7/29/86 XR RE 32,216

United States Patent [19]

Theissen

[11] E **Patent Number: Re. 32,216**

[45] **Reissued Date of Patent: Jul. 29, 1986**

[54] **SALTS OF SUBSTITUTED PHENOXYBENZOIC ACIDS, COMPOSITIONS OF THE SAME AND HERBICIDAL USE THEREOF**

[75] Inventor: **Robert J. Theissen**, Bridgewater, N.J.

[73] Assignee: **Rhone-Poulenc Agrochimie**, Lyons, France

[21] Appl. No.: **469,565**

[22] Filed: **Feb. 23, 1983**

Related U.S. Patent Documents

Reissue of:

[64] Patent No.: **4,164,408**
Issued: **Aug. 14, 1979**
Appl. No.: **836,885**
Filed: **Sep. 26, 1977**

U.S. Applications:

[63] Continuation of Ser. No. 279,288, Jun. 25, 1981, abandoned, and a continuation of Ser. No. 702,367, Jul. 2, 1976, which is a continuation-in-part of Ser. No. 617,569, Sep. 29, 1975, Pat. No. 3,979,437, which is a continuation of Ser. No. 398,610, Sep. 19, 1973, Pat. No. 3,941,830, which is a continuation of Ser. No. 114,712, Feb. 11, 1971, Pat. No. 3,784,635, which is a continuation-in-part of Ser. No. 819,412, Apr. 25, 1969, Pat. No. 3,652,645, said Ser. No. 702,367, is a continuation-in-part of Ser. No, 545,232, Jan. 29, 1975, Pat. No. 4,002,662, which is a continuation-in-part of Ser. No. 398,610.

[51] **Int. Cl.**⁴ **A01N 33/22; C07C 79/35**

[52] **U.S. Cl.** **71/98;** 71/103; 71/105; 71/111; 71/115; 260/501.1; 260/501.16; 260/501.17; 560/12; 560/13; 560/17; 560/21; 562/430; 562/432; 562/435; 558/416

[58] **Field of Search** .... 71/98, 103, 105, 115, 71/111; 260/465 D; 562/430, 432, 435; 560/12, 13, 17, 21

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,080,225	3/1963	Wilson et al.	71/124
3,316,080	4/1967	Inoue et al.	71/124
3,322,525	5/1967	Martin et al.	71/103 X
3,423,470	1/1969	Rohr et al.	71/105
3,463,639	8/1969	Baltazzi	260/559 R
3,475,427	10/1969	Blank et al.	260/244
3,652,645	3/1972	Theissen	560/21
3,776,715	12/1973	Theissen	71/115 X
3,784,635	1/1974	Theissen	71/105 X
3,798,276	3/1974	Bayer et al.	71/98 X
3,812,184	5/1974	Theissen	71/115 X
3,839,444	10/1974	Theissen	71/115 X
3,873,302	3/1975	Theissen	71/115
3,873,303	3/1975	Theissen	71/118
3,907,866	9/1975	Theissen	71/111 X
3,928,416	12/1975	Bayer et al.	71/105 X
3,929,455	12/1975	Theissen	71/92 X
3,941,830	3/1976	Theissen	562/430 X
3,953,489	4/1976	Tamura et al.	260/455 R
3,979,437	9/1976	Theissen	71/111 X
3,983,168	9/1976	Theissen	71/108 X
4,001,005	1/1977	Theissen	71/108
4,002,662	1/1977	Theissen	71/105 X
4,015,975	4/1977	Tamura et al.	71/100
4,039,588	8/1977	Wilson et al.	71/105 X
4,046,798	9/1977	Bayer et al.	260/465 D
4,063,929	12/1977	Bayer et al.	260/520 E X
4,070,178	1/1978	Johnson et al.	71/105
4,093,446	6/1978	Bayer et al.	560/21 X
4,164,408	8/1979	Theissen	71/105 X
4,164,409	8/1979	Theissen	71/105 X
4,164,410	8/1979	Theissen	71/105 X

FOREIGN PATENT DOCUMENTS

7303590	9/1973	Netherlands .
951651	3/1964	United Kingdom .

OTHER PUBLICATIONS

Scarborough, et al., J. Chem. Soc., London (1934), pp. 52-56.

Sus, et al., Annalen Der Chemie, vol. 593 (1955), pp. 91-126.

Cook, et al., J. Am. Chem. Soc., (1902) vol. 24, pp. 1200-1204; pp. 486-490.

Mayer, et al., Ber., (1922), pp. 1659-1666.

Borsche, Ber., (1923), pp. 1488-1493.

McCombie, et al., J. Chem. Soc., London, (1931), pp. 529-536.

Brewster, et al., J. Am. Chem. Soc., (1934), vol. 56, pp. 117-120.

Tozer, et al., J. Chem. Soc., London, (1938), pp. 1897-1900.

Koelsch, et al., J. Am. Chem. Soc., (1949), vol. 71, pp. 3556-3558.

Barry, et al., Proceedings of the Royal Irish Academy, Dublin (1949), pp. 55-59.

Vanderhaeghe, et al., Bull. Soc. Chem. Belg., (1952), vol. 61, pp. 310-321.

Mann, et al., J. Chem. Soc., London, (1951), pp. 747-756.

Julia; Bull. Soc. Chem. Fr., (1952), pp. 546-549.

Julia, C. R.; 1st, Semestre, Academie des Sciences, Paris, (1952), vol. 234, pp. 1179-1181.

Goldberg, et al., J. Chem. Soc., London (1953), pp. 1348-1357; pp. 2049-2052.

Thompson, et al.; Antibiotics and Chemotherapy, N.Y., (1953), vol. 3, pp. 399-408.

Southwick, et al., J. Am. Chem. Soc., (1953), pp. 5877-5880.

Tomita, et al.; J. Pharm. Soc., Japan, (1955), vol. 75, pp. 449-461.

Fults, et al.; J. Amer. Soc. Agronomy, vol. 31, (1947), pp. 667-681.

Primary Examiner—Joseph Paul Brust

Attorney, Agent, or Firm—Morgan, Finnegan, Pine, Foley & Lee

[57] **ABSTRACT**

2-Nitro-5-(substituted-phenoxy)benzoic acids and esters, salts, amides, and acyl halides thereof comprise a class of compounds that are highly effective herbicides.

6 Claims, No Drawings

SALTS OF SUBSTITUTED PHENOXYBENZOIC ACIDS, COMPOSITIONS OF THE SAME AND HERBICIDAL USE THEREOF

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation of application Ser. No. 279,288, filed June 25, 1981, now abandoned.

This application is a continuation of copending application Ser. No. 702,367, filed July 2, 1976, which is a continuation-in-part of copending application Ser. No. 617,569, filed Sept. 29, 1975, now U.S. Pat. No. 3,979,437, issued Sept. 7, 1976, which is a continuation of copending application Ser. No. 398,610, filed Sept. 19, 1973, now U.S. Pat. No. 3,941,830, issued Mar. 2, 1976, which is a continuation of application Ser. No. 114,712, filed Feb. 11, 1971, now U.S. Pat. No. 3,784,635, issued Jan. 8, 1974, which is a continuation-in-part of application Ser. No. 819,412, filed Apr. 25, 1969, now U.S. Pat. No. 3,652,645, issued Mar. 28, 1972. Said application Ser. No. 702,367 pending is also a continuation-in-part of application Ser. No. 545,232 filed Jan. 29, 1975 now U.S. Pat. No. 4,002,662, issued Jan. 11, 1977 which in turn is a continuation-in-part of said application Ser. No. 398,610 filed Sept. 19, 1973 now U.S. Pat. No. 3,941,830 issued Mar. 2, 1976.

BACKGROUND OF THE INVENTION

1. Field of the Invention

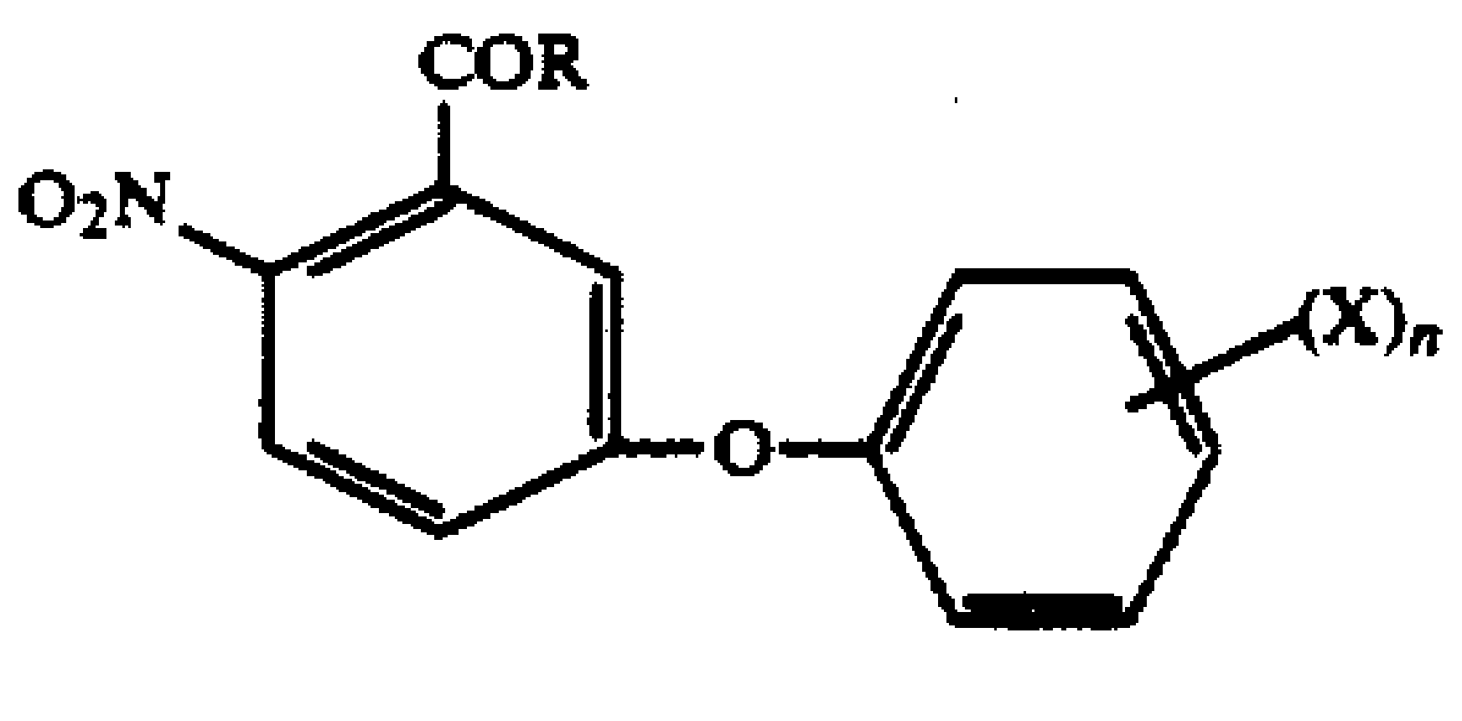
This invention is concerned with certain phenoxybenzoic acid compounds and their use as herbicides.

2. Description of the Prior Art

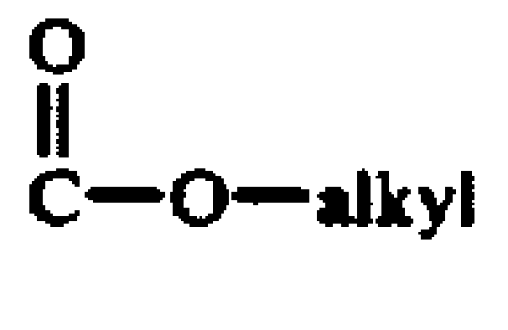
It has been proposed to use as herbicides 2-methoxybenzoic acids (U.S. Pat. No. 3,013,054) and 4-phenoxybenzoic acids (France 1,502,538). It is the discovery of this invention, however, that benzoic acids having a phenoxy substituent in the 5-position are very effective herbicides.

SUMMARY OF THE INVENTION

This invention provides herbicidal compounds having the formula:

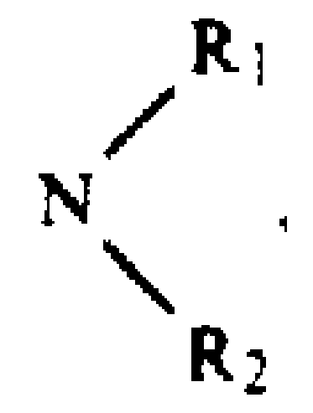


wherein X is a member selected from the group consisting of hydrogen, halogen (e.g., iodine, fluorine, chlorine and bromine), nitro, trifluoromethyl, cyano, COOH,



$$\overset{O}{\overset{\|}{C}}-O-\text{alkyl}$$

(eg. alkyl of 1 to 4 carbon atoms), hydroxy, alkoxy of 1 to 4 carbon atoms, alkyl of 1 to 4 carbon atoms,



SH, SR_1, SOR_1, SO_2R_1, SO_2NH_2 and combinations thereof, R_1 and R_2 are selected from the group consisting of alkyl of 1 to 4 carbon atoms, R is selected from the group consisting of hydroxy, alkoxy of 1 to 5 carbon atoms, aryloxy, chloro, amido, alkylamido of 1 to 4 carbon atoms, dialkylamido of 2 to 6 carbon atoms, SH, SR_1, and OM in which M is an alkali metal (eg., lithium, sodium and potassium), alkylammonium of 1 to 4 carbon atoms or alkanolammonium of 1 to 4 carbon atoms, n is an integer of 1 to 5, and in which compound at least one X is other than hydrogen; their use as herbicides; and a herbicidal composition comprising at least one of said compounds and a carrier therefor.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The compounds of this invention are readily prepared by the Ullmann ether synthesis reaction between the alkali metal, (eg., Na, K) salt of a suitable substituted phenol and a 5-halo (eg., F, Cl, Br)-2-nitrobenzoic acid or an ester, amide, or salt thereof. The 5-halo-2-nitrobenzoic acid or ester is readily prepared by nitrating a m-halotoluene, followed by oxidation of the methyl group by well-known procedures. Also, the m-halobenzoic acid or ester may be directly nitrated by well-known procedures.

Non-limiting examples of the compounds of this invention are:

propyl 2-nitro-5-(2',4',6'-tribromophenoxy)benzoate;
phenyl 2-nitro-5-(2',4',5'-trifluorophenoxy)benzoate;
2-nitro-5-(2',4',6'-triiodophenoxy)benzoic acid;
2-nitro-5-(2',4',6'-trichlorophenoxy)benzoyl chloride;
2-nitro-5-(2',4',6'-trichlorophenoxy)benzamide;
N-ethyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzamide;
N-isopropyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzamide;
N,N-dimethyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzamide;
ethylammonium 2-nitro-5-(2',4',6'-trichlorophenoxy)-benzoate;
ethanolammonium 2-nitro-5-(2',4',6'-trichlorophenoxy)-benzoate;
methyl 2-nitro-5-(2',3',4',5',6'-pentachlorophenoxy)benzoate;
n-pentyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoate;
2-nitro-5-(2',4'-dichlorophenoxy)benzoic acid;
methyl 2-nitro-5-(2'-chlorophenoxy)benzoate;
methyl 2-nitro-5-(4'-chloro-3'-methylphenoxy)benzoate;
methyl 2-nitro-5-(3'-methylphenoxy)benzoate;
ethyl 2-nitro-5-(2',6'-dichlorophenoxy)benzoate;
isopropyl 2-nitro-5-(2',4'-dichloro-6'-methylphenoxy)-benzoate;
ethyl 2-nitro-5-(2'-chloro-4'-fluorophenoxy)benzoate;
2-nitro-5-(2'-chloro-4'-fluorophenoxy)benzoic acid;
methyl 2-nitro-5-(2',4'-dinitrophenoxy)benzoate;
2-nitro-5-(2',4'-dinitrophenoxy)benzoic acid;
2-nitro-5-(2'-chloro-4'-nitrophenoxy)benzoic acid;
isopropyl 2-nitro-5-[3'-(α, α, α-trifluoromethyl)phenoxy]benzoate;
isopropyl 2-nitro-5-[3',5'-dicarbomethoxyphenoxy]benzoate;

methyl 2-nitro-5-(2'-methoxyphenoxy)benzoate;
methyl 2-nitro-5-(4'-chloro-2'-nitrophenoxy)benzoate;
2-nitro-5-(2',4'-dichloro-6'-fluorophenoxy)benzoic acid;
methyl 2-nitro-5-(2',4'-dichloro-6'-fluorophenoxy)benzoate;
methyl 2-nitro-5-(2',4'-dicarbomethoxyphenoxy)benzoate;
methyl 2-nitro-5-[2'-cyano-4'-(α, α, α-trifluoromethyl)-phenoxy]benzoate;
methyl 2-nitro-5-(3'-carbomethoxy-4'-hydroxyphenoxy)benzoate;
methyl 2-nitro-5-[4'-chloro-2'-(α, α, α-trifluoromethyl)-phenoxy]benzoate;
methyl 2-nitro-5-(3'-carbomethoxy-4'-nitrophenoxy)-benzoate;
methyl 2-nitro-5-(4'-chloro-2',6'-dibromophenoxy)benzoate;
methyl 2-nitro-5-(2',4'-dicyanophenoxy)benzoate;
methyl 2-nitro-5-[2'-dimethylamino-4'-(α, α, α-trifluoromethyl)phenoxy]benzoate;
ethyl 2-nitro-5-[2'-amino-4'-(α,α,α-trifluoromethyl)-phenoxy]benzoate
methyl 2-nitro-5-[2'-methyl-4'-methylthiophenoxy]benzoate;
N,N-dimethyl 2-nitro-5[2',6'-dimethyl-4'-methylthiophenoxy]benzamide;
methyl 2-nitro-5-[2'-methyl-4'-methylsulfonylphenoxy]-benzoate;
ethyl 2-nitro-5-[2'-chloro-4'-methylsulfinylphenoxy]-benzoate;
methyl 2-nitro-5-[4'-(N-trifluoromethylsulfonamido)-phenoxy]benzoate;
methyl 2-nitro-5-(4'-cyanophenoxy)benzoate;
ethyl 2-nitro-5-(4'-carboethoxyphenoxy)benzoate;
methyl 2-nitro-5'-(4'-hydroxyphenoxy)benzoate
2-nitro-5-[2'-t-butylphenoxy]benzoic acid;
2-nitro-5-[2'-carboxyphenoxy]benzoic acid;
methyl 2-nitro-5-(4'-aminophenoxy)benzoate;
methyl 2-nitro-5-(4'-diethylaminophenoxy)benzoate;
methyl 2-nitro-5-(2'-methylaminophenoxy)benzoate;
methyl 2-nitro-5-(4'-mercaptophenoxy)benzoate;
ethyl 2-nitro-5-(4'-methylthiophenoxy)benzoate;
methyl 2-nitro-5-(2'-sulfonamidophenoxy)benzoate;
ethyl 2-nitro-5-(4'-methylsulfinylphenoxy)benzoate;
methyl 2-nitro-5-(4'-methylsulfonylphenoxy)benzoate; and
2-nitro-5-(2',4'-dichlorophenoxy)thiobenzoic acid.

The following example illustrates the preparation of a typical compound of this invention and demonstrates a method for product recovery.

EXAMPLE 1

Methyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoate

A stirred solution of methyl 5-chloro-2-nitro-benzoate (17.0 g., 0.079 mole) and the potassium salt of 2,4,6-trichlorophenol (18.6 g., 0.079 mole) in dimethyl sulfoxide (100 ml.) was heated at 90° C. for 17 hours. The cooled reaction mixture was diluted with water (500 ml.) and then extracted with ether (3×100 ml.). The combined ether fractions were washed with 10% sodium hydroxide solution (2×30 ml.) and then with a saturated aqueous sodium chloride solution. The ether solution was dried (Na_2SO_4) and the solvent evaporated to give a dark oil. Two crystallizations (petroleum ether) gave 1.91 g. of a pale yellow solid, m.p. 101°-103° C.

EXAMPLE 1

IR(nujol): c=o 1723, c-o 1240, and 1260 cm^{-1}

NMR ($CDCl_3$): methyl 3.91 ppm (3H), quartet: 6.96 ppm (1H, J=2.5 and 8 c.p.s.), doublet: 7.05 ppm (1H, J=2.5 c.p.s.), broad singlet: 7.05 ppm (2H), and doublet 8.01 ppm (1H, J=8 c.p.s.).

EXAMPLES 2 through 24

Using procedures similar to that described in Example 1, twenty-three other compounds within the scope of this invention were prepared. These compounds are:

(2) 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoic acid, m.p. 184°-189° C.
(3) sodium 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoate m.p. >300° C.
(4) methyl 2-nitro-5-(2',4',5'-trichlorophenoxy)benzoate m.p. 100°-103° C.
(5) methyl 2-nitro-5-(2',4'-dichlorophenoxy)benzoate, m.p. 84°-86° C.
(6) ethyl 2-nitro-5-(2',4',6'-trichlorophenoxy)benzoate, m.p. 60°-64° C.
(7) methyl 2-nitro-5-(2',4'-dibromophenoxy)benzoate, m.p. 98°-100° C.
(8) methyl 2-nitro-5-(4'-chloro-2'-methylphenoxy)benzoate, m.p. 70°-72° C.
(9) methyl 2-nitro-5-(2',4'-dimethylphenoxy)benzoate, oil.
(10) 2-nitro-5-(2',4'-dichlorophenoxy)benzamide, m.p. 130°-133° C.
(11) isopropyl 2-nitro-5-(2', 4',6'-trichlorophenoxy)benzoate, m.p. 71°-74° C.
(12) ethyl 2-nitro-5-(2',4'-dichlorophenoxy)benzoate, m.p. 83°-85° C.
(13) isopropyl 2-nitro-5-(2',4'-dichlorophenoxy)benzoate, m.p. 59°-62° C.
(14) methyl 2-nitro-5-(2',4',6'-trichlorophenoxy)thiobenzoate, m.p. 96°-100° C.
(15) methyl 2-nitro-5-(2',4'-dichloro-6'-methylphenoxy)benzoate, m.p. 85°-89° C.
(16) methyl 2-nitro-5-(2'-chloro-4'-fluorophenoxy)benzoate, m.p. 67°-70° C.
(17) isopropyl 2-nitro-5-(2'-chloro-4'-fluorophenoxy)-benzoate, m.p. 48°-51° C.
(18) N-methyl 2-nitro-5-(2',4'-dichlorophenoxy)benzamide, m.p. 137° C.
(19) ethyl 2-nitro-5-(4'-nitrophenoxy)benzoate, m.p. 75°-82° C.
(20) methyl 2-nitro-5-(3'-methyl-4'-nitrophenoxy)benzoate, m.p. 75°-82° C.
(21) isopropyl 2-nitro-5-[2'-nitro-4'-(α,α,α-trifluoromethyl)phenoxy]benzoate, oil.
(22) ethyl 2-nitro-5-[2'-nitro-4'-(α,α,α-trifluoromethyl)-phenoxy]benzoate, oil.
(23) methyl 2-nitro-5-[2'-chloro-4'-nitrophenoxy]benzoate, m.p. 97°-102° C.
(24) 2-nitro-5-(2'-chloro-4'-nitrophenoxy)benzoic acid, m.p. 185° C.

EXAMPLE 25

2-Nitro-5-[2'-nitro-4'-(α,α,α-trifluoromethyl)phenoxy]-benzoic acid

A stirred solution of 4-chloro-3-nitrobenzotrifluoride (22.55 g, 0.1 mole) and the potassium salt of 3-methyl-4-nitrophenol (19.12 g, 0.1 mole) in dimethyl acetamide (75 ml) was heated at 150° for 4 hours. The cooled reaction solution was diluted with water (300 ml) to precipitate a brown solid which was filtered and dried to give 28.9 g (85%) of 4-nitro-3-tolyl-2'-nitro- α,α,α-trifluoro-4'-tolyl ether, which had an m.p. of 82°-85° C. To a stirred solution of the above diphenyl ether product (25.0 g, 0.073 mole) and sodium dichromate (35.8 g. 0.12 mole) in glacial acetic acid (200 ml) was added concentrated sulfuric acid (60 ml, 1.15 moles) over about 30 minutes. The temperature was maintained below 70° C. during the addition and then raised to 110° C. for 15 hours. The reaction solution was cooled to 60° C. and extracted with hot chloroform. The extract was evaporated to dryness to give an oily solid, which was leached free of starting material with an ether-ligroin mixture. The resulting off-white solid acid weighed 13.6 g (51%), m.p. 185°-187°.

EXAMPLE 26

2-Nitro-5-[2'-nitro-4'-(α,α,α-trifluoromethyl)phenoxy]-benzoic acid methyl ester

A stirred solution of the acid from Example 25 (3.5 g, 0.0094 mole) in a 25 wt. %/vol. solution of borontrifluoride in methanol (50 ml) was refluxed for 10 hours. The cooled solution was poured onto water (250 ml) and the resulting oil separated and dried to give 3.4 g (93.5%) of the desired product.

EXAMPLE 27

Methyl 2-nitro-5-(2',4'-dichlorophenoxy)thiobenzoate

Into a solution of 2-nitro-5-(2', 4'-dichlorophenoxy) benzoyl chloride (4.16 g., 0.012 mole), prepared from the corresponding acid, in 40 ml. benzene was bubbled methanethiol gas for 0.5 hour at room temperature. The gas bubbling was stopped and the reaction mixture was refluxed for 15 minutes and then cooled. The mixture was diluted with diethyl ether, washed twice with 10% aqueous NaOH, once with NaCl solution, dried, and evaporated to dryness to give 4.3 g. of an oil. Infrared analysis showed a large amount of initial benzoyl chloride was unreacted. The oil was dissolved in 100 ml. benzene and 1.5 g. triethylamine was added. The reaction mixture was heated to 65°-70° C. and methanethiol was bubbled in. There was an immediate precipitate. After 1.5 hours, the reaction mixture was cooled, filtered, and evaporated to dryness to give 4.6 g. of the desired product.

EXAMPLE 28

Ethyl 2-nitro-5-(2',4'-dichlorophenoxy)thiobenzoate

A mixture of 2-nitro-5-(2',4'-dichlorophenoxy)benzoyl chloride (4.16 g., 0.012 mole) and ethanethiol (2.24 g., 0.036 mole) in 40 ml. benzene was heated at reflux for 2 hours and 50 minutes and then cooled. The mixture was diluted with diethyl ether, washed twice with 10% aqueous NaOH, once with NaCl solution, dried, and evaporated to dryness to give 4.2 g. of an oil. Infrared analysis showed a large amount of initial benzoyl chloride and some desired product. The oil was dissolved in 100 ml. benzene and 3.0 g. ethanethiol and about 1.5 g. triethylamine were added. A precipitate formed immediately. The reaction mixture was refluxed for 1.5 hours, cooled, filtered and evaporated to dryness to give 4.65 g. of the desired product.

COMPARATIVE EXAMPLES

A series of compounds were prepared which are position isomers of the compounds of Example 1 through 4. Each compound is designated by the number of the corresponding isomeric compound of Examples 1 through 4, followed by "a" or "b". These compounds are:

(1a) methyl 5-nitro-2-(2',4',6'-trichlorophenoxy)benzoate, m.p. 128°-133° C.
(2a) 5-nitro-2-(2',4',6'-trichlorophenoxy)benzoic acid, m.p. 175°-177° C.
(2b) 4-nitro-2-(2',4',5'-trichlorophenoxy)benzoic acid, m.p. 190°-193° C.
(3a) sodium 5-nitro-2-(2',4',6'-trichlorophenoxy)benzoate, m.p. >300° C.
(4a) methyl 5-nitro-2-(2',4',5'-trichlorophenoxy)benzoate, m.p. 104°-106° C.
(4b) methyl 4-nitro-2-(2',4',5'-trichlorophenoxy)benzoate, m.p. 127°-131° C.

As is apparent from the data in the Table set forth hereinafter, the compounds embodied herein in which the nitro group is in the 2-position and the substituted phenoxy group is in the 5-position exhibit markedly higher effectiveness as herbicides than do the comparable compounds in which the nitro group and the substituted phenoxy group are in different positions.

The compounds of this invention can be applied in various ways to achieve herbicidal action. They can be applied, per se, as solids or in vaporized form, but are preferably applied as the toxic components in pesticidal compositions of the compound and a carrier. The compositions can be applied as dusts, as liquid sprays, or as gas-propelled sprays and can contain, in addition to a carrier, additives such as emulsifying agents, binding agents, gases compressed to the liquid state, odorants, stabilizers, and the like. A wide variety of liquid and solid carriers can be used. Non-limiting examples of solid carriers include talc, bentonite, diatomaceous earth, pyrophyllite, fullers earth, gypsum, flours derived from cotton seeds and nut shells, and various natural and synthetic clays having a pH not exceeding about 9.5. Non-limiting examples of liquid carriers, include water; organic solvents, such as alcohols, ketones, amides and esters; mineral oils, such as kerosene, light oils, and medium oils and vegetable oils, such as cottonseed oil.

In practice, herbicidal application is measured in terms of pounds of herbicide applied per acre. The compounds of this invention are effective herbicides when applied in herbicidal amounts, i.e., at rates between about 0.2 pounds and about 10 pounds per acre.

HERBICIDAL EFFECTIVENESS
Method of Propagating Test Species

Crabgrass	*Digitaria sanguinalis*
Yellow Foxtail grass	*Setaria glauca*
Johnson grass	*Sorgum Halepense*
Barnyard grass	*Echinochloa crus-galli*
Amaranth pigweed	*Amaranthus retroflexus*
Turnip	Brassica sp.
Cotton	*Gossypium hirsutum* var. DPL smooth leaf
Corn	*Zea Mays* var. Golden Bantam
Bean	*Phaseolus vulgaris* var. Black Valentine

All crop and weed species are planted individually in 3" plastic pots containing potting soil. Four seeds of each of corn, cotton, and snapbeans are seeded to a depth equal to the diameter of the seed. All other species are surface seeded and sprinkled with screened soil in an amount sufficient to cover the seeds. Immediately after planting, all pots are watered by sub-irrigation in greenhouse trays. Pots for the pre-emergence phase are seeded one day before treatment.

Planting dates for the post-emergence phase are varied so that all the seedlings will reach the desired state of development simultaneously. The proper state of seedling development for treatment in the post-emergence phase is as follows:

GRASSES:	2 inches in height
PIGWEED & TURNIPS:	1 or 2 true leaves visible above cotyledons.
COTTON:	first true leaf 1 inch in length; expanded cotyledons.
CORN:	3 inches-4 inches in height
BEANS:	primary leaves expanded, growing point at primary leaf node.

METHOD OF TREATMENT

Spray applications are made in a hood containing movable belt and fixed spray nozzle. For passage through the spray hood, one pot of each species (pre-emergence phase) is placed on the forward half of a wooden flat and one pot of established plants (post-emergence phase) is placed on the rear half of the flat. Treatments are moved to the greenhouse after spraying. Watering during the observation period is applied only by sub-irrigation.

Compounds are screened initially at a rate of application equivalent to four or eight pounds per acre. Two weeks after treatment the pre- and post-emergence percent effectiveness is visually rated. Subsequent testing is carried out at 2.1 and 0.5 pounds per acre.

Herbicidal testing of the compounds of Examples 1 through 28 and of the comparative compounds provided the results set forth in the Table. The plants are tabulated using the following abbreviations:

Crabgrass	CG	Pigweed	PW
Yellow Foxtail grass	YF	Turnip	TP
Johnson grass	JG	Cotton	CT
Barnyard grass	BG	Corn	CN
Bean	BN		

TABLE

PRE/POST-EMERGENCE HERBICIDAL ACTIVITY* OF CERTAIN SUBSTITUTED PHENOXYBENZOIC ACIDS AND DERIVATIVES THEREOF

Compound of Example	Compound Concentration, Lbs./Acre	CG	YF	JG	BG	PW	TP	CT	CN	BN
1	4	100/100	100/100	60/50	60/70	100/100	80/100	0/100	0/40	30/100
	2	100/100	80/100	30/70	20/80	100/100	0/100	90/100	30/20	70/100
	1	100/90	80/100	20/60	0/60	100/100	30/90	0/100	0/20	80/100
	0.5	40/50	60/80	30/60	0/40	100/70	0/80	40/20	0/20	30/70
1a(Comparative)	4	20/20	0/20	0/20	0/20	20/0	0/30	100/0	50/0	20/80
2	4	70/70	—/—	70/90	60/70	—/—	100/100	0/100	0/70	80/70
2a(Comparative)	4	20/30	0/20	20/30	0/20	—/20	30/90	50/20	0/0	50/70
2b(Comparative)	4	0/30	40/0	50/30	20/20	20/20	0/50	40/20	30/30	80/0
3	4	50/80	—/—	30/60	40/60	—/—	95/100	50/100	0/40	50/100
3a(Comparative)	4	0/20	0/20	0/20	0/20	50/50	0/60	100/0	30/0	50/40
4	4	90/60	—/—	80/90	50/50	—/—	40/70	80/70	0/50	80/80
4a(Comparative)	8	30/30	0/20	20/30	0/20	30/30	40/0	0/30	0/0	60/0
4b(Comparative)	4	20/20	0/20	0/20	0/20	0/20	0/60	30/50	0/30	0/60
5	4	100/95	—/—	90/90	90/90	—/—	80/100	50/80	0/40	50/100
6	4	100/80	—/—	80/50	50/70	100/100	40/90	30/100	0/100	100/100
7	8	80/60	—/—	50/40	60/50	100/100	20/100	30/90	0/50	100/100
8	8	50/60	—/—	20/30	0/20	100/100	0/40	0/40	0/30	100/100
9	8	30/30	—/—	0/40	20/20	90/90	20/50	0/70	0/40	100/90
10	4	80/70	—/—	40/40	40/30	100/100	20/70	100/40	0/20	100/100
11	4	60/70	—/—	30/60	20/50	90/100	0/50	30/70	0/30	80/60
12	8	90/90	—/—	90/90	60/90	100/100	0/100	0/100	0/70	0/100
	4	100/90	—/—	90/100	60/60	100/100	0/100	30/90	0/70	30/100
	2	100/100	100/—	40/60	80/70	—/100	30/100	80/70	0/70	100/100
	1	100/100	—/—	40/90	50/80	—/—	30/100	20/80	0/20	50/80
13	8	70/90	—/—	30/90	20/80	90/100	0/30	30/70	0/20	100/100
14	4	70/80	—/—	20/90	0/40	100/100	70/100	90/90	20/20	0/80
15	8	100/100	100/—	50/70	50/—	—/100	70/90	0/90	0/30	50/100
	4	90/90	0/—	40/60	0/60	—/—	60/90	100/60	0/40	0/100
	2	90/70	—/—	30/40	20/70	—/—	70/60	0/60	0/50	0/100
16	8	100/90	100/100	80/100	100/90	100/100	100/100	40/100	80/40	80/100
	4	100/100	100/100	100/100	80/80	100/100	70/100	40/90	20/80	80/100
	2	100/100	100/100	90/100	80/90	100/100	80/100	30/90	0/80	0/90
	0.8	90/60	100/80	70/50	40/50	100/100	40/100	80/60	30/20	50/100
17	8	100/40	90/40	70/40	50/30	100/100	0/60	0/80	0/30	0/90
	4	100/90	100/100	80/90	50/70	100/100	0/40	0./50	0/30	0/90
	2	100/90	100/90	30/90	30/90	100/100	20/30	0/50	0/30	0/90
	1	60/50	100/80	90/60	20/30	100/100	0/40	90/30	30/0	80/80
18	8	90/80	—/—	60/80	70/40	—/—	90/100	30/80	0/80	0/100
19	10	40/30	—/—	90/—	—/—	—/—	0/90	—/60	—/—	—/60
20	10	50/20	—/—	90/—	—/—	—/—	20/20	—/30	—/—	—/40
21	3	100/—	100/—	100/—	30/—	—/—	50/—	30/—	0/—	0/—
22	1	90/—	100/—	100/—	30/—	—/—	30/—	50/—	60/—	0/—
23	10	80/—	100/—	100/—	30/—	—/—	80/—	—/—	—/—	—/—
24	10	100/—	—/—	30/—	—/—	—/—	100/—	—/—	—/—	—/—
25	8	80/60	90/100	50/40	30/60	100/100	100/100	30/50	0/30	30/90
26	8	100/80	100/90	40/20	90/60	100/100	90/90	0/50	0/20	70/90
	4	100/90	100/100	70/90	80/50	100/100	100/100	0/50	0.20	0.90
	2	90/70	100/100	60/60	40/70	100/100	90/90	0/50	0/30	0.90

TABLE-continued

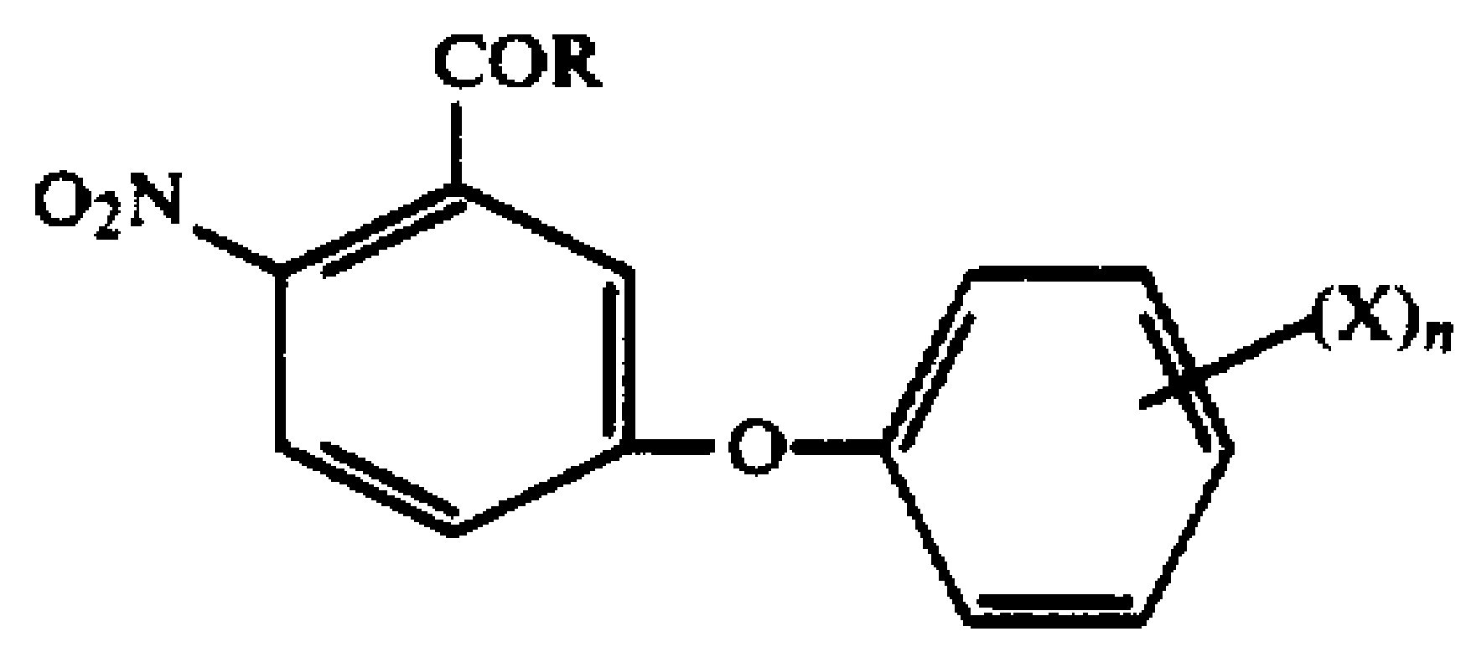
Compound of Example	Compound Concentration, Lbs./Acre	PRE/POST-EMERGENCE HERBICIDAL ACTIVITY* OF CERTAIN SUBSTITUTED PHENOXYBENZOIC ACIDS AND DERIVATIVES THEREOF								
		CG	YF	JG	BG	PW	TP	CT	CN	BN
27	8	20/30	80/—	—/—	—/—	—/—	100/100	—/100	—/—	—/100
28	8	0/30	—/—	—/—	—/—	—/—	100/100	—/100	—/—	—/100

*Herbicidal activity is measured in percent effectiveness

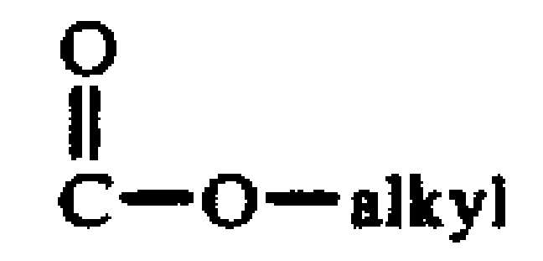
Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the appended claims.

What is claimed is:

[1. Herbicidal compounds having the formula:

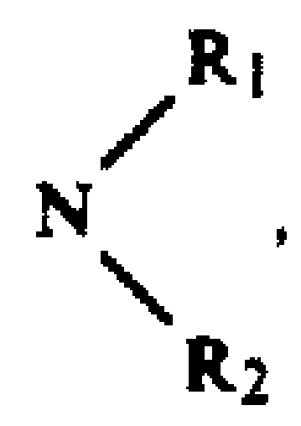


wherein X is a member selected from the group consisting of halogen, nitro, trifluoromethyl, cyano, COOH,



$$\overset{O}{\overset{\|}{C}}\text{—O—alkyl}$$

(alkyl of 1 to 4 carbon atoms), hydroxy, alkoxy of 1 to 4 carbon atoms, alkyl of 1 to 4 carbon atoms,

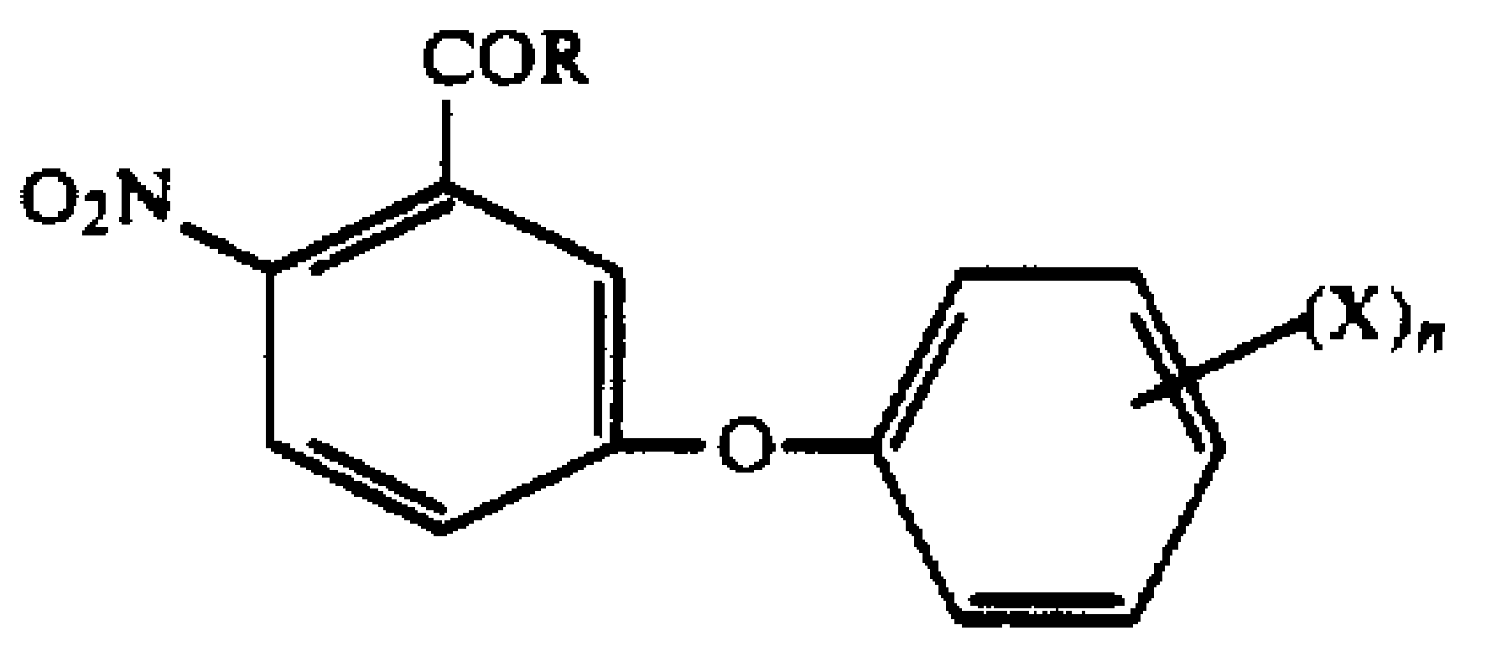


SH, SR_1, SOR_1, SO_2R_1, SO_2NH_2 and combinations thereof, R_1 and R_2 are selected from the group consisting of alkyl of 1 to 4 carbon atoms, R is OM in which M is an alkali metal (lithium, sodium and potassium), alkylammonium of 1 to 4 carbon atoms or alkanolammonium of 1 to 4 carbon atoms, n is an integer of 1 to 5.]

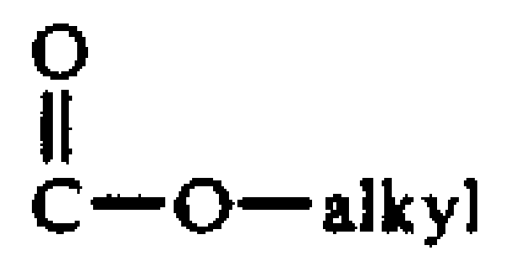
[2. The method for controlling plant growth that comprises applying an herbicidal amount of a compound defined in claim 1.]

[3. An herbicidal composition comprising a carrier for an herbicide and an herbicidal amount of a compound defined in claim 1.]

4. Herbicidal compounds having the formula:

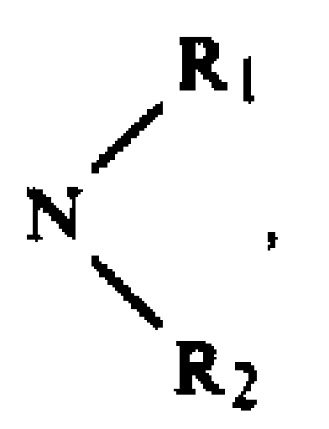


wherein $(X)_n$ *is a combination of the members selected from the group consisting of halogen, trifluoromethyl, COOH,*



$$\overset{O}{\overset{\|}{C}}\text{—O—alkyl}$$

(alkyl of 1 to 4 carbon atoms), hydroxy, alkoxy of 1 to 4 carbon atoms,



SH, SR_1, SOR_1, SO_2R_1, SO_2NH_2, R_1 *and* R_2 *are selected from the group consisting of alkyl of 1 to 4 carbon atoms, R is OM in which M is an alkali metal (lithium, sodium and potassium), alkylammonium of 1 to 4 carbon atoms or alkanolammonium of 1 to 4 carbon atoms, n is an integer of 2 to 5.*

5. The method for controlling plant growth that comprises applying an herbicidal amount of a compound defined in claim 4.

6. An herbicidal composition comprising a carrier for an herbicide and an herbicidal amount of a compound defined in claim 4.

* * * * *