	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	80%
wetting agent	1%
crude ligninsulfonate salt (containing 5-20% of the natural sugars)	10%
attapulgite clay	9%

The ingredients are blended and milled to pass through a 100 mesh screen. This material is then added to a fluid bed granulator, the air flow is adjusted to gently fluidize the material, and a fine spray of water is sprayed onto the fluidized material. The fluidization and spraying are continued until granules of the desired size range are made. The spraying is stopped, but fluidization is continued, optionally with heat, until the water content is reduced to the desired level, generally less than 1%. The material is then discharged, screened to the desired size range, generally 14-100 mesh (1410-149 microns), and packaged for use.

Example G

Aqueous Suspension	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	40%
polyacrylic acid thickener	0.3%
dodecylphenol polyethylene glycol ether	0.5%
disodium phosphate	1%
monosodium phosphate	0.5%
polyvinyl alcohol	1.0%
water	56.7%

The ingredients are blended and ground together in a sand mill to produce particles essentially all under 5 microns in size.

Example H

High Strength Concentrate	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	99%
silica aerogel	0.5%
synthetic amorphous silica	0.5%

The ingredients are blended and ground in a hammer-mill to produce a material essentially all passing a U.S.S. No. 50 screen (0.3 mm opening). The concentrate may be formulated further if necessary.

Example I

Wettable Powder	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	90%
dioctyl sodium sulfosuccinate	0.1%
synthetic fine silica	9.9%

The ingredients are blended and ground in a hammer-mill to produce particles essentially all below 100 microns. The material is sifted through a U.S.S. No. 50 screen and then packaged.

Example J

Wettable Powder	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	40%
sodium ligninsulfonate	20%
montmorillonite clay	40%

The ingredients are thoroughly blended, coarsely hammer-milled and then air-milled to produce particles essentially all below 10 microns in size. The material is reblended and then packaged.

Example K

Oil Suspension	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	35%
blend of polyalcohol carboxylic esters and oil soluble petroleum sulfonates	6%
xylene	59%

The ingredients are combined and ground together in a sand mill to produce particles essentially all below 5 microns. The product can be used directly, extended with oils, or emulsified in water.

Example L

Dust	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	10%
attapulgite	10%
Pyrophyllite	80%

The active ingredient is blended with attapulgit and then passed through a hammer-mill to produce particles substantially all below 200 microns. The ground concentrate is then blended with powdered pyrophyllite until homogeneous.

Example M

Oil Suspension	
α -(difluoromethoxy)-6-methyl-8-[3-(trifluoromethyl)phenyl]quinoxaline	25%
polyoxyethylene sorbitol hexaoleate	5%
highly aliphatic hydrocarbon oil	70%

The ingredients are ground together in a sand mill until the solid particles have been reduced to under about 5 microns. The resulting thick suspension may be applied directly, but preferably after being extended with oils or emulsified in water.

UTILITY

Test results indicate compounds of this invention are active postemergence and preemergence herbicides. Many compounds in this invention are useful for the control of selected grass and broadleaf weeds with tolerance to important agronomic crops such as barley (*Hordeum vulgare*), corn (*Zea mays*), cotton (*Gossypium hirsutum*), rice (*Oryza sativa*), sorghum (*Sorghum bicolor*), soybean (*Glycine max*), wheat (*Triticum aestivum*), and to vegetable crops. Grass and broadleaf weed species controlled include, but are not limited to, barnyardgrass (*Echinochloa crusgalli*), bedstraw (*Galium aparine*), blackgrass (*Alopecurus myosuroides*), cheatgrass (*Bromus secalinus*), chickweed (*Stellaria media*), crabgrass (*Digitaria* spp.), foxtail (*Setaria* spp.), lambsquarters (*Chenopodium* spp.), velvetleaf (*Afutilon theophrasti*), wild buckwheat (*Polygonum convolvulus*) and wild oats (*Avena fatua*).

These compounds also have utility for weed control of selected vegetation in specified areas such as around storage tanks, parking lots, highways, and railways; in fallow crop areas; and in citrus and plantation crops such as banana, coffee, oil palm, and rubber. Alternatively, these compounds are useful to modify plant growth.

Rates of application for compounds of this invention are determined by a number of factors. These factors include: formulation selected, method of application, amount and type of vegetation present, growing conditions, etc. In general terms, the subject compounds should be applied at rates from 0.01 to 20 kg/ha with a preferred rate range of 0.02 to 2 kg/ha. Although a small number of compounds show slight herbicidal activity at the rates tested, it is anticipated these compounds are herbicidally active at higher application rates. One skilled in the art can easily determine application rates necessary for desired level of weed control.

Compounds of this invention may be used alone or in combination with other commercial herbicides, insecticides, or fungicides. The following list exemplifies some of the herbicides suitable for use in mixtures. A combination of a compound from this invention with one or more of the following herbicides may be particularly useful for weed control.

Common Name	Chemical Name
acetochlor	2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide
5 acifluorfen	5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid
aclonifen	2-chloro-6-nitro-3-phenoxybenzenamine
acrolein	2-propenal
alachlor	2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide
10 alloxydim	methyl 2,2-dimethyl-4,6-dioxo-5-[1-[(2-propenyloxy)amino]butylidene]-cyclohexanecarboxylate
ametryn	N-ethyl-N'-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
15 amitrole	1H-1,2,4-triazol-3-amine
AMS	ammonium sulfamate
anilofos	S-[2-[(4-chlorophenyl)(1-methylethyl)amino]-2-oxoethyl][0,0-dimethylphosphorodithioate
asulam	methyl [(4-aminophenyl)sulfonyl]-carbamate
20 atrazine	6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine
aziprotrotryne	4-azido-N-(1-methylethyl)-6-methylthio-1,3,5-triazin-2-amine
azoluron	N-(1-ethyl-1H-pyrazol-5-yl)-N'-phenylurea
25 barban	4-chloro-2-butynyl 3-chlorocarbamate
benazolin	4-chloro-2-oxo-3(2H)-benzothiazole acetic acid
benfluralin	N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine
bensulfuron	2-[[[[[4,6-dimethoxy-2-pyrimidinyl]amino]methylcarbonyl]amino]sulfonyl]methyl]benzoic acid, methyl ester
30 bensulide	0,0-bis(1-methylethyl) S-[2-[(phenylsulfonyl)amino]ethyl]phosphorodithioate
bentazon	3-(1-methylethyl)-(1H)-2,1,3-benzothiazidin-4(3H)-one, 2,2-dioxide
35 benzofluor	N-[4-(ethylthio)-2-(trifluoromethyl)phenyl]methanesulfonamide
benzoylprop	N-benzoyl-N-(3,4-dichlorophenyl)-DL-alanine
benzthiazuron	N-2-benzothiazolyl-N'-methylurea
40 bialaphos	4-(hydroxymethylphosphinyl)-L-2-aminobutanoyl-L-alanyl-L-alanine
bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate
bromacil	5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1H,3H)pyrimidinedione
45 *bromobutide	(+)-2-bromo-3,3-dimethyl-N-(1-methyl-1-phenylethyl)butanamide
bromofenoxim	3,5-dibromo-4-hydroxybenzaldehyde 0-(2,4-dinitrophenyl)oxime
bromoxynil	3,5-dibromo-4-hydroxybenzoxonitrile
bromuron	N'-(4-bromophenyl)-N,N-dimethylurea
50 buminafos	dibutyl [1-(butylamino)cyclohexyl]phosphonate
butachlor	N-(butoxymethyl)-2-chloro-N-(2,6-diethylphenyl)acetamide
butamifos	0-ethyl 0-(5-methyl-2-nitrophenyl)(1-methylpropyl)phosphoramidodithioate
55 buthidazole	3-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-4-hydroxy-1-methyl-2-imidazolidinone
butralin	4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamine
butylate	S-ethyl bis(2-methylpropyl)-carbamothioate
60 cacodylic acid	dimethyl arsinic oxide
carbetamide	(R)-N-ethyl-2-[[[phenylamino]carbonyl]oxy]propanamide
CDA	2-chloro-N,N-di-2-propenylacetamide
CDEC	2-chloroallyl diethyldithiocarbamate
65 chlomethoxyfen	4-(2,4-dichlorophenoxy)-2-methoxy-1-nitrobenzene
chloramben	3-amino-2,5-dichlorobenzoic acid
chlorbromuron	3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea
chlorbufam	1-methyl-2-propynyl(3-chlorophenyl)-

-continued

Common Name	Chemical Name
	carbamate
chlorfenac	2,3,6-trichlorobenzeneacetic acid
chlorfluorecol- methyl	methyl 2-chloro-9-hydroxy-9H- fluorene-9-carboxylate
chloridazon	5-amino-4-chloro-2-phenyl-3(2H)- pyridazinone
chlorimuron	2-[[[(4-chloro-6-methoxy-2- pyrimidinyl)ethylamino]carbonyl]- amino]sulfonyl]benzoic acid, ethyl ester
chlornitrofen	1,3,5-trichloro-2-(4-nitrophenoxy)- benzene
chloropicrin	trichloronitromethane
chloroxuron	N'-[4-(4-chlorophenoxy)phenyl]-N,N- dimethylurea
chlorpropham	1-methylethyl 3-chlorophenylcarbamate
chlorsulfuron	2-chloro-N-[[[(4-methoxy-6-methyl- 1,3,5-triazin-2-yl)-amino]- carbonyl]benzenesulfonamide
chlorthal- dimethyl	dimethyl 2,3,5,6-tetrachloro-1,4- benzenedicarboxylate
chlorthiamid	2,6-dichlorobenzene carbothioamide
chlortoluron	N'-(3-chloro-4-methylphenyl)-N,N- dimethylurea
cinmethylin	exo-1-methyl-4-(1-methylethyl)-2-[(2- methylphenyl)methoxy]-7-oxabicyclo- [2.2.1]heptane
clethodim	(E,E)-(+)-2-[1-[[[(3-chloro-2- propenyl)oxy]imino]propyl]-5-[2- (ethylthio)propyl]-3-hydroxy-2- cyclohexen-1-one
clomazone	2-[(2-chlorophenyl)methyl]-4,4- dimethyl-3-isoxazolidinone
cloproxydim	(E,E)-2-[1-[[[(3-chloro-2-propenyl)- oxy]imino]butyl]-5-[2-(ethylthio)- propyl]-3-hydroxy-2-cyclohexen-1- one
clopyralid	3,6-dichloro-2-pyridinecarboxylic acid
CMA	calcium salt of MAA
cyazazine	2-[[4-chloro-6-(ethylamino)-1,3,5- triazin-2-yl]amino]-2-methyl- propanenitrile
cycloate	S-ethyl cyclohexylethylcarbamothioate
cycloxydim	2-[1-ethoxyimino]butyl]-3-hydroxy-5- (tetrahydro-2H-thiopyran-3-yl)-2- cyclohexene-1-one
cycluron	3-cyclooctyl-1,1-dimethylurea
cyperquat	1-methyl-4-phenylpyridinium
cyprazine	2-chloro-4-(cyclopropylamino)-6- (isopropylamino)-s-triazine
cyprazole	N-[5-(2-chloro-1,1-dimethylethyl)- 1,3,4-thiadiazol-2-yl]cyclopropane- carboxamide
cypromid	3',4'-dichlorocyclopropane- carboxanilide
dalapon	2,2-dichloropropanoic acid
dazomet	tetrahydro-3,5-dimethyl-2H-1,3,5- thiadiazine-2-thione
DCPA	dimethyl 2,3,5,6-tetrachloro-1,4- benzenedicarboxylate
desmedipham	ethyl [3-[[[(phenylamino)carbonyl]- oxy]phenyl]carbamate
desmetryn	2-(isopropylamino)-4-(methylamino)-6- (methylthio)-s-triazine
diallate	S-(2,3-dichloro-2-propenyl)bis(1- methylethyl)carbamothioate
dicamba	3,6-dichloro-2-methoxybenzoic acid
dichlobenil	2,6-dichlorobenzonitrile
dichlorprop	(+)-2-(2,4-dichlorophenoxy)propanoic acid
*diclofopmethyl	(+)-2-[4-(2,4-dichlorophenoxy)- phenoxy]propanoic acid, methyl ester
diethatyl	N-(chloroacetyl)-N-(2,6-diethyl- phenyl)glycine
difenoxuron	N'-[4-(4-methoxyphenoxy)phenyl]-N,N- dimethylurea
difenzoquat	1,2-dimethyl-3,5-diphenyl-1H- pyrazolium ion
diflufenican	N-(2,4-difluorophenyl)-2-(3-

-continued

Common Name	Chemical Name
	trifluoromethylphenoxy)pyridine-3- carboxamide
5 dimefuron	N'-[3-chloro-4-[5-(1,1-dimethyl- ethyl)-2-oxo-1,3,4-oxadiazol-3(2H)- yl]phenyl]-N,N-dimethylurea
dimethachlor	2-chloro-N-(2,6-dimethylphenyl)-N-(2- methoxyethyl)acetamide
10 dimethametryn	N-(1,2-dimethylpropyl)-N'-ethyl-6- (methylthio)-1,3,5-triazine-2,4- diamine
dimethipin	2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetraoxide
dimethylarsinic dinitramine	dimethylarsinic acid N ³ ,N ² -diethyl-2,4-dinitro-6-(tri- fluoromethyl)-1,3-benzenediamine
15 dinoseb	2-(1-methylpropyl)-4,6-dinitrophenol
dinoterb	2-(1,1-dimethylethyl)-4,6-dinitro- phenol
diphenamid	N,N-dimethyl- α -phenylbenzeneacetamide
20 dipropetryn	6-(ethylthio)-N,N'-bis(1-methyl- ethyl)-1,3,5-triazine-2,4-diamine
diquat	6,7-dihydrodipyrido[1,2-a:2',1'-c]- pyrazinedium ion
diuron	N'-(3,4-dichlorophenyl)-N,N- dimethylurea
DNOC	2-methyl-4,6-dinitrophenol
25 DPX-V9360	2-[[[(4,6-dimethoxypyrimidin-2-yl)- aminocarbonyl]aminosulfonyl]-N,N- dimethyl-3-pyridinecarboxamide
DSMA	disodium salt of MAA
dymron	N-(4-methylphenyl)-N'-(1-methyl-1- phenylethyl)urea
30 eglazine-ethyl	N-[4-chloro-6-(ethylamino)-1,3,5- triazin-2-yl]glycine ethyl ester
endothall	7-oxabicyclo[2.2.1]heptane-2,3- dicarboxylic acid
EPTC	S-ethyl dipropylcarbamothioate
ethalfuralin	N-ethyl-N-(2-methyl-2-propenyl)-2,6- dinitro-4-(trifluoromethyl) benzenamine
35 ethidimuron	N-[5-(ethylsulfonyl)-1,3,4-thia- diazol-2-yl]-N,N'-dimethylurea
*ethofumesate	(+)-2-ethoxy-2,3-dihydro-3,3- dimethyl-5-benzofuranyl methane- sulfonate
40 fenac	2,3,6-trichlorobenzeneacetic acid
*fenoprop	(+)-2-(2,4,5-trichlorophenoxy)- propanoic acid
*fenoxaprop	(+)-2-[4-[[6-chloro-2-benzoxazolyl]- oxy]phenoxy]propanoic acid
fenuron	N,N-dimethyl-N'-phenylurea
45 fenuron TCA	Salt of fenuron and TCA
flamprop-M- isopropyl	1-methylethyl N-benzoyl-N-(3-chloro- 4-fluorophenyl)-D-alanine
flamprop-methyl	methyl N-benzoyl-N-(3-chloro-4- fluorophenyl)-DL-alaninate
*fluazifop	(+)-2-[4-[[5-(trifluoromethyl)-2- pyridinyl]oxy]phenoxy]propanoic acid
50 fluazifop-P	(R)-2-[4-[[5-(trifluoromethyl)-2- pyridinyl]oxy]phenoxy]propanoic acid
fluchloralin	N-(2-chloroethyl)-2,6-dinitro-N- propyl-4-(trifluoromethyl)- benzenamine
55 fluometuron	N,N-dimethyl-N'-[3-(trifluoro- methyl)phenyl]urea
fluralin	N-butyl-N-ethyl-2,6-dinitro-4- (trifluoromethyl)benzenamine
flurodifen	p-nitrophenyl α,α,α -trifluoro-2- nitro-p-tolyl ether
60 fluoroglycofen	carboxymethyl 5-[2-chloro-4-(tri- fluoromethyl)phenoxy]-2-nitro- benzoate
flurecol-butyl	butyl 9-hydroxy-9H-fluorene-9- carboxylate
65 fluridone	1-methyl-3-phenyl-5-[3-(trifluoro- methyl)phenyl]-4(IH)-pyridinone
flurochloridone	3-chloro-4-(chloromethyl)-1-[3- (trifluoromethyl)phenyl]-2- pyrrolidinone

-continued

Common Name	Chemical Name
fluroxypyr	[(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid
fomesafen	5-[2-chloro-4-(trifluoromethyl)phenoxy]-N-(methylsulfonyl)-2-nitrobenzamide
fosamine-ammonium	ethyl hydrogen (aminocarbonyl)-phosphonate ammonium ethyl
glufosinate-ammonium	ammonium 2-amino-4-(hydroxymethyl)-phosphinyl)butanoate
glyphosate	N-(phosphonomethyl)glycine
haloxyfop	2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]-phenoxy]propanoic acid
hexaflurate	potassium hexafluoroarsenate
hexazinone	3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4-(1H, 3H) dione
imazamethabenz	6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester
imazapyr	(+)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid
imazaquin	2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid
imazethapyr	(+)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridine carboxylic acid
ioxynil	4-hydroxy-3,5-diiodobenzonitrile
isocarbamid	N-(2-methylpropyl)-2-oxo-1-imidazolidinecarboxamide
isopropalin	4-(1-methylethyl)-2,6-dinitro-N,N-dipropylbenzenamine
isoproturon	N-(4-isopropylphenyl)-N',N'-dimethylurea
isouron	N'-[5-(1,1-dimethylethyl)-3-isoxazolyl]-N,N-dimethylurea
isoxaben	N-[3-(1-ethyl-1-methylpropyl)-5-isoxazolyl]-2,6-dimethoxybenzamide
karbutilate	3-[[[(dimethylamino)carbonyl]-amino]phenyl-(1,1-dimethylethyl)-carbamate
lactofen	(+)-2-ethoxy-1-methyl-2-oxoethyl-5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate
lenacil	3-cyclohexyl-6,7-dihydro-1H-cyclopentapyrimidine-2,4-(3H,5H)-dione
linuron	N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea
MAA	methylarsonic acid
MAMA	monoammonium salt of MAA
MCPA	(4-chloro-2-methylphenoxy)acetic acid
MCPA-thioethyl	S-ethyl (4-chloro-2-methylphenoxy)-ethanethioate
MCPB	4-(4-chloro-2-methylphenoxy)butanoic acid
mecoprop	(+)-2-(4-chloro-2-methylphenoxy)-propanoic acid
mefenacet	2-(2-benzothiazolyloxy)-N-methyl-N-phenyl acetamide
mefluidide	N-[2,4-dimethyl-5-[[trifluoromethyl)sulfonyl]amino]phenyl]-acetamide
metamitron	4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one
metazachlor	2-chloro-N-(2,6-dimethylphenyl)-N-(1H-pyrazol-1-ylmethyl)acetamide
methabenz-thiazuron	1,3-dimethyl-3-(2-benzothiazolyl)urea
methalpropalin	N-(2-methyl-2-propenyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)-benzenamide
metham	methylcarbamidithioic acid
methazole	2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione
methoxuron	N'-(3-chloro-4-methoxyphenyl)-N,N-dimethylurea

-continued

Common Name	Chemical Name
methoxyphenone	(4-methoxy-3-methylphenyl)(3-methylphenyl)methanone
5 methylodymron	N-methyl-N'-(1-methyl-1-phenylethyl)-N-phenylurea
metobromuron	N'-(4-bromophenyl)-N-methoxy-N-methylurea
metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide
10 metoxuron	N'-(3-chloro-4-methoxyphenyl)-N,N-dimethylurea
metribuzin	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one
15 metsulfuron methyl	2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoic acid, methyl ester
MH molinate	1,2-dihydro-3,6-pyridazinedione
20 monalide	S-ethyl hexahydro-1H-azepine-1-carbothioate
monolinuron	N-(4-chlorophenyl)-2,2-dimethyl-pentanamide
monuron	3-(p-chlorophenyl)-1-methoxy-1-methyl-urea
MSMA	N'-(4-chlorophenyl)-N,N-dimethylurea
25 naproanilide	monosodium salt of MAA
napropamide	2-(2-naphthalenyloxy)-N-phenylpropanamide
naptalam	N,N-diethyl-2-(1-naphthalenyloxy)-propanamide
neburon	2-[(1-naphthalenylamino)carbonyl]-benzoic acid
30 nitralin	1-butyl-3-(3,4-dichlorophenyl)-1-methylurea
nitrofen	4-methylsulfonyl-2,6-dinitro-N,N-dipropylaniline
nitrofluorfen	2,4-dichloro-1-(4-nitrophenoxy)-benzene
35 norea	2-chloro-1-(4-nitrophenoxy)-4-(trifluoromethyl)benzene
norflurazon	N,N-dimethyl-N'-(octahydro-4,7-methano-1H-inden-5-yl)urea-3 α , 4 α , 5 α , 7 α -isomer
40 orbencarb	4-chloro-5-(methylamino)-2-[3-(trifluoromethyl)phenyl]-3(2H)-pyridazinone
oryzalin	S-[2-(chlorophenyl)methyl]diethyl-carbamothioate
oxadiazon	4-(dipropylamino)-3,5-dinitrobenzenesulfonamide
45 oxyfluorfen	3-[2,4-dichloro-5-(1-methylethoxy)phenyl]-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2(3H)-one
paraquat	2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene
pebulate	1,1'-dimethyl-4,4'-dipyridinium ion
50 pendimethalin	S-propyl butylethylcarbamothioate
perfluidone	N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine
phenisopham	1,1,1-trifluoro-N-[2-methyl-4-(phenylsulfonyl)phenyl]methanesulfonamide
55 phenmedipham	3-[[[(1-methylethoxy)carbonyl]-amino]phenyl ethylphenylcarbamate
picloram	3-[(methoxycarbonyl)amino]phenyl(3-methylphenyl)carbamate
piperophos	4-amino-3,5,6-trichloro-2-pyridine-carboxylic acid
60 pretilachlor	S-[2-(2-methyl-1-piperidinyl)-2-oxoethyl]0,0-dipropyl phosphorodithioate
procyazine	2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide
65 prodiamine	2-[[4-chloro-6-(cyclopropylamino)-1,3,5-triazine-2-yl]amino]-2-methylpropanenitrile
profluralin	2,4-dinitro-N3,N3-dipropyl-6-(trifluoromethyl)-1,3-benzenediamine
	N-(cyclopropylmethyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)-benzenamine

-continued

Common Name	Chemical Name
proglinazine-ethyl	N-[4-chloro-6-[(1-methylethyl)amino]-1,3,5-triazin-2-yl]-glycine ethyl ester
prometon	6-methoxy-N,N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine
prometryn	N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
pronamide	3,5-dichloro-N-(1,1-dimethyl-2-propynyl)benzamide
propachlor	2-chloro-N-(1-methylethyl)-N-phenyl acetamide
propanil	N-(3,4-dichlorophenyl)propanamide
propaquizafop	2-[[[(1-methylethylidene)amino]oxy]-ethyl-2-[4-[(6-chloro-2-quinoxalinyloxy)phenoxy]-propanoate
propazine	6-chloro-N,N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine
propham	1-methylethyl phenylcarbamate
propyzamide	3,5-dichloro-N-(1,1-dimethyl-2-propynyl)benzamide
prosulfalin	N-[[4-(dipropylamino)-3,5-dinitrophenyl]sulfonyl]-S,S-dimethylsulfilimine
prosulfocarb	S-benzylidipropylthiocarbamate
prynachlor	2-chloro-N-(1-methyl-2-propynyl)-acetanilide
pyrazon	5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone
pyrazosulfuron-ethyl	ethyl 5-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-1-methyl-1H-pyrazole-4-carboxylate
pyrazoxyfen	2-[[4-(2,4-dichlorobenzoyl)-1,3-dimethyl-1H-pyrazol-5-yl]oxy]-1-phenylethanone
pyridate	O-(6-chloro-3-phenyl-4-pyridazinyl) S-octyl carbonothioate
quizalofop ethyl	(+)-2-[4-[(6-chloro-2-quinoxalinyloxy)phenoxy]propanoic acid, ester
sebumeton	N-ethyl-6-methoxy-N'-(1-methylpropyl)-1,3,5-triazine-2,4-diamine
sethoxydim	2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one
siduron	N-(2-methylcyclohexyl)-N'-phenylurea
simazine	6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine
simetryn	N,N'-diethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine
sodium chlorate	sodium chlorate
sodium monochloroacetate	chloroacetic acid, sodium salt
sulfometuron methyl	2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-benzoic acid, methyl ester
2,4,5-T	(2,4,5-trichlorophenoxy)acetic acid
2,3,6-TBA	2,3,6-trichlorobenzoic acid
TCA	trichloroacetic acid
tebutam	2,2-dimethyl-N-(1-methylethyl)-N-(phenylmethyl)propanamide

-continued

Common Name	Chemical Name
tebuthiuron	N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea
5 terbacil	5-chloro-3-(1,1-dimethylethyl)-6-methyl-2,4(1H,3H)-pyrimidinedione
terbuchlor	N-(butoxymethyl)-2-chloro-N-[2-(1,1-dimethylethyl)-6-methylphenyl]-acetamide
10 terbumeton	N-(1,1-dimethylethyl)-N'-ethyl-6-methoxy-1,3,5-triazine-2,4-diamine
terbutylazine	2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine
terbutol	2,6-di-tert-butyl-p-tolyl methylcarbamate
15 terbutryn	N-(1,1-dimethylethyl)-N'-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine
thifensulfuron	3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid, methyl ester
20 thiameturonmethyl	methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate
thiazafluron	N,N'-dimethyl-N-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]urea
25 thiobencarb	S-[(4-chlorophenyl)methyl]diethylcarbamothioate
tiocarbazil	S-(phenylmethyl) bis(1-methylpropyl)carbamothioate
tralkoxydim	2-[1-(ethoxyimino)propyl]-3-hydroxy-5-(2,4,6-trimethylphenyl)-2-cyclohexen-1-one
30 triallate	S-(2,3,3-trichloro-2-propenyl)bis(1-methylethyl)carbamothioate
triasulfuron	2-(2-chloroethoxy)-N-[[4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide
35 tribenuron methyl	2-[[[N-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-N-methylamino]carbonyl]amino]sulfonyl]benzoic acid, methyl ester
40 triclopyr	[(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid
*tridiphane	(+)-2-(3,5-dichlorophenyl)-2-(2,2,2-trichloroethyl)oxirane
trietazine	6-chloro-N,N,N'-triethyl-1,3,5-triazine-2,4-diamine
45 trifluralin	2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine
trimeturon	1-(p-chlorophenyl)-2,3,3-trimethylpseudourea
2,4-D	(2,4-dichlorophenoxy)acetic acid
2,4-DB	4-(2,4-dichlorophenoxy)butanoic acid
50 vernolate	S-propyl dipropylcarbamothioate
xylachlor	2-chloro-N-(2,3-dimethylphenyl)-N-(1-methylethyl)acetamide

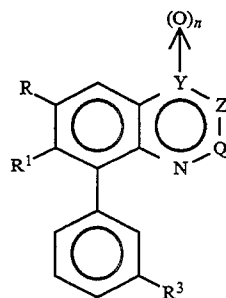
Selective herbicidal properties of the subject compounds were discovered in greenhouse tests as described below.

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TABLE OF COMPOUNDS



CMPD	R	R ¹	R ³	Y	Z	O	n	m.p. (°C.)
1	Me	H	CF ₃	CH	CH	C—OCH ₂ CF ₃	0	oil
2	Me	H	CF ₃	N	C—OCH ₂ CF ₃	CH	0	114-117
3	Me	H	CF ₃	N	C—OMe	CH	0	141-142
4	Me	H	CF ₃	N	CH	C—OMe	0	119-121
5	Me	H	CF ₃	N	N	C—OCH ₂ CF ₃	1	168-169
6	Me	H	CF ₃	N	N	C—OCH ₂ CF ₃	0	140-141
7	Me	H	CF ₃	N	CH	C—OCH ₂ CF ₃	0	46-48
8	Me	H	CF ₃	N	C—CF ₃	CH	0	93-94
9	Me	H	CF ₃	N	CH	C—CF ₃	0	117-118
10	Me	H	CF ₃	N	N	C—OCHF ₂	1	128-129
11	Me	H	CF ₃	N	N	C—OCHF ₂	0	109-110
12	Me	H	CF ₃	N	N	C—OMe	1	147-148
13	Me	H	CF ₃	N	N	C—OMe	0	117-118
14	Me	H	CF ₃	N	C—OCHF ₂	CH	0	105-106
15	Me	H	CF ₃	N	CH	C—OCHF ₂	0	103-104
16	Me	H	CN	N	C—CF ₃	CH	0	165-166
17	Me	H	CN	N	CH	C—CF ₃	0	171-172
18	Me	H	CF ₃	CH	CH	C—OCHF ₂	0	74-75
19	Et	H	CF ₃	N	CH	C—CF ₃	0	65-67
20	Me	H	OCF ₃	N	C—CF ₃	CH	0	55-58
21	Me	H	OCF ₃	N	CH	C—CF ₃	0	102-105
22	Et	H	OCF ₃	N	CH	C—CF ₃	0	48-50
23	Et	H	OCF ₃	N	C—CF ₃	CH	0	oil
24	Me	H	OCF ₃	N	CH	C—OCHF ₂	0	101-103
25	Me	H	OCF ₃	N	C—OCHF ₂	CH	0	61-64
26	MeO	H	CF ₃	N	CH	C—OCHF ₂	0	127-131
27	MeO	H	OCF ₃	N	CH	C—OCHF ₂	0	103-106
28	MeO	H	OCF ₃	N	C—OCHF ₂	CH	0	62-65
29	MeO	H	CF ₃	N	C—OCHF ₂	CH	0	80-84
30	Me	Me	OCHF ₂	N	CH	C—OCHF ₂	0	109-113
31	Me	Me	OCHF ₂	N	C—OCHF ₂	CH	0	85-88
32	MeO	H	OCF ₃	N	CH	C—CF ₃	0	85-88
33	MeO	H	CF ₃	N	CH	C—CF ₃	0	110-112
34	Et	H	CF ₃	N	C—CF ₃	CH	0	139-140

TEST A

Seeds of barley (*Hordeum vulgare*), barnyardgrass (*Echinochloa crus-galli*), bedstraw (*Galium aparine*), blackgrass (*Alopecurus myosuroides*), cheatgrass (*Bromus secalinus*), chickweed (*Stellaria media*), cocklebur (*Xanthium pensylvanicum*), corn (*Zea mays*), cotton (*Gossypium hirsutum*), crabgrass (*Digitaria* spp.), giant foxtail (*Setaria faberii*), lambsquarters (*Chenopodium album*), morningglory (*Ipomoea hederacea*), rape (*Brassica napus*), rice (*Oryza sativa*), sorghum (*Sorghum bicolor*), soybean (*Glycine max*), sugar beet (*Beta vulgaris*), velvetleaf (*Abutilon theophrasti*), wheat (*Triticum aestivum*), wild buckwheat (*Polygonum convolvulus*), and

wild oat (*Avena fatua*) and purple nutsedge (*Cyperus rotundus*) tubers were planted and treated preemergence with test chemicals dissolved in a non-phytotoxic solvent. At the same time, these crop and weed species were also treated with postemergence applications of test chemicals. Plants ranged in height from two to eighteen cm (one to four leaf stage) for postemergence treatments. Treated plants and controls were maintained in a greenhouse for twelve to sixteen days, after which all species were compared to controls and visually evaluated. Plant response ratings, summarized in Table A, are based on a scale of 0 to 10 where 0 is no effect and 10 is complete control. A dash (—) response means no test result.

TABLE A

COMPOUND	POSTEMERGENCE										POSTEMERGENCE																		
	Rate (2000 g/ha)					Rate (400 g/ha)					Rate (100 g/ha)					Rate (50 g/ha)													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Barley	0	0	0	2	3	3	2	3	2	3	4	5	4	2	2	2	0	2	2	2	2	4	6	3	4	3	3	3	
Barnyardgrass	1	1	3	—	—	—	4	2	3	5	2	3	5	9	9	8	1	1	1	1	3	3	1	9	6	5	4	6	2
Bedstraw	5	1	6	5	0	0	3	2	3	4	6	7	6	7	3	5	4	5	2	2	5	6	7	9	8	9	8	7	7
Blackgrass	0	0	4	3	5	0	0	2	3	6	5	5	7	4	8	2	3	0	1	4	8	5	5	7	6	7	5	5	5
Cheatgrass	0	0	2	2	6	0	1	0	3	2	5	6	2	4	4	1	2	0	2	1	2	2	1	7	4	5	6	1	5
Chickweed	4	1	7	5	7	2	3	4	5	7	6	7	7	7	4	7	4	3	5	4	5	7	7	8	8	8	7	7	7
Cocklebur	5	2	8	—	—	2	4	2	4	—	—	—	—	7	8	3	—	2	4	3	7	7	4	7	8	7	6	6	6
Corn	0	2	1	2	3	0	1	2	3	2	2	3	3	5	2	2	2	0	1	2	1	1	5	2	2	2	2	2	2
Cotton	8	3	5	3	6	0	8	0	1	9	2	3	8	4	9	5	8	4	2	2	2	2	10	10	9	9	10	9	9
Crabgrass	—	1	2	2	3	—	1	1	2	1	2	1	4	3	4	9	2	7	1	9	4	7	8	9	9	8	9	7	7
Giant foxtail	0	2	1	3	5	0	2	1	2	3	3	5	5	4	5	3	5	2	1	2	3	2	3	2	2	3	6	6	3
Lambsquarters	4	6	6	8	10	3	5	2	4	4	8	9	6	7	8	10	10	10	10	10	9	9	10	9	8	7	6	6	7
Morningglory	2	4	7	8	8	2	6	4	5	3	4	8	7	8	7	8	6	3	8	5	9	9	7	10	9	8	7	6	7
Nutsedge	1	5	1	0	—	1	0	0	—	1	1	—	—	2	2	7	—	0	0	0	—	0	1	2	—	—	—	—	—
Rape	0	4	4	8	9	0	6	3	2	5	7	5	0	4	9	8	9	8	1	1	1	1	5	4	8	7	7	5	7
Rice	1	0	1	1	3	1	0	0	1	1	1	2	1	2	3	1	2	1	1	3	5	1	0	2	1	2	2	2	1
Sorghum	3	0	2	1	3	0	0	0	1	1	2	2	2	2	3	2	1	3	1	2	2	1	0	3	2	2	1	3	1
Soybean	5	5	6	6	7	1	5	4	6	6	7	5	5	6	7	8	7	5	3	3	6	5	3	8	8	4	5	4	3
Sugar beet	6	9	8	8	9	2	8	8	5	8	7	8	9	9	9	9	9	9	2	7	9	9	8	7	9	9	9	8	9
Velvetleaf	1	0	3	2	8	1	3	0	1	3	5	6	2	2	7	8	1	1	2	5	0	6	3	1	1	4	0	6	1
Wheat	0	0	2	1	2	0	0	0	0	0	2	2	2	4	3	3	0	3	0	3	0	3	2	1	6	4	3	2	2
Wild buckwheat	2	1	2	3	3	2	3	2	1	1	2	3	6	7	6	7	4	6	—	10	4	7	4	—	—	—	—	—	—
Wild oat	1	0	2	6	7	0	0	0	1	3	3	4	4	8	6	8	8	4	2	1	5	1	1	8	7	3	4	4	3

COMPOUND	POSTEMERGENCE										POSTEMERGENCE																										
	Rate (400 g/ha)					Rate (200 g/ha)					Rate (100 g/ha)					Rate (50 g/ha)																					
	31	32	33	34	30	2	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30						
Barley	2	1	1	0	0	0	1	0	0	0	2	2	2	2	0	0	0	0	0	0	1	1	1	2	3	1	0	1	0	0							
Barnyardgrass	0	2	4	7	0	0	2	2	1	2	2	3	1	2	4	2	3	2	3	1	3	3	5	3	7	6	7	4	5	0	0						
Bedstraw	0	4	7	0	0	0	2	4	3	6	4	5	4	3	3	2	2	2	0	0	1	3	5	3	7	6	7	4	5	0	0						
Blackgrass	0	5	5	2	0	0	2	2	2	3	2	2	4	4	2	2	2	0	0	0	1	5	4	1	3	5	3	3	2	5	0	0					
Cheatgrass	0	1	2	0	0	0	1	2	0	3	1	2	3	2	2	1	0	0	0	1	1	0	1	0	2	1	3	2	3	0	0	0					
Chickweed	0	5	7	0	0	3	7	5	4	5	3	5	5	4	7	1	2	2	3	5	3	7	5	7	6	6	6	6	0	0	0						
Cocklebur	0	6	6	0	0	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—						
Corn	0	1	2	0	0	0	1	1	1	1	2	2	1	2	2	1	2	1	2	1	1	1	0	1	2	1	1	1	1	1	0	0					
Cotton	0	2	6	6	4	0	7	2	0	3	8	5	6	3	9	5	5	2	1	0	1	0	0	10	8	9	9	9	0	0	0	0					
Crabgrass	2	6	6	4	0	0	1	2	1	2	4	2	3	2	3	7	2	3	1	5	3	6	1	2	8	6	4	6	4	5	2	4	1	0			
Giant foxtail	1	2	3	0	0	0	1	2	1	1	3	1	4	2	3	2	3	1	1	2	1	2	1	2	2	2	2	2	2	0	1	1	0	0			
Lambsquarters	0	9	—	0	0	0	3	5	4	2	4	5	3	5	9	10	6	10	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
Morningglory	3	6	7	0	0	0	3	6	2	5	5	3	2	6	2	3	5	2	6	3	6	2	4	8	4	8	4	7	5	6	7	0	3	7	0	0	
Nutsedge	0	0	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
Rape	0	4	5	0	0	0	7	2	0	0	6	7	6	2	4	6	5	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Rice	2	2	3	0	0	0	0	0	0	0	1	1	2	2	1	2	1	1	2	1	1	1	3	1	1	1	1	1	1	1	1	1	1	1	1	1	0
Sorghum	0	2	2	0	0	0	1	1	1	1	2	1	2	2	2	2	2	1	3	1	2	2	1	3	1	2	2	1	2	2	1	2	2	1	3	1	1
Soybean	5	5	6	6	7	1	5	4	6	6	7	5	8	5	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
Sugar beet	6	9	8	8	9	2	8	8	5	8	7	8	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
Velvetleaf	1	0	3	2	8	1	3	0	1	3	5	6	2	2	7	3	4	5	7	8	1	1	1	2	5	0	6	3	1	1	4	0	6	1	2	2	
Wheat	0	0	2	1	2	0	0	0	0	0	2	2	2	2	4	3	4	3	3	0	3	0	3	0	3	0	3	0	3	2	1	1	3	2	2	1	2
Wild buckwheat	2	1	2	3	3	2	3	2	1	1	2	3	6	8	7	6	7	6	7	7	4	6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Wild oat	1	0	2	6	7	0	0	0	1	3	3	4	4	8	6	8	8	4	4	2	1	5	1	1	8	7	3	4	4	3	4	4	3	4	4	3	

TEST B

The compounds evaluated in this test were formulated in a non-phytoxic solvent and applied to the soil surface before plant seedlings emerged (preemergence application), to water that covered the soil surface (paddy application), and to plants that were in the one-to-four leaf stage (postemergence application). A sandy loam soil was used for the preemergence and postemergence tests, while a silt loam soil was used in the paddy test. Water depth was approximately 2.5 cm for the paddy test and was maintained at this level for the duration of the test.

Plant species in the preemergence and postemergence tests consisted of barley (*Hordeum vulgare*), bedstraw (*Galium aparine*), blackgrass (*Alopecurus myosuroides*), chickweed (*Stellaria media*), corn (*Zea mays*), cotton (*Gossypium hirsutum*), crabgrass (*Digitaria sanguinalis*), downy brome (*Bromus tectorum*), duck salad (*Heteranthera limosa*), giant foxtail (*Setaria faberii*), lambsquarters (*Chenopodium album*), morningglory (*Ipomoea hederacea*), pigweed (*Amaranthus retroflexus*), rape (*Brassica napus*), ryegrass (*Lolium multiflorum*), sorghum (*Sorghum bicolor*), soybean (*Glycine max*), speedwell (*Veronica persica*), sugar beet (*Beta vulgaris*), velvetleaf (*Abutilon theophrasti*), wheat (*Triticum aestivum*), wild buckwheat (*Polygonum convolvulus*) and wild oat (*Avena fatua*) and purple nutsedge (*Cyperus rotundus*). All plant species were planted one day before application of the compound for the preemergence portion of this test. Plantings of these species were adjusted to produce plants of appropriate size for the postemergence portion of the test. Plant species in the paddy test consisted of barnyardgrass (*Echinochloa crus-galli*), rice (*Oryza sativa*), and umbrella sedge (*Cyperus difformis*).

All plant species were grown using normal greenhouse practices. Visual evaluations of injury expressed on treated plants, when compared to untreated controls, were recorded approximately fourteen to twenty-one days after application of the test compound. Plant response ratings, summarized in Table B, were recorded on a 0 to 10 scale where 0 is no injury and 10 is complete control. A dash (—) response means no test result.

TABLE B

	POSTEMERGENCE				
	COMPOUND				
	5	9	15	21	24
Rate (500 g/ha)					
Barley Igri	4	3	4	1	2
Bedstraw	4	10	9	9	9
Blackgrass	3	8	9	6	9
Chickweed	5	10	9	9	9
Corn	3	4	4	5	4
Cotton	5	6	4	3	5
Crabgrass	3	7	9	6	8
Downy brome	1	4	5	—	2
Duck salad	4	5	2	0	2
Giant foxtail	4	6	6	3	5
Lambsquarters	6	10	10	10	10
Morningglory	6	7	10	8	8
Pigweed	8	8	8	8	8
Rape	5	7	9	6	6
Ryegrass	0	3	4	2	1
Sorghum	2	3	4	4	4
Soybean	5	7	9	6	9
Speedwell	10	10	10	10	10
Sugar beet	8	10	9	10	10
Velvetleaf	0	7	8	4	6
Wheat	2	3	3	1	3
Wild buckwheat	3	9	7	10	10

TABLE B-continued

Wild oat	4	7	6	3	10
Barnyardgrass	5	10	9	9	10
Rice Japonica	2	6	6	5	4
Umbrella sedge	7	9	9	3	6
Rate (250 g/ha)					
Barley Igri	2	3	2	1	2
Bedstraw	3	8	9	9	9
Blackgrass	2	7	9	6	9
Chickweed	5	7	9	9	6
Corn	3	3	3	4	3
Cotton	4	6	3	3	4
Crabgrass	3	6	9	6	8
Downy brome	0	2	4	—	1
Duck salad	2	3	1	0	1
Giant foxtail	3	4	5	3	3
Lambsquarters	4	10	10	10	9
Morningglory	5	6	9	7	7
Pigweed	6	8	8	8	8
Rape	4	6	9	5	3
Ryegrass	0	0	3	—	0
Sorghum	2	2	3	4	3
Soybean	4	7	8	5	3
Speedwell	10	10	10	10	10
Sugar beet	8	10	9	10	8
Velvetleaf	0	6	7	4	5
Wheat	1	2	2	—	2
Wild buckwheat	2	7	6	10	10
Wild oat	3	5	5	2	—
Barnyardgrass	5	10	9	9	10
Rice Japonica	0	5	6	4	4
Umbrella sedge	6	8	8	1	5
Rate (125 g/ha)					
Barley Igri	2	2	2	—	1
Bedstraw	0	8	7	9	8
Blackgrass	0	7	9	5	6
Chickweed	3	7	9	7	—
Corn	3	3	3	4	2
Cotton	3	5	3	2	4
Crabgrass	3	5	9	4	7
Downy brome	0	0	3	0	0
Duck salad	2	3	0	0	0
Giant foxtail	3	3	4	2	0
Lambsquarters	3	10	10	10	9
Morningglory	5	6	9	7	5
Pigweed	6	8	8	7	5
Rape	4	5	8	3	2
Ryegrass	0	0	2	0	0
Sorghum	2	2	2	3	3
Soybean	4	6	8	5	3
Speedwell	10	10	10	10	10
Sugar beet	6	8	9	9	6
Velvetleaf	0	4	6	2	0
Wheat	1	1	2	0	1
Wild buckwheat	1	5	5	9	7
Wild oat	3	3	4	0	3
Barnyardgrass	4	10	9	9	10
Rice Japonica	0	3	4	2	3
Umbrella sedge	5	8	5	0	1
Rate (62 g/ha)					
Barley Igri	1	2	1	0	1
Bedstraw	0	7	7	4	5
Blackgrass	0	2	7	1	3
Chickweed	2	6	8	4	5
Corn	3	2	2	3	2
Cotton	3	4	3	2	3
Crabgrass	3	4	9	2	7
Downy brome	0	0	2	0	0
Duck salad	1	2	0	0	0
Giant foxtail	3	3	3	2	0
Lambsquarters	3	10	10	9	9
Morningglory	3	6	7	5	5
Pigweed	6	7	7	5	5
Rape	3	5	7	2	—
Ryegrass	0	0	2	0	0
Sorghum	2	1	2	3	2
Soybean	4	6	7	5	2
Speedwell	9	10	10	10	10
Sugar beet	6	8	8	9	6
Velvetleaf	0	3	6	2	0
Wheat	1	0	2	0	0
Wild buckwheat	0	5	4	7	6

TABLE B-continued

Wild oat	3	2	3	0	3
Barnyardgrass	3	10	9	9	10
Rice Japonica	0	0	3	0	2
Umbrella sedge	0	5	2	0	0 5
<u>Rate (31 g/ha)</u>					
Barley Igri	1	1	1	0	—
Bedstraw	0	0	5	4	5
Blackgrass	0	0	4	—	2
Chickweed	0	5	8	4	4
Corn	2	1	2	3	2 10
Cotton	2	3	3	2	3
Crabgrass	3	3	8	2	7
Downy brome	0	0	2	0	0
Duck salad	0	0	0	0	0
Giant foxtail	3	3	3	0	0
Lambsquarters	2	7	10	9	6 15
Morningglory	2	4	6	5	0
Pigweed	5	7	7	5	5
Rape	2	3	6	0	—
Ryegrass	0	0	2	0	0
Sorghum	2	1	2	2	2
Soybean	3	4	6	4	0 20
Speedwell	4	9	10	10	10
Sugar beet	5	6	7	9	6
Velvetleaf	0	0	4	0	0
Wheat	0	0	1	0	0
Wild buckwheat	0	0	2	4	3
Wild oat	2	2	2	0	0 25
Barnyardgrass	0	9	9	5	7
Rice Japonica	0	0	2	0	1
Umbrella sedge	0	3	0	0	0

PREEMERGENCE

COMPOUND

	5	9	15	21	24 30
<u>Rate (500 g/ha)</u>					
Barley Igri	—	2	5	4	3
Bedstraw	10	10	10	5	10
Blackgrass	6	10	10	10	10
Chickweed	10	10	10	9	10 35
Corn	7	4	2	3	0
Cotton	4	3	5	2	0
Crabgrass	10	10	10	10	10
Downy brome	—	6	10	4	10
Duck salad	—	—	—	—	—
Giant foxtail	10	10	10	10	10 40
Lambsquarters	10	10	10	10	10
Morningglory	8	4	8	3	6
Pigweed	10	10	10	10	10
Rape	10	10	10	4	4
Ryegrass	6	10	10	5	10
Sorghum	4	8	8	5	— 45
Soybean	3	0	6	4	—
Speedwell	10	10	10	10	10
Sugar beet	10	9	10	10	10
Velvetleaf	9	7	10	4	8
Wheat	0	1	6	4	4
Wild buckwheat	9	9	10	6	10
Wild oat	3	10	10	10	10 50
<u>Rate (250 g/ha)</u>					
Barley Igri	2	1	3	2	2
Bedstraw	7	10	10	5	0
Blackgrass	6	10	10	10	10
Chickweed	10	10	10	9	10
Corn	7	3	0	2	0 55
Cotton	3	0	4	0	0
Crabgrass	10	10	10	10	10
Downy brome	0	6	10	4	4
Duck salad	—	—	—	—	—
Giant foxtail	9	10	10	10	10
Lambsquarters	10	10	10	8	10 60
Morningglory	6	3	7	2	5
Pigweed	10	10	10	10	10
Rape	8	10	8	2	4
Ryegrass	6	10	10	4	10
Sorghum	3	7	7	5	—
Soybean	3	0	3	2	0 65
Speedwell	10	10	10	10	10
Sugar beet	10	9	10	9	10
Velvetleaf	8	7	8	4	6
Wheat	—	—	3	1	4

TABLE B-continued

Wild buckwheat	8	8	10	6	10
Wild oat	3	5	9	7	9
<u>Rate (125 g/ha)</u>					
Barley Igri	0	—	1	0	0
Bedstraw	4	8	10	3	0
Blackgrass	3	10	10	10	10
Chickweed	8	8	10	5	10
Corn	4	3	0	2	0
Cotton	3	0	3	0	0
Crabgrass	9	10	10	10	10
Downy brome	0	4	6	4	4
Duck salad	—	—	—	—	—
Giant foxtail	9	10	10	9	10
Lambsquarters	10	10	10	5	10
Morningglory	4	2	6	2	0
Pigweed	10	10	10	10	10
Rape	5	7	4	0	0
Ryegrass	2	5	10	3	9
Sorghum	2	6	5	3	0
Soybean	3	0	2	2	0
Speedwell	10	10	10	10	10
Sugar beet	10	9	10	5	9
Velvetleaf	6	5	4	4	0
Wheat	0	0	3	0	0
Wild buckwheat	4	7	10	6	—
Wild oat	3	3	8	5	9
<u>Rate (62 g/ha)</u>					
Barley Igri	0	0	1	0	0
Bedstraw	3	7	10	2	0
Blackgrass	3	8	10	8	10
Chickweed	5	6	10	5	5
Corn	3	3	0	0	0
Cotton	2	0	0	0	0
Crabgrass	8	10	10	9	10
Downy brome	0	2	4	3	0
Duck salad	—	—	—	—	—
Giant foxtail	8	10	10	8	10
Lambsquarters	10	6	10	5	9
Morningglory	3	1	5	0	0
Pigweed	9	10	10	9	10
Rape	4	3	4	0	0
Ryegrass	0	5	9	2	3
Sorghum	0	4	4	2	0
Soybean	0	0	0	0	0
Speedwell	10	10	10	8	10
Sugar beet	7	8	10	5	5
Velvetleaf	4	0	3	4	0
Wheat	0	0	3	0	0
Wild buckwheat	4	5	10	2	9
Wild oat	3	1	5	4	3
<u>Rate (31 g/ha)</u>					
Barley Igri	0	0	1	0	0
Bedstraw	0	0	5	0	0
Blackgrass	0	5	9	8	10
Chickweed	5	0	9	5	1
Corn	0	0	0	0	0
Cotton	0	0	0	0	0
Crabgrass	7	9	10	5	10
Downy brome	0	0	1	3	0
Duck salad	—	—	—	—	—
Giant foxtail	7	7	10	6	7
Lambsquarters	7	3	10	5	2
Morningglory	3	0	0	0	0
Pigweed	9	10	10	3	8
Rape	0	0	1	0	0
Ryegrass	0	0	5	2	3
Sorghum	0	3	4	0	0
Soybean	0	0	0	0	0
Speedwell	9	9	10	8	9
Sugar beet	2	0	8	2	3
Velvetleaf	0	0	2	2	0
Wheat	0	0	3	0	0
Wild buckwheat	4	2	7	0	0
Wild oat	2	0	4	2	0

TEST C

Seeds of barnyardgrass (*Echinochloa crus-galli*), cassia (*Cassia obtusifolia*), cocklebur (*Xanthium pensylvanicum*), common ragweed (*Ambrosia elatior*), corn

(*Zea mays*), cotton (*Gossypium hirsutum*), crabgrass (*Digitaria* spp.), fall panicum (*Panicum dicholomiflorum*), giant foxtail (*Setaria faberii*), green foxtail (*Setaria viridis*), jimson weed (*Datura stramonium*), johnson grass (*Sorghum halepense*), morningglory (*Ipomoea* spp.), prickly sida (*Sida spinosa*), signalgrass (*Brachiaria platyphylla*), soybean (*Glycine max*), velvetleaf (*Abutilon theophrasti*), wild proso (*Panicum miliaceum*) and purple nutsedge (*Cyperus rotundus*) tubers were planted into a silt loam soil. Test chemicals, dissolved in a non-phytotoxic solvent, were then applied to the soil surface within one day after the seeds were planted. Pots receiving these preemergence treatments were placed in the greenhouse and maintained according to routine greenhouse procedures.

Treated plants and untreated controls were maintained in the greenhouse approximately 21 days after application of the test compound. Visual evaluations of plant injury responses were then recorded. Plant response ratings, summarized in Table C, are reported on a 0 to 10 scale where 0 is no effect and 10 is complete control.

TABLE C

	PREEMERGENCE	
	COMPOUND	
	9	15
<u>Rate (500 g/ha)</u>		
Barnyardgrass	8	
Cassia	6	
Cocklebur	0	
Common Ragweed	8	
Corn G4689A	3	
Cotton	0	
Crabgrass	10	
Fall Panicum	10	
Giant Foxtail	10	
Green Foxtail	10	
Jimson weed	8	
Johnson Grass	9	
Morningglory	7	
Prickly sida	7	
Signalgrass	10	
Soybean	1	
Velvetleaf	4	
Wild Proso	9	
<u>Rate (250 g/ha)</u>		
Barnyardgrass	7	10
Cassia	0	8
Cocklebur	0	0
Common Ragweed	8	10
Corn G4689A	1	2
Cotton	0	0
Crabgrass	10	10
Fall Panicum	10	10
Giant Foxtail	10	10
Green Foxtail	10	10
Jimson weed	6	7
Johnson Grass	6	6
Nutsedge	6	—
Prickly sida	5	6
Signalgrass	10	10
Velvetleaf	4	6
Wild Proso	9	9
<u>Rate (125 g/ha)</u>		
Barnyardgrass	5	8
Cassia	0	0
Cocklebur	0	0
Common Ragweed	1	0
Corn G4689A	1	1
Cotton	0	—
Crabgrass	10	10
Fall Panicum	1	10
Giant Foxtail	9	10
Green Foxtail	10	10
Jimson weed	2	1
Johnson Grass	1	6

TABLE C-continued

	PREEMERGENCE	
	COMPOUND	
	9	15
Nutsedge	0	—
Prickly sida	0	6
Signalgrass	—	10
Soybean	0	—
Velvetleaf	0	2
Wild Proso	8	8
<u>Rate (62 g/ha)</u>		
Barnyardgrass	2	7
Cassia	0	0
Cocklebur	—	0
Common Ragweed	0	0
Corn G4689A	—	1
Cotton	0	—
Crabgrass	10	10
Fall Panicum	0	8
Giant Foxtail	9	10
Green Foxtail	7	10
Jimson weed	0	0
Johnson Grass	—	6
Morningglory	0	—
Nutsedge	0	2
Prickly sida	0	0
Signalgrass	—	10
Soybean	0	—
Velvetleaf	0	0
Wild Proso	7	8
<u>Rate (31 g/ha)</u>		
Barnyardgrass	0	2
Cassia	0	0
Cocklebur	0	0
Common Ragweed	0	0
Corn G4689A	—	1
Cotton	0	0
Crabgrass	2	9
Fall Panicum	—	0
Giant Foxtail	8	8
Green Foxtail	6	8
Jimson weed	0	0
Johnson Grass	0	6
Morningglory	—	0
Prickly sida	0	0
Signalgrass	—	9
Soybean	0	0
Velvetleaf	0	0
Wild Proso	6	7
<u>Rate (16 g/ha)</u>		
Barnyardgrass		0
Cassia		0
Cocklebur		0
Common Ragweed		0
Cotton		0
Crabgrass		6
Fall Panicum		0
Giant Foxtail		2
Green Foxtail		4
Jimson weed		0
Johnson Grass		2
Morningglory		0
Nutsedge		0
Prickly sida		0
Signalgrass		0
Soybean		0
Velvetleaf		0
Wild Proso		6

TEST D

Plastic pots were partially filled with silt loam soil. The soil was then saturated with water. Japonica rice (*Oryza sativa*) seedlings at the 2.0 to 2.5 leaf stage, seeds selected from barnyardgrass (*Echinochloa crus-galli*), umbrella sedge (*Cyperus difformis*), and tubers selected from arrowhead (*Sagittaria* spp.), waterchestnut (*Eleocharis* spp.), were planted into this soil. After planting,

water levels were raised to 3 cm above the soil surface and maintained at this level throughout the test. Chemical treatments were formulated in a non-phytotoxic solvent and applied directly to the paddy water. Treated plants and controls were maintained in a greenhouse for approximately 21 days, after which all species were compared to controls and visually evaluated. Plant response ratings, summarized in Table D, are reported on a 0 to 10 scale where 0 is no effect and 10 is complete control. A dash (—) response means no test result.

TABLE D

PADDY		COMPOUND	9
<u>Rate (500 g/ha)</u>			
Arrowhead	0		
Barnyardgrass	10		
Japonica rice	4		
Umbrella sedge	6		
Waterchestnut	0		
<u>Rate (250 g/ha)</u>			
Arrowhead	0		
Barnyardgrass	10		
Japonica rice	3		
Umbrella sedge	4		
Waterchestnut	0		
<u>Rate (125 g/ha)</u>			
Arrowhead	0		
Barnyardgrass	9		
Japonica rice	2		
Umbrella sedge	3		
Waterchestnut	0		
<u>Rate (64 g/ha)</u>			
Arrowhead	0		
Barnyardgrass	3		
Japonica rice	1		
Umbrella sedge	4		
Waterchestnut	0		
<u>Rate (32 g/ha)</u>			
Arrowhead	0		
Barnyardgrass	1		
Japonica rice	0		
Umbrella sedge	3		
Waterchestnut	0		

TEST E

Plastic pots were partially filled with silt loam soil. The soil was then flooded with water, Japonica rice (*Oryza sativa*) sprouted seeds and 1.5 leaf transplants were planted in the soil. Seeds of barnyardgrass (*Echinochloa crus-galli*) were planted in saturated soil and plants grown to the 1 leaf, 2 leaf and 3 leaf stages for testing. At testing, the water level for all plantings was raised to 2 cm above the soil surface. Chemical treatments were formulated in a non-phytotoxic solvent and applied directly to the paddy water. Treated plants and controls were maintained in a greenhouse for approximately 21 days, after which all species were compared to controls and visually evaluated. Plant response ratings, summarize in Table E are reported on a 0 to 10 scale where 0 is no effect and 10 is complete control. A dash (—) response means no test result.

TABLE E

Flood		COMPOUND	9
<u>Rate (500 g/ha)</u>			
1-LF B.Y.Grass	10		
2-LF B.Y.Grass	9		

TABLE E-continued

Flood		COMPOUND	9
<u>Rate (250 g/ha)</u>			
3-lf B.Y.Grass	8		
Jap Direct Seed	3		
Jap Rice Eff	3		
<u>Rate (125 g/ha)</u>			
1-LF B.Y.Grass	10		
2-LF B.Y.Grass	8		
3-lf B.Y.Grass	9		
Jap Direct Seed	1		
Jap Rice Eff	1		
<u>Rate (64 g/ha)</u>			
1-LF B.Y.Grass	9		
2-LF B.Y.Grass	5		
3-lf B.Y.Grass	3		
Jap Direct Seed	1		
Jap Rice Eff	0		
<u>Rate (32 g/ha)</u>			
1-LF B.Y.Grass	8		
2-LF B.Y.Grass	4		
3-lf B.Y.Grass	2		
Jap Direct Seed	1		
Jap Rice Eff	0		
<u>Rate (16 g/ha)</u>			
1-LF B.Y.Grass	6		
2-LF B.Y.Grass	2		
3-lf B.Y.Grass	0		
Jap Direct Seed	0		
Jap Rice Eff	0		
<u>Rate (8 g/ha)</u>			
1-LF B.Y.Grass	0		
2-LF B.Y.Grass	0		
3-lf B.Y.Grass	0		
Jap Direct Seed	0		
Jap Rice Eff	0		

TEST F

Compounds evaluated in this test were formulated in a non-phytotoxic solvent and applied to the soil surface before plant seedlings emerged (preemergence application) and to plants that were An the one-to-four leaf stage (postemergence application). A sandy loam soil was used for the preemergence test while a mixture of sandy loam soil and greenhouse potting mix in a 60:40 ratio was used for the postemergence test. Test compounds were applied within approximately one day after planting seeds for the preemergence test. Plantings of these crops and weed species were adjusted to produce plants of appropriate size for the postemergence test. All plant species were grown using normal greenhouse practices. Crop and weed species include winter barley (*Hordeum vulgare* cv. 'Igrí'), bedstraw (*Galium aparine*), blackgrass (*Alopecurus myosuroides*), chickweed (*Stellaria media*), downy brome (*Bromus tectorum*), field violet (*Viloa arvensis*), green foxtail (*Setaria viridis*), kochia (*Kochia scoparia*), lambsquarters (*Chenopodium album*), Persian speedwell (*Veronica persica*), rape (*Brassica napus* cv. 'Jet Neuf'), ryegrass (*Lolium multiflorum*), sugar beet (*Beta vulgaris* cv. 'US1'), sunflower (*Helianthus annuus* cv. 'Russian Giant'), spring wheat (*Triticum aestivum* cv. 'ERA'), winter wheat (*Triticum aestivum* cv. 'Talent'), wild buckwheat (*Polygonum convolvulus*), wild mustard (*Sinapis arvensis*), wild oat (*Avena fatua*), and wild radish (*Raphanus raphanistrum*).

trum). Blackgrass and wild oat were treated postemergence at two growth stages. The first stage (1) was when the plants had two to three leaves. The second stage (2) was when the plants had approximately four leaves or in the initial stages of tillering. Treated plants and untreated controls were maintained in a greenhouse for approximately 21 to 28 days, after which all treated plants were compared to untreated controls and visually evaluated. Plant response ratings, summarized in Table F, are based upon a 0 to 10 scale where 0 is no effect and 10 is complete control. A dash response (—) means no test result.

TABLE F

	POSTEMERGENCE	
	COMPOUND	
	9	15
<u>Rate (500 g/ha)</u>		
Blackgrass (1)	—	7
Blackgrass (2)	—	5
Chickweed	0	3
Downy brome	—	2
Field violet	4	10
Galium (1)	0	2
Galium (2)	—	—
Green foxtail	—	6
Kochia	8	6
Lambsquarters	7	10
Persn Speedwell	6	10
Rape	—	10
Ryegrass	—	3
Sugar beet	8	9
Sunflower	7	10
Wheat (Spring)	0	3
Wheat (Winter)	—	2
Wild buckwheat	2	2
Wild mustard	7	10
Wild oat (1)	—	4
Wild oat (2)	—	4
Wild radish	7	9
Winter Barley	—	2
<u>Rate (250 g/ha)</u>		
Blackgrass (1)	0	3
Blackgrass (2)	0	3
Chickweed	0	0
Downy brome	0	0
Field violet	2	9
Galium (1)	0	0
Galium (2)	—	—
Green foxtail	4	4
Kochia	6	4
Lambsquarters	5	8
Persn Speedwell	4	10
Rape	—	10
Ryegrass	0	0
Sugar beet	6	6
Sunflower	6	10
Wheat (Spring)	0	0
Wheat (Winter)	0	0
Wild buckwheat	0	0
Wild mustard	4	8
Wild oat (1)	2	2
Wild oat (2)	3	2
Wild radish	3	8
Winter Barley	0	0
<u>Rate (125 g/ha)</u>		
Blackgrass (1)	0	0
Blackgrass (2)	0	0
Chickweed	0	0
Downy brome	0	0
Field violet	0	8
Galium (1)	0	0
Galium (2)	—	—
Green foxtail	2	2
Kochia	3	2
Lambsquarters	2	5
Persn Speedwell	2	7
Rape	—	9
Ryegrass	0	0

TABLE F-continued

Sugar beet	4	3
Sunflower	3	10
Wheat (Spring)	0	0
Wheat (Winter)	0	0
Wild buckwheat	0	0
Wild mustard	0	5
Wild oat (1)	0	0
Wild oat (2)	0	0
Wild radish	0	4
Winter Barley	0	0
<u>Rate (64 g/ha)</u>		
Blackgrass (1)	0	
Blackgrass (2)	0	
Chickweed	0	
Downy brine	0	
Field violet	0	
Galium (1)	0	
Galium (2)	—	
Green foxtail	0	
Kochia	0	
Lambsquarters	0	
Persn Speedwell	0	
Rape	—	
Ryegrass	0	
Sugar beet	3	
Sunflower	0	
Wheat (Spring)	0	
Wheat (Winter)	0	
Wild buckwheat	0	
Wild mustard	0	
Wild oat (1)	0	
Wild oat (2)	0	
Wild radish	0	
Winter Barley	0	
<u>Rate (32 g/ha)</u>		
Blackgrass (1)	0	4
Blackgrass (2)	2	5
Chickweed	2	2
Downy brome	0	0
Field violet	4	9
Galium (1)	0	3
Galium (2)	—	2
Green foxtail	7	9
Kochia	0	0
Lambsquarters	2	8
Persn Speedwell	3	10
Rape	2	4
Ryegrass	0	3
Sugar beet	3	7
Sunflower	0	2
Wheat (Spring)	0	0
Wheat (Winter)	0	0
Wild buckwheat	0	0
Wild mustard	0	4
Wild oat (1)	2	3
Wild oat (2)	2	2
Wild radish	0	2
Winter Barley	0	0
<u>PREEMERGENCE</u>		
	COMPOUND	
	9	15
<u>Rate (500 g/ha)</u>		
Blackgrass (1)	10	10
Blackgrass (2)	10	10
Chickweed	10	10
Downy brome	10	10
Field violet	10	10
Galium (1)	10	10
Galium (2)	—	10
Green foxtail	10	10
Kochia	10	10
Lambsquarters	10	10
Persn Speedwell	10	10
Rape	9	10
Ryegrass	10	10
Sugar beet	10	10
Sunflower	0	10
Wheat (Spring)	4	4
Wheat (Winter)	3	4
Wild buckwheat	10	10

TABLE F-continued

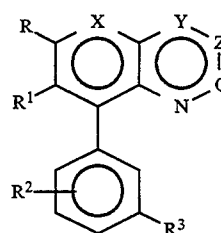
Wild mustard	9	10
Wild oat (1)	10	10
Wild oat (2)	10	10
Wild radish	10	10
Winter Barley	4	4
<u>Rate (250 g/ha)</u>		
Blackgrass (1)	8	10
Blackgrass (2)	8	10
Chickweed	10	10
Downy brome	9	10
Field violet	10	10
Galium (1)	10	10
Galium (2)	—	10
Green foxtail	10	10
Kochia	7	10
Lambsquarters	10	10
Persn Speedwell	10	10
Rape	8	10
Ryegrass	10	10
Sugar beet	10	10
Sunflower	0	10
Wheat (Spring)	2	2
Wheat (Winter)	2	2
Wild buckwheat	10	10
Wild mustard	7	10
Wild oat (1)	8	10
Wild oat (2)	10	9
Wild radish	8	10
Winter Barley	2	2
<u>Rate (125 g/ha)</u>		
Blackgrass (1)	6	10
Blackgrass (2)	6	10
Chickweed	8	10
Downy brome	6	7
Field violet	10	10
Galium (1)	8	8
Galium (2)	—	8
Green foxtail	10	10
Kochia	3	8
Lambsquarters	8	10
Persn Speedwell	10	10
Rape	6	7
Ryegrass	8	8
Sugar beet	8	10
Sunflower	0	9
Wheat (Spring)	0	0
Wheat (Winter)	0	0
Wild buckwheat	6	8
Wild mustard	3	10
Wild oat (1)	6	8
Wild oat (2)	7	8
Wild radish	6	7
Winter Barley	0	0
<u>Rate (64 g/ha)</u>		
Blackgrass (1)	4	8
Blackgrass (2)	4	8
Chickweed	5	7
Downy brome	4	3
Field violet	8	10
Galium (1)	4	4
Galium (2)	—	5
Green foxtail	10	10
Kochia	0	4
Lambsquarters	6	10
Persn Speedwell	6	10
Rape	4	5
Ryegrass	3	6
Sugar beet	6	9
Sunflower	0	4
Wheat (Spring)	0	0
Wheat (Winter)	0	0
Wild buckwheat	2	3
Wild mustard	0	7
Wild oat (1)	4	6
Wild oat (2)	5	5
Wild radish	2	3
Winter Barley	0	0
<u>Rate (16 g/ha)</u>		
Blackgrass (1)	0	2
Blackgrass (2)	0	2
Chickweed	0	0

TABLE F-continued

Downy brome	0	0
Field violet	0	6
Galium (1)	0	0
Galium (2)	—	0
Green foxtail	3	4
Kochia	0	0
Lambsquarters	0	5
Persn Speedwell	0	7
Rape	0	2
Ryegrass	0	0
Sugar beet	0	3
Sunflower	0	0
Wheat (Spring)	0	0
Wheat (Winter)	0	0
Wild buckwheat	0	0
Wild mustard	0	2
Wild oat (1)	0	0
Wild oat (2)	0	0
Wild radish	0	0
Winter Barley	0	0

20 What is claimed is:

1. A compound of the formula



wherein

- 35 X is CH₃;
 Y is CR⁸;
 Z is N;
 Q is N CR⁵;
 R is C₁-C₄ alkyl, C₂-C₄ alkoxyalkyl, C₂-C₄ alkenyl,
 C₂-C₄ alkynyl, C₁-C₄ alkoxy, C₁-C₄ alkylthio,
 C₁-C₃ alkylamino or N(C₁-C₃ alkyl)(C₁-C₃ alkyl);
 R¹ is H, F, Cl or CH₃;
 R² is H, halogen, C₁-C₃ alkyl, C₁-C₃ haloalkyl,
 C₁-C₃ alkoxy or C₁-C₃ haloalkoxy;
 R³ is H, halogen, C₁-C₄ alkyl, C₂-C₄ alkenyl, C₂-C₄
 40 alkynyl, C₁-C₄ haloalkyl, C₃-C₄ halocycloalkyl,
 C₂-C₄ haloalkenyl, C₂-C₄ haloalkynyl, OR⁶,
 S(O)_nR⁷ or CN;
 R⁵ is C₁-C₄ haloalkyl, C₃-C₅ halocycloalkyl, C₂-C₄
 50 haloalkenyl, C₂-C₄ haloalkynyl, OR⁶, S(O)_nR⁷ or
 halogen;
 R⁶ is C₁-C₄ alkyl, C₃-C₄ alkenyl, C₃-C₄ alkynyl,
 C₁-C₄ haloalkyl, C₂-C₄ haloalkenyl or C₂-C₄ halo-
 alkynyl;
 R⁷ is C₁-C₂ alkyl or C₁-C₂ haloalkyl;
 R⁸ is H, CN, C₁-C₃ alkyl, C₁-C₃ alkoxy or halogen;
 and
 n is 0, 1 or 2;
 or their mono N-oxides or their agriculturally suitable
 60 salts.
2. The compounds of claim 1 wherein
 R¹ is H or F; and
 R² is H or F.
3. The compounds of claim 2 wherein
 65 R³ is F, Cl, Br, C₁-C₄ haloalkyl, OR⁶, S(O)_nR⁷ or CN;
 n is 0;
 Y is CH or C-CN; and
 their mono N-oxides.

4. The compounds of claim 3 wherein
R is C₁-C₃ alkyl, C₂-C₃ alkoxyalkyl, C₂-C₃ alkenyl,
C₂-C₃ alkynyl, C₁-C₂ alkoxy, C₁-C₂ alkylthio,
C₁-C₂ alkylamino and N(C₁-C₂ alkyl)(C₁-C₂ al-

kyl);
R⁶ is C₁-C₃ alkyl, allyl, propargyl, C₁-C₃ haloalkyl,
C₂-C₃ haloalkenyl.

5. A composition suitable for controlling the growth
of undesired vegetation which comprises an effective
amount of a compound of claim 1 and at least one of the
following: surfactant, solid or liquid diluent.

6. A composition suitable for controlling the growth
of undesired vegetation which comprises an effective
amount of a compound of claim 2 and at least one of the
following: surfactant, solid or liquid diluent.

7. A composition suitable for controlling the growth
of undesired vegetation which comprises an effective
amount of a compound of claim 3 and at least one of the
following: surfactant, solid or liquid diluent.

8. A composition suitable for controlling the growth
of undesired vegetation which comprises an effective
amount of a compound of claim 4 and at least one of the
following: surfactant, solid or liquid diluent.

9. A method for controlling the growth of undesired
vegetation which comprises applying to the locus to be
protected an effective amount of a compound of claim
1.

10. A method for controlling the growth of undesired
vegetation which comprises applying to the locus to be
protected an effective amount of a compound of claim
2.

11. A method for controlling the growth of undesired
vegetation which comprises applying to the locus to be
protected an effective amount of a compound of claim
3.

12. A method for controlling the growth of undesired
vegetation which comprises applying to the locus to be
protected an effective amount of a compound of claim
4.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,389,600
DATED : FEBRUARY 14, 1995
INVENTOR(S) : THOMAS P. SELBY

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 15, line 53:

Change "78°C" to -- -78°C --.

Column 19, line 46:

Change "starred" to --stirred --.

Columns 45 and 46, table heading:

Change "O" to --Q--.

Signed and Sealed this
Thirtieth Day of July, 1996

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks