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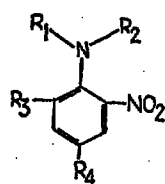


(54) CONTROL OF PESTS WITH CYCLOALKANE DERIVATIVES OF NITRATED ARYL COMPOUNDS

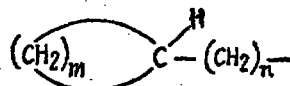
We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to cycloalkane derivatives of nitrated aryl compounds and to their use as pesticides, particularly as herbicides. When so used the compounds are preferably formulated with a diluent and/or carrier.

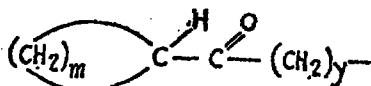
According to the present invention there is provided a compound of the formula:



wherein R₁ represents a



or a



[Price 25p]

group in which the ring may be substituted, for example with an alkyl, alkenyl or cyano group or a halogen atom, or unsubstituted; m represents an integer from 2 to 4; n represents zero or an integer from 1 to 3; and y represents an integer from 1 to 3;

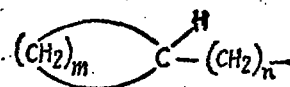
R₂ represents a hydrogen atom or a C₁ to C₁₂ straight or branched chain monovalent aliphatic group, for example an alkyl, alkenyl or alkynyl group, a C₃ to C₈ cycloalkyl group, a C₄ to C₁₀ cycloalkylalkyl group, a C₂ to C₁₂ alkoxyalkyl group, a C₁ to C₁₂ haloalkyl group, a C₂ to C₁₂ cyanoalkyl group, a C₂ to C₆ acyl group, or a C₂ to C₆ alkylmercaptoalkyl group or a sulfoxide or sulphone thereof;

R₃ represents a hydrogen or halogen atom or a nitro group, a C₁ to C₆ alkyl group, or a cyano group; and

R₄ represents a hydrogen or halogen atom or a C₁ to C₁₂ alkyl group, a haloalkyl, for example trifluoromethyl group, a cycloalkyl group, a nitro group, a cyano group, a substituted or unsubstituted phenyl group, a C₆H₅—N=N— group, a C₁ to C₃ alkyl mercapto group or a sulfoxide or sulphone thereof, or an R₅R₆NSO₂— group in which R₅ and R₆, which may be the same or different, each represent R₂ as hereinabove defined.

Such compounds are biologically active and useful as herbicides.

Suitable such compounds include those wherein R₁ represents a



group in which m and n are as defined hereinabove;

R₂ represents a hydrogen atom or a C₁ to

C₁₂ straight or branched chain monovalent aliphatic group, a C₃ to C₈ cycloalkyl group, a C₄ to C₁₀ cycloalkylalkyl group, a C₂ to C₁₂ alkoxyalkyl group or a C₁ to C₁₂ haloalkyl group;

5 R₃ represents a nitro group; and

R₄ represents a hydrogen atom or a C₁ to C₁₂ alkyl group, a haloalkyl, for example a trifluoromethyl group, a cyano group, a substituted or unsubstituted phenyl group or a C₁ to C₃ alkylmercapto group or a sulfoxide or sulphone thereof.

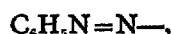
10 The preferred compounds of the present invention are those cyclopropane derivatives wherein

15 R₁ represents a cyclopropylmethyl group;

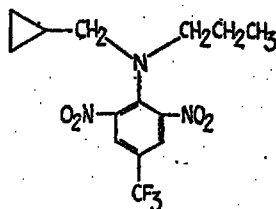
R₂ represents a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, isobutyl, cyclopropylmethyl, n-amyl, isoamyl, 20 sec-amyl, allyl, propargyl, crotyl, methallyl, methoxyethyl, ethoxyethyl, n-propoxyethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-methylmercaptoethyl, 3-methylmercaptoethyl, trifluoromethyl, pentafluoroethyl, 3-chloropropyl, 25 trichloromethyl or bromomethyl group;

R₃ represents a nitro group; and

R₄ represents a hydrogen, chlorine, bromine or fluorine atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, isobutyl, 30 t-butyl, n-pentyl, n-hexyl, trifluoromethyl, chloromethyl, trichloromethyl, bromomethyl, chloroethyl, bromoethyl, chloropropyl, bromopropyl, cyano, cyclopentyl, cyclohexyl,



35 unsubstituted or alkyl, halogen or nitro substituted phenyl, a C₁ to C₃ alkylmercapto group or a sulfoxide or sulphone thereof, or an R₅R₆NSO₂— group in which R₅ and R₆, which may be the same or different, each 40 represent a hydrogen atom or an alkyl, alkenyl, alkynyl or cycloalkyl group, especially preferred being the compound



Typical of such preferred compounds are:

45 N - cyclopropylmethyl - N - methyl - 4-trifluoromethyl - 2,6 - dinitroaniline;

N - cyclopropylmethyl - N - ethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline;

50 N - cyclopropylmethyl - N - isopropyl - 4-trifluoromethyl - 2,6 - dinitroaniline;

N - cyclopropylmethyl - N - n - butyl - 4 - trifluoromethyl - 2,6 - dinitroaniline;

N - cyclopropylmethyl - N - (3 - methyl-

mercaptoethyl) - 4 - trifluoromethyl - 2,6-dinitroaniline;

N,N - bis(cyclopropylmethyl) - 4 - trifluoromethyl - 2,6 - dinitroaniline;

4 - (methylsulfonyl) - 2,6 - dinitro - N-cyclopropyl - N - methylaniline;

4 - (methylsulfonyl) - 2,6 - dinitro - N-cyclopropylmethyl - N - ethylaniline;

4 - (methylsulfonyl) - 2,6 - dinitro - N-cyclopropylmethyl - N - n - propylaniline;

4 - (methylsulfonyl) - 2,6 - dinitro - N-cyclopropylmethyl - N - n - butylaniline;

4 - (methylsulfonyl) - 2,6 - dinitro - N-cyclopropylmethyl - N - (3 - methylmercaptoethyl)aniline;

N - cyclopropylmethyl - N - n - propyl - 2,6 - dinitroaniline;

N - cyclopropylmethyl - N - ethyl - 2,6-dinitroaniline;

N - cyclopropylmethyl - N - n - propyl - 2,6 - dinitro - p - toluidine;

N - cyclopropylmethyl - N - ethyl - 2,6-dinitro - p - toluidine;

N - cyclopropylmethyl - N - n - propyl - 4 - cyano - 2,6 - dinitroaniline;

N - cyclopropylmethyl - N - ethyl - 4 - cyano - 2,6 - dinitroaniline;

N - cyclopropylmethyl - N - n - propyl - 2 - nitro - 4 - trifluoromethylaniline;

N - cyclobutylmethyl - N - ethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline;

N - cyclopentylmethyl - N - ethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline;

4 - (methylsulfonyl) - 2,6 - dinitro - N-cyclopentyl - methyl - N - ethylaniline;

4 - (methylsulfonyl) - 2,6 - dinitro - N-cyclopropyl - N - ethylaniline;

N - cyclopropyl - N - ethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline; and

N - cyclopropyl - N - cyclopropylmethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline.

The foregoing compounds can be prepared readily by the following synthetic methods. For example, the preferred method for preparation of these products comprises reaction of the highly reactive compound 3,5-dinitro-4-chlorobenzotrifluoride with an amine of the general structure R₁R₂NH, where R₁ and R₂ can have the same designation as previously expressed above. During this reaction, elimination of hydrogen chloride occurs and this reacts with excess of the amine R₁R₂NH to form the corresponding amine hydrochloride salt; alternatively, if desired, any tertiary amine, such as dimethylaniline or triethylamine can be reacted with the eliminated HCl to form the corresponding amine hydrochloride salt.

If it is desired that a suitable organic solvent such as ether, benzene, toluene, hexane or a chlorinated hydrocarbon be used in this method, the resulting amine hydrochloride, which is insoluble in such solvent, is ordinarily removed by filtration. The filtrate, upon

removal of the solvent, yields the desired product.

Furthermore, the intermediate amines can themselves be prepared *via* a two-step process in which the first step involves the reaction of a cycloalkyl carbonylchloride with various types of primary amines to form the corresponding N-substituted cycloalkanecarboxamide. In a second step, these amides are reduced to the desired secondary amines with an appropriate reducing agent, such as lithium aluminum hydride or diborane.

Typical illustrative reactants employed for the preferred method of this invention include, below:

- 10 removal of the solvent, yields the desired product.
- 15 Furthermore, the intermediate amines can themselves be prepared *via* a two-step process in which the first step involves the reaction of a cycloalkyl carbonylchloride with various types of primary amines to form the corresponding N-substituted cycloalkanecarboxamide. In a second step, these amides are reduced to the desired secondary amines with an appropriate reducing agent, such as lithium aluminum hydride or diborane.
- 20 Typical illustrative reactants employed for the preferred method of this invention include, below:
- 25 removal of the solvent, yields the desired product.

The typical reaction conditions for the aforesaid methods are tabulated in Table I below:

TABLE I

Typical Reaction Conditions for Preparation of
N-Cyclopropylmethyl-N-n-Propyl-4-Trifluoromethyl-2,6-Dinitroaniline
Would Include:

Molar Ratio of Reactants	Temperature, °C.	P. Atm	Single Step Reaction	
				Preferred Solvents
3,5-dinitro-4-chlorobenzotrifluoride (1 mole) + N-cyclopropylmethyl-N-n-propyl amine (1.1 mole) + triethyl amine (1.1-2.0 mole)	0°C.-150°C.	1 Atm.		benzene, toluene, ethers, alcohols, chlorinated hydrocarbons

TABLE I (continued)

Typical Reaction Conditions for Preparation of Amines Would Include:

Molar Ratio of Reactants	Temperature, °C.	Two-Step Reaction	
		Preferred Solvents	Undesirable Solvents
Step (a)			
Cyclopropanecarboxylic acid chloride (1 mole) + n-propyl- amine (2.1—3.0 mole)	-10°C. to 100°C.	benzene, toluene, ethers, chlorinated hydrocarbons	alcohols, water
Step (b)			
N-n-propylcyclopropane- carboxamide (1.0 mole) + lithium aluminum hydride (1.1 — 2.0 moles)	-75°C. to 75°C.	diethylether, tetra- hydrofuran, benzene	aqueous or alcoholic solvents

Preferred solid carriers can be natural occurring minerals including, for example, gypsum; tripolite; diatomaceous earth; mineral silicates such as mica, vermiculite, talc, and pyrophyllite; clays of the montmorillonite, kaolinite, or attapulgite groups; calcium or magnesium limes, or calcite and dolomite. Carriers produced synthetically, as for example, synthetic hydrated silica oxides and synthetic calcium silicates or an elemental substance such as sulfur or carbon, preferably an activated carbon, can also be used.

For some purposes, a resinous or waxy carrier can be used, preferably one which is solvent-soluble or thermoplastic, including fusible types. Examples of such carriers are natural or synthetic resins such as a coumarone resin, rosin, copal, shellac, dammar, polyvinyl chloride, styrene polymers and copolymers, a solid grade of polychlorophenol such as is

available under the registered trademark "Aroclor", a bitumen, an asphaltite, a wax for example beeswax or a mineral wax such as paraffin wax or montan wax, or a chlorinated mineral wax, or a microcrystalline wax such as those available under the registered trademark "Mikrovan Wax." Compositions comprising such resinous or waxy carriers are preferably in granular or pelleted form.

Fluid carriers can be liquids, as for example, water, or an organic fluid, including a liquefied normally vaporous or gaseous material, or a vaporous or gaseous material, and can be solvents or non-solvents for the active material. For example, the horticultural petroleum spray oils boiling in the range of from about 275° to about 575°F., or boiling in the range of about 575° to about 1,000°F. and having an unsulfonatable residue of at least about 75% and preferably of at

least types carrier

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The wetting agents used can be non-ionic type surfactants, as for example, the condensation products of fatty acids containing at least 12, preferably 16 to 20, carbon atoms in the molecule, or abiestic acid or naphthenic acid obtained in the refining of petroleum lubricating oil fractions with alkylene oxides such as ethylene oxide or propylene oxide, or with both, as, for example, the condensation product of oleic acid and ethylene oxide containing about 6 to 15 ethylene oxide units in

3,5 - Dinitro - 4 - chlorobenzotrifluoride (14.6 grams, 0.054 mole) and *N* - cyclopropylmethyl - *N* - *n* - propylamine (13.0 grams, 0.115 mole) were mixed in a reaction flask, whereupon an exothermic reaction occurred with the temperature rising to a maximum of 80°C. The resultant deep orange-colored reaction mixture was heated at 100° to 120°C. for two hours with occasional stirring. After

chloride, styrene polymers and copolymers, a solid grade of polychlorophenol such as is of at least about 75% and preferably of at least about 80% and having an unsaturation

cooling the mixture, ether was added and the insoluble by-product, the amine hydrochloride, was removed by filtration. The filtrate was washed with 60 ml. portions of 5% hydrochloric acid and water, and then dried with K_2CO_3 . The ether was removed under vacuum, leaving the red, oily residue of *N*-cyclopropyl-

methyl - *N* - *n* - propyl - 4 - trifluoromethyl - 2,6 - dinitroaniline (14.4 grams). The material was then crystallized by dissolving in hexane and chilling the solution with stirring in a dry-ice bath. The resulting bright yellow solids which were obtained upon filtering melted at 27—28°C.

15 Elemental Analysis: Calculated: C, 48.43; H, 4.65; N, 12.12.
Found: C, 48.22; H, 4.69; N, 12.45.

The nuclear magnetic resonance spectrum of this compound was consistent with its proposed structure.

20 EXAMPLE 2.

Preparation of *N* - cyclopropylmethyl - *N* - ethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline.

25 In a reaction flask was placed 3,5-dinitro-4-chlorobenzotrifluoride (85.4 grams, 0.316 mole) and triethylamine (40.5 grams, 0.40 mole), dissolved in 800 ml of benzene. The solution was cooled to approximately 10°C. with stirring and *N* - cyclopropylmethyl - *N* -

ethylamine (35 grams, 0.347 mole), dissolved in 100 ml of benzene, was added dropwise over 1½ hours. The mixture was refluxed for 2½ hours and then allowed to cool. Filtration of the solids (amine hydrochloride) gave a red-colored filtrate which was washed with 5% HCl and water. After drying the solution with K_2CO_3 , the solvent was removed at reduced pressure to yield a yellow solid which was recrystallized from cold hexane. The product obtained was *N* - cyclopropylmethyl - *N* - ethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline, melting point 32—33°C., in a yield of 80 grams.

45 Elemental Analysis: Calculated: C, 46.8; H, 4.23; N, 12.61.
Found: C, 47.2; H, 4.93; N, 12.69.

The nuclear magnetic resonance spectrum substantiated its proposed structure.

50 EXAMPLE 3.

Preparation of *N* - cyclopropylmethyl - *N* - methyl - 4 - trifluoromethyl - 2,6 - dinitroaniline.

50 Addition of an ether solution of 3,5-dinitro-4-chloro - benzotrifluoride (10.7 grams, 0.039 mole) to *N* - cyclopropylmethyl - *N* - methyl-

amine (3.84 grams, 0.045 mole) and triethylamine (4.95 grams, 0.056 mole), dissolved in ether, yielded a precipitate of amine hydrochloride. The mixture was heated at reflux for one hour, cooled, and filtered. The filtrate, after workup in the usual manner, yielded yellow-orange solids, in a yield of 11.9 grams. The product was recrystallized from petroleum ether and had a melting point range of 59—60°C.

65 Elemental Analysis: Calculated: C, 45.2; H, 3.78; N, 13.1.
Found: C, 44.8; H, 4.19; N, 13.3.

70 EXAMPLE 4.

Preparation of *N* - cyclopropylmethyl - *N* - isopropyl - 4 - trifluoromethyl - 2,6 - dinitroaniline.

70 Following the general procedure of Example 1, *N* - cyclopropyl - *N* - isopropyl - amine

(13 grams, 0.115 mole) was reacted with 3,5-dinitro - 4 - chlorobenzotrifluoride (14.6 grams, 0.054 mole) to yield 12.5 grams of product, after recrystallization from hexane. The material melted at 42.5—43.5°C.

Elemental Analysis: Calculated: C, 48.43; H, 4.65; N, 12.12.
Found: C, 49.02; H, 4.79; N, 12.14.

80 EXAMPLE 5.

Preparation of *N* - cyclopropylmethyl - *N* - *n* - butyl - 4 - trifluoromethyl - 2,6 - dinitroaniline.

85 According to the general procedure of Example 1, *N* - cyclopropylmethyl - *N* - *n* -

butylamine (15.0 grams, 0.118 mole) was reacted with 3,5 - dinitro - 4 - chlorobenzotrifluoride (14.16 grams, 0.054 mole) to yield the product, which was recrystallized from hexane and had a melting point range of 30—32°C.

Elemental Analysis: Calculated: C, 49.9; H, 5.03; N, 11.64.
Found: C, 50.08; H, 5.21; N, 11.68.

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anilin
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50 Prepara
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propy
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65 Prepara
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EXAMPLE 6.

Preparation of *N,N* - bis(cyclopropylmethyl)-4 - trifluoromethyl - 2,6 - dinitroaniline.

Following the general procedure of Example 1, *N,N* - bis - (cyclopropylmethyl)amine (9.0 grams, 0.072 mole) was reacted with 3,5-

dinitro - 4 - chlorobenzotrifluoride (9.73 grams, 0.036 mole) to yield 12.5 grams of crude product. Recrystallization of this material from hexane gave a product having a melting point range of 61—62°C.

Elemental Analysis: Calculated: C, 50.1; H, 4.49; N, 11.70.
Found: C, 50.05; H, 4.72; N, 11.36.

EXAMPLE 7.

Preparation of 4 - (methylsulfonyl) - 2,6-dinitro - *N* - cyclopropylmethyl - *N* - methylaniline.

To a suspension of 4 - chloro - 3,5 - dinitrophenyl methylsulfone (7.5 grams, 0.027 mole) in 60 ml of methanol was added *N* - cyclopropylmethyl - *N* - methylamine (5.1 grams, 0.06 mole) dissolved in twice its volume of methanol over a period of 10 minutes. A slight exothermic reaction was noted as orange-

yellow colored solids formed during the addition. The mixture was heated at reflux for approximately one hour, chilled to 0°C., and then filtered. This process effected the separation of the methanol-insoluble product from the methanol-soluble amine hydrochloride by-product. The golden crystalline product (8.4 grams) was recrystallized from hot methanol. The melting point range of this final product was 143—145°C.

Elemental Analysis: Calculated: C, 43.8; H, 4.59.
Found: C, 44.1; H, 4.82.

EXAMPLE 8.

Preparation of 4 - (methylsulfonyl) - 2,6-dinitro - *N* - cyclopropylmethyl - *N* - ethylaniline.

Following the general procedure of Example 7, *N* - cyclopropyl - methyl - *N* - ethylamine

(5.9 grams, 0.06 mole) was reacted with 4-chloro - 3,5 - dinitrophenyl methylsulfone (7.5 grams, 0.027 mole) to give crystalline product melting at 110—111°C. after recrystallization from methanol.

Elemental Analysis: Calculated: C, 45.4; H, 4.98.
Found: C, 45.7; H, 5.31.

EXAMPLE 9.

Preparation of 4 - (methylsulfonyl) - 2,6-dinitro - *N* - cyclopropylmethyl - *N* - *n*-propylaniline.

Following the procedure of Example 7, *N*-

cyclopropylmethyl - *N* - *n* - propylamine (7.1 grams, 0.06 mole) was reacted with 4 - chloro - 3,5 - dinitrophenyl methylsulfone (7.5 grams, 0.027 mole) to yield a product melting at 132—133°C.

Elemental Analysis: Calculated: C, 47.1; H, 5.36; N, 8.97.
Found: C, 46.9; H, 5.54; N, 8.96.

EXAMPLE 10.

Preparation of 4 - (methylsulfonyl) - 2,6-dinitro - *N* - cyclopropylmethyl - *N* - *n*-butylaniline.

According to the general procedure of Ex-

ample 7, *N* - cyclopropylmethyl - *N* - *n*-butylamine (8.0 grams, 0.06 mole) was reacted with 4 - chloro - 3,5 - dinitrophenyl methylsulfone to give a product melting at 88—90°C.

Elemental Analysis: Calculated: C, 48.5; H, 5.69; N, 8.63.
Found: C, 48.0; H, 5.58; N, 8.59.

EXAMPLE 11.

Preparation of *N* - cyclopropylmethyl - *N* - *n* - propyl - 2,6 - dinitroaniline.

In a suitable reaction flask was placed 1-chloro - 2,6 - dinitrobenzene (10.1 grams, 0.05 mole), triethylamine (7.1 grams, 0.07 mole, 9.7 ml), and benzene (100 ml). To this stirred solution, *N* - cyclopropylmethyl - *N* - *n*-propylamine (6.8 grams, 0.06 mole), dissolved in 10 ml of benzene, was added dropwise at room temperature. The resulting solution was

refluxed for 15 hours. After cooling the solution and filtering off the amine hydrochloride, the filtrate was washed with 9% HCl, then with water, and finally dried with MgSO₄. Removal of the solvent under reduced pressure yielded a viscous red oil which soon crystallized to a yellow solid weighing 12.7 grams. Recrystallization from a heptane-petroleum ether mixture gave a product melting at 47—48°C.

Elemental Analysis: Calculated: C, 55.9; H, 6.14; N, 15.05.
Found: C, 56.0; H, 6.33; N, 14.79.

EXAMPLE 12.

Preparation of *N* - cyclopropylmethyl - *N* - *n* - propyl - 2,6 - dinitro - *p* - toluidine.
Following the general procedure of Example 1, *N* - cyclopropylmethyl - *N* - *n* - propylamine (11.3 grams, 0.10 mole) was reacted with 3,5 - dinitro - 4 - chlorotoluene (10.8 grams, 0.05 mole) to yield a product melting at 26—28°C. after the usual workup and recrystallization from hexane.

Elemental Analysis: Calculated: N, 14.33.
Found: N, 14.68.

Elemental Analysis: Calculated: C, 55.25; H, 5.30; N, 18.41.
Found: C, 55.22; H, 5.48; N, 18.07.

EXAMPLE 14.

Preparation of *N* - cyclopropylmethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline.
Cyclopropylmethylamine hydrochloride (5.3 grams, 0.05 mole), prepared according to the procedure of Roberts and Mazur (JACS 73, pp. 2509—20, 1951), was dissolved in 20 ml of water. A solution of 4.0 grams (0.1 mole) of sodium hydroxide was added, fol-

Elemental Analysis: Calculated: C, 43.5; H, 3.3; N, 13.8.
Found: C, 43.3; H, 3.6; N, 13.7.

EXAMPLE 15.

Preparation of *N* - cyclopropylmethyl - *N* - *n* - propyl - 2 - nitro - 4 - trifluoromethylaniline.

According to the general procedure of Example 2, *N* - cyclopropylmethyl - *N* - *n* - propylamine (6.79 grams, 0.06 mole) was reacted with 4 - chloro - 3 - nitrobenzotrifluoride (11.3 grams, 0.05 mole), using benzene as a solvent. The reflux time was extended to 21 hours. Workup of the reaction mixture in the usual way yielded a red oil, which when subjected to vacuum distillation, gave a main

Elemental Analysis: Calculated: C, 54.33; H, 5.7; N, 15.84.
Found: C, 54.53; H, 6.09; N, 15.59.

(b) *N* - cyclopropylmethyl - *N* - ethyl - 2,6-dinitro - *p* - toluidine, m.p. 44—46°C.

Elemental Analysis: Calculated: C, 55.90; H, 6.14; N, 15.05.
Found: C, 55.83; H, 6.54; N, 15.14.

(c) *N* - cyclopropylmethyl - *N* - (3 - methyl-mercaptopropyl) - 4 - trifluoromethyl - 2,6-dinitroaniline, m.p. 36—38°C.

Elemental Analysis: Calculated: C, 46.0; H, 4.61; N, 10.7.
Found: C, 45.75; H, 4.40; N, 10.66.

EXAMPLE 13.

Preparation of *N* - cyclopropylmethyl - *N* - *n* - propyl - 4 - cyano - 2,6 - dinitroaniline.
N - cyclopropylmethyl - *N* - *n* - propylamine (11.1 grams, 0.098 mole) was dissolved in 100 ml of benzene. To this stirred solution was added a solution of 4 - chloro - 3,5-dinitrobenzonitrile (10 grams, 0.044 mole) dropwise over a period of $\frac{1}{2}$ hour. The resulting solution was refluxed for 40 hours. Workup of the product in the usual manner gave a bright yellow solid melting at 106.5—108°C.

lowed by a portion-wise addition of solid 3,5-dinitro - 4 - chlorobenzotrifluoride. The resulting mixture was refluxed for one hour. After cooling, the oily product was separated from the aqueous phase and dissolved in boiling methanol. Chilling of the alcoholic solution precipitated solids which were filtered and air dried, and had a melting point range of 90—91°C.

cut (7.0 grams) of red oil having a boiling point range of 143—145°C. at 0.5 mm Hg of pressure.

Elemental Analysis: Calculated: N, 9.27.
Found: N, 9.75.

EXAMPLE 16.

According to the general procedures outlined in the preceding examples, the following additional compounds were synthesized:

(a) *N* - cyclopropylmethyl - *N* - ethyl - 2,6-dinitrobenzene, m.p. 47.5—49°C.

(d)
cyclopropyl

Elem

(e)
cyano

Elem

(f)

(i)
71—

(j)
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(k)
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(d) 4 - (methylsulfonyl) - 2,6 - dinitro - *N*-cyclopropylmethyl - *N* - (3 - methylmercapto-propyl)aniline, m.p. 72—76°C.

Elemental Analysis: Calculated: N, 10.4.
Found: N, 9.58.

(e) *N* - cyclopropylmethyl - *N* - ethyl - 4-cyano - 2,6 - dinitroaniline, m.p. 93—94°C.

Elemental Analysis: Calculated: N, 19.3.
Found: N, 19.39.

(f) *N* - cyclobutylmethyl - *N* - ethyl - 4-

Elemental Analysis: Calculated
Found:

trifluoromethyl - 2,6 - dinitroaniline, (oil).

Elemental Analysis: Calculated: N, 12.1.
Found: N, 11.83.

(g) *N* - cyclopentylmethyl - *N* - ethyl - 4-trifluoromethyl - 2,6 - dinitroaniline, m.p. 60—62°C.

Elemental Analysis: Calculated: N, 11.6.
Found: N, 11.36.

(h) 4 - (methylsulfonyl) - 2,6 - dinitro - *N*-cyclopentyl - methyl - *N* - ethylaniline, m.p. 119—122°C.

Elemental Analysis: Calculated: C, 48.6; H, 5.69; N, 11.32.
Found: C, 48.3; H, 5.40; N, 11.32.

(i) *N* - cyclopropyl - *N* - ethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline, m.p. 71—73°C.

Elemental Analysis: Calculated: C, 45.2; H, 3.79; N, 13.15.
Found: C, 45.16; H, 3.65; N, 13.34.

(j) 4 - (methylsulfonyl) - 2,6 - dinitro - *N*-cyclopropyl - *N* - ethylaniline, m.p. 170—171°C.

Elemental Analysis: Calculated: C, 43.8; H, 4.59; N, 12.78.
Found: C, 43.99; H, 4.96; N, 12.81.

(k) *N* - cyclopropyl - *N* - cyclopropylmethyl - 4 - trifluoromethyl - 2,6 - dinitroaniline, m.p. 45—54°C.

Elemental Analysis: Calculated: N, 12.2.
Found: N, 12.23.

yield a crude oil (108.6 grams) which crystallized to a solid upon standing. A sample was recrystallized from petroleum ether at sub-zero temperatures to give material melting at 34—35°C.

Elemental Analysis: Calculated: N, 11.01.
Found: N, 10.92.

The procedures described in Examples 17 and 18 illustrate the general mode of preparation of the intermediate amides and amines. The physical constants of these compounds are consolidated in the table which follows, Table II.

EXAMPLE 17.

Preparation of *N* - *n* - propylcyclopropanecarboxamide.

In 600 ml of benzene was dissolved *n*-propylamine (130 grams, 2.2 moles, 181 ml). This well-stirred solution was cooled to about 10°C., and a solution of cyclopropanecarboxylic acid chloride (104.5 grams, 1.0 mole) in 100 ml of benzene was added dropwise over a period of 1½ hours. During this time, white solids formed in the reaction medium. The mixture was heated at reflux for about 3 hours, cooled to room temperature, and filtered to remove the insoluble white *n*-propylamine hydrochloride salt. The filtrate was washed successively with 150 ml portions of water, 5% HCl, water, 10% NaHCO₃, and water. The solution after being dried with anhydrous MgSO₄ was stripped of solvent to

EXAMPLE 18.

Preparation of *N* - cyclopropylmethyl - *N* - *n*-propylamine.

In a reaction flask was placed a suspension of lithium aluminum hydride (30 grams, 0.786 mole) in anhydrous ether (1 liter). A nitrogen blanket was held over the mixture throughout the reaction. To the stirred mixture was added dropwise a solution of *N* - *n* - propylcyclopropanecarboxamide (50 grams, 0.393 mole) in 300 ml of dry ether over a period of two hours. Gentle refluxing of the solvent was evident during the addition. After the addition was complete, the mixture was heated at reflux for approximately 10 hours. The solution was cooled with an ice bath, while 6% aqueous sodium hydroxide was cautiously added dropwise to destroy the unreacted lithium aluminum hydride. The resulting white aluminate salts were removed by filtration and the clear ethereal filtrate was dried with potassium hydroxide pellets. After the ether was removed by distillation, the *N*-cyclopropylmethyl - *N* - *n* - propylamine was dis-

tilled at atmospheric pressure and found to have a boiling point range of 136—138°C. The yield was 27 grams.

Elemental Analysis: Calculated: N, 11.01. Found: N, 10.97.

As an alternate workup procedure, the ethereal solution obtained after filtration was extracted two or three times with 10% HCl. The acidic aqueous solution was basified with

excess aqueous sodium hydroxide, and the amine which formed an insoluble upper layer was extracted with ether. After drying the ether solution with KOH pellets, the distillation procedure as described above was carried out.

Exemplary of products prepared in accordance with the procedures set forth in Examples 17—18 above, are those listed in Table II below.

TABLE II

N-alkylcycloalkancarboxamides

N-cycloalkylmethyl-N-alkylamines

R₁ CONHR₂

R₁ CH₂NHR₂

R ₁	R ₂	m.p. °C.	Nitrogen Analysis		b.p. °C./1 Atm.	Nitrogen Analysis	
			Found	Calculated		Found	Calculated
	CH ₃	48 — 51	13.99	14.13	91 — 93.5	16.85	16.4
	CH ₂ CH ₃	(oil)	11.81	12.39	110 — 12	13.39	14.12
	n-C ₃ H ₇	34 — 35	10.92	11.01	136 — 38	12.40	12.3
	i-C ₃ H ₇	91 — 92	10.87	11.01	125	12.65	12.3

TABLE II (continued)

N-alkylcycloalkancarboxamides

TABLE II (continued)

N-alkylcycloalkanecarboxamides *N*-cycloalkylmethyl-*N*-alkylamines

	R_2	m.p. °C.	Nitrogen Analysis		b.p. °C./1 Atm.	Nitrogen Analysis	
			Found	Calculated		Found	Calculated
	n-C ₄ H ₉	36 — 37	9.98	9.92	158 — 59	11.06	11.0
		56 — 58	10.15	10.06	168 — 72	10.92	11.1
	(CH ₂) ₃ SCH ₃	48 — 50	8.09	8.09	62 — 3/0.1 mm	8.65	8.82
	CH ₂ CH ₃				136		
	CH ₂ CH ₃				164 — 165.5	10.51	11.01

NMR spectroscopy was used to verify the structures indicated in this table.

EXAMPLE 19.

N - cyclopropyl - *N* - alkylamines which are used in the preparation of compounds illustrated by Example 14(i), 14(j) and 14(k) may be synthesized by reduction of the corresponding *N*-cyclopropyl amides under mild conditions. The method of Brown and Heim (see JACS 86, 3566 (1964)) utilizing diborane as the reducing agent, can be used to prepare these amines. The following synthesis shows the general technique.

N - cyclopropyl - *N* - ethylamine.

In a flask was placed 338 ml of a 1 M borane in tetrahydrofuran solution (nitrogen atmosphere). The solution was cooled to approximately 0°C., and a solution of *N*-cyclopropylacetamide (16.6 grams, 0.169 mole) in tetrahydrofuran was added dropwise with stirring over a period of 60 minutes, maintaining a temperature of 0—5°C. The solution was heated at reflux for three hours and then cooled to room temperature. About 90 ml of 5 *N* HCl solution was added dropwise and the reaction mixture was heated to reflux for 30 minutes. The tetrahydrofuran was removed by distillation at atmospheric pressure and the residue was made basic with excess 50% NaOH solution. This basic solution was extracted with ether and the extracts were dried over KOH pellets. Distillation afforded 7.2 grams of *N* - cyclopropyl - *N* - ethylamine boiling at 101—103°/1 atm. The structure was confirmed by its nuclear magnetic resonance spectrum.

EXAMPLE 20.

Representative nitrated aryl cycloalkane derivatives from those prepared in the previous examples were evaluated for pre-emergence herbicidal activity in this example. The test procedure employed was as follows:

Two flats seeded with six crops (cotton, soybean, tomato, corn, rice and oats) and six weeds (mustard, morning glory, velvet leaf, crabgrass, Johnson grass, and foxtail) were sprayed with a formulation containing the test chemical at a rate equivalent to 10 lbs./acre. The test chemicals were sprayed as acetone solutions or very small particle acetone suspensions onto the test plants. Sprayers were calibrated to deliver a certain volume of liquid and the calculated amount of active ingredient which would give a rate corresponding to the indicated lbs./acre. The flats were then held in the greenhouse and a response rated after 12 days to 16 days. Response was rated by a scale of 0—10. The 0—10 scale is defined as: 0=no injury; 1—3=slight injury; 4—6=moderate injury, plants may die; 7—9=severe injury, plants will probably die; and 10=all plants dead (complete kill). Treflan was used as the standard in the amount of 5 and 1.25 lbs./acre, respectively. Results of this test are shown below in Table III and it is indicative that many of these compounds show a high degree of herbicidal activity against certain weed species, yet remain highly tolerant of desirable crop species.

TABLE III
Herbicide Activity

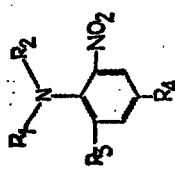
	Preemergence Test																
	R ₁	R ₂	R ₃	R ₄	Rate lbs./acre	Corn	Soybean	Cotton	Rice	Morning Glory	Tomato	Oats	Crabgrass	Johnson Grass	Yellow Foxtail	Velvet Leaf	Mustard
	CH ₂	CH ₃	NO ₂	CF ₃	10 1.25	1 0	0 0	0 0	0 0	0 0	0 0	3 0	10 9	9 5	9 7	2 0	2 0
	CH ₂	C ₂ H ₅	NO ₂	CF ₃	5 1.25	4 0	0 2	3 0	9 2	0 0	0 0	3 0	10 8	10 8	9 8	2 2	4 0
	CH ₂	n-C ₃ H ₇	NO ₂	CF ₃	10 1.25	6 1	4 0	8 4	5 1	5 0	5 0	7 1	10 10	10 9	10 9	5 0	3 0
	CH ₂	i-C ₃ H ₇	NO ₂	CF ₃	10 1.25	1 1	0 0	5 8	3 1	0 0	0 0	0 0	9 0	7 0	8 0	0 0	5 3
	CH ₂	n-C ₄ H ₉	NO ₂	CF ₃	10 1.25	1 1	0 0	8 0	2 2	0 0	0 0	2 0	9 7	9 5	8 2	0 1	1 0

TABLE III (Continued)

Herbicide Activity

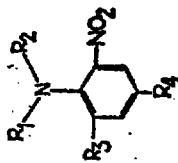
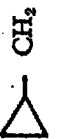
	Preemergence Test													Rate lbs./acre		
	R ₁	R ₂	R ₃	R ₄	Corn	Soybean	Cotton	Rice	Morning Glory	Tomato	Oats	Crabgrass	Johnson Grass		Yellow Foxtail	Velvet Leaf
	CH ₂		CH ₂	NO ₂	CF ₃	10	0	0	5	0	0	1	9	9	0	3
						1.25	0	0	2	0	0	0	9	6	0	2
	CH ₂	CH ₃	CH ₃	NO ₂	SO ₂ CH ₃	10	0	0	3	0	0	0	10	7	0	2
						1.25	0	0	0	0	0	1	0	0	0	0
	CH ₂	C ₆ H ₅	NO ₂	SO ₂ CH ₃	10	1	0	3	0	0	2	10	9	9	8	6
					1.25	0	0	7	0	0	0	10	8	7	0	1
	CH ₂	n-C ₈ H ₇	NO ₂	SO ₂ CH ₃	10	1	1	3	0	0	3	10	9	7	0	2
					1.25	0	0	3	1	0	0	9	3	2	0	2
	CH ₂	n-C ₆ H ₅	NO ₂	SO ₂ CH ₃	10	1	0	2	0	0	2	8	5	4	0	0
					1.25	0	1	0	0	1	0	6	3	0	0	2
	CH ₂	(CH ₂) ₃ SCH ₃	NO ₂	SO ₂ CH ₃	10	0	0	3	0	0	4	5	0	0	0	0

TABLE III (Continued)

Herbicide Activity

TABLE III (Continued)

Herbicide Activity

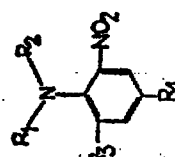
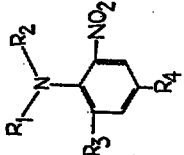
	Preemergence Test												
	Rate lbs./acre	Corn	Soybean	Cotton	Rice	Morning Glory	Tomato	Oats	Crabgrass	Johnson Grass	Yellow Foxtail	Velvet Leaf	Mustard
	R ₁	R ₂	R ₃	R ₄									
	CH ₂	C ₂ H ₅	NO ₂	SO ₂ CH ₃	10	0	0	0	0	8	5	0	0
	CH ₂	n-C ₃ H ₇	NO ₂	H	10 1.25	0	0	10	5	9	8	5	0
	CH ₂	C ₂ H ₅	NO ₂	H	10 1.25	0	0	6	1	9	9	2	0
	CH ₂	n-C ₃ H ₇	NO ₂	CH ₃	10 1.25	0	0	5	4	10	9	6	3
	CH ₂	C ₂ H ₅	NO ₂	CH ₃	10 1.25	1	3	3	5	10	9	2	2
	CH ₂	n-C ₃ H ₇	NO ₂	C≡N	10 1.25	1	0	0	2	10	9	0	0

TABLE III (Continued)
Herbicide Activity

	Preemergence Test																
	Rate lbs./acre	Corn	Soybean	Cotton	Rice	Morning Glory	Tomato	Oats	Crabgrass	Johnson Grass	Yellow Foxtail	Velvet Leaf	Mustard				
	R ₁	R ₂	R ₃	R ₄													
	CH ₂	C ₂ H ₅	NO ₂	C≡N	10	0	0	5	0	0	0	0	9	8	9	2	0
	CH ₂	n-C ₃ H ₇	H	CF ₃	10	1	0	4	2	0	0	0	7	5	5	0	4
	CH ₂	(CH ₂) ₃ SCH ₃	NO ₂	CF ₃	10	0	0	0	0	0	0	1	9	6	7	0	0
	CH ₂	H	NO ₂	CF ₃	10	0	0	5	5	0	1	0	0	5	0	6	3
n-C ₃ H ₇		n-C ₃ H ₇ TREFLAN	NO ₂	CF ₃	5 1.25	1 0	4 1	3 0	5 3	3 0	5 0	3 0	10 10	10 7	10 8	2 0	4 1
	CH ₂	C ₂ H ₅	NO ₂	CF ₃	10	0	0	10	0	0	0	2	10	9	9	0	0
	CH ₂	C ₂ H ₅	NO ₂	CF ₃	10	0	0	0	0	0	0	0	9	6	7	0	7
	CH ₂	C ₂ H ₅	NO ₂	SO ₂ CH ₃	10	0	0	0	0	0	0	0	8	5	5	0	0

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EXAMPLE 21.

5 In this example representative cycloalkane derivatives of the nitrated aryl compounds of this invention were evaluated for post-emergence activity. The test procedure was as follows:

10 Flats were seeded, as described in the previous example, and held until the first true leaves had appeared on all plants, which were then sprayed in the same fashion as in the preceding example at a rate of 10 lbs./acre. The plant responses were rated 12—16 days after treatment on the same scale as described previously. The test results are shown in 15 Table IV.

EXAMPLE 22.

In this example a pre-emergence herbicide study was carried out to compare the activity of the commercial material Treflan (*N,N*-di-

n - propyl - 4 - trifluoromethyl - 2,6 - dinitro- 20
aniline) with that of a specific example disclosed in this invention, namely *N*-cyclopropyl- 25
methyl - *N* - *n* - propyl - 4 - trifluoromethyl - 2,6 - dinitroaniline. Tests were carried out on a number of crop and weed species and the chemical were applied to the surface of the 30
soil as well as incorporated into the soil. Observations were made four weeks after the planting date to determine the relative effects on the crops as well as the overall effect on broadleaf weed species and grassy weed species. 35
The data is summarized in Table V. The results show that in general the scope of activity of both compounds against weed species is quite similar. However, in addition, the cyclopropyl derivative appears to show some unexpected crop tolerance which exceeds the tolerance of Treflan to these same species.

TABLE IV

Herbicide Activity

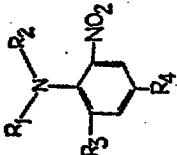
	Post Emergence Test										Rate lbs./acre					
	R ₁	R ₂	R ₃	R ₄	Corn	Soybean	Cotton	Rice	Morning Glory	Tomato			Oats	Crabgrass	Johnson Grass	Yellow Foxtail
 -CH ₂		CH ₃	NO ₂	CF ₃	2	1	2	2	1	5	5	1	7	5	5	5
 -CH ₂		C ₂ H ₅	NO ₂	CF ₃	1	3	1	—	2	1	1	0	—	1	—	2
 -CH ₂		n-C ₈ H ₁₇	NO ₂	CF ₃	7	5	8	5	5	6	5	9	8	8	5	5
 -CH ₂		i-C ₈ H ₁₇	NO ₂	CF ₃	2	3	3	3	2	2	5	7	6	5	4	2
 -CH ₂		n-C ₄ H ₉	NO ₂	CF ₃	0	3	1	1	2	3	3	8	4	4	5	4
 -CH ₂		 -CH ₂	NO ₂	CF ₃	0	1	0	0	1	0	5	0	0	0	3	3

TABLE IV (Continued)

Herbicide Activity

TABLE IV (Continued)

Herbicide Activity

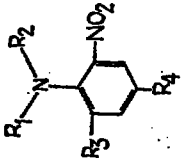
	Post Emergence Test											Rate lbs./acre					
	Corn	Soybean	Cotton	Rice	Morning Glory	Tomato	Oats	Crabgrass	Johnson Grass	Yellow Foxtail	Velvet Leaf			Mustard			
	R ₁	R ₂	R ₃	R ₄													
	 -CH ₂	(CH ₂) ₃ SCH ₃	NO ₂	CF ₃	10	2	2	0	2	3	2	6	8	3	6	1	3
	 -CH ₂	CH ₃	NO ₂	SO ₂ CH ₃	10	1	2	0	2	0	1	1	5	5	0	0	0
	 -CH ₂	C ₂ H ₅	NO ₂	SO ₂ CH ₃	10	4	2	10	2	1	1	0	6	5	2	3	0
	 -CH ₂	n-C ₃ H ₇	NO ₂	SO ₂ CH ₃	10	3	3	8	4	2	6	1	7	4	0	2	0
	 -CH ₂	n-C ₄ H ₉	NO ₂	SO ₂ CH ₃	10	0	1	6	0	0	0	1	0	0	0	0	1
	 -CH ₂	(CH ₂) ₃ SCH ₃	NO ₂	SO ₂ CH ₃	10	0	1	1	0	1	0	1	0	0	0	0	0

TABLE IV (Continued)
Herbicide Activity

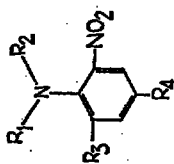
	Post Emergence Test										Rate lbs./acre						
	R ₁	R ₂	R ₃	R ₄	Corn	Soybean	Cotton	Rice	Morning Glory	Tomato		Oats	Crabgrass	Johnson Grass	Yellow Foxtail	Velvet Leaf	Mustard
	CH ₂	n-C ₈ H ₇	NO ₂	H	3	2	1	3	2	4	5	7	6	5	5	4	
	CH ₂	C ₂ G ₅	NO ₂	H	2	2	6	2	2	6	3	9	5	7	4	9	
	CH ₂	n-C ₈ H ₇	NO ₂	CH ₃	3	3	1	2	3	5	6	7	7	5	3	5	
	CH ₂	C ₂ H ₅	NO ₂	CH ₃	5	5	3	3	2	6	5	9	9	7	2	7	
	CH ₂	n-C ₈ H ₇	NO ₂	C≡N	0	0	0	0	0	4	1	5	3	2	0	0	

TABLE IV (Continued)
Herbicide Activity

TABLE IV (Continued)

Herbicide Activity

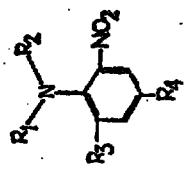
	Rate lbs./acre	Post Emergence Test														
		R ₁	R ₂	R ₃	R ₄	Corn	Soybean	Cotton	Rice	Morning Glory	Tomato	Oats	Crabgrass	Johnson Grass	Yellow Foxtail	Velvet Leaf
 -CH ₂	10	0	1	0	0	0	0	0	0	1	1	4	2	0	2	1
 -CH ₂	10	3	2	1	3	2	3	2	2	2	0	3	2	2	1	1
 -CH ₂	10	0	1	10	2	0	2	0	1	1	0	0	0	0	0	0
 -CH ₂	10	0	1	10	0	1	0	1	3	6	7	6	6	4	1	2
 -CH ₂	10	8	6	0	0	1	0	1	8	5	9	8	8	8	2	5
 -CH ₂	10	3	1	0	0	0	0	0	3	2	6	1	1	0	1	0

TABLE V

Treatment	Rate Lbs./A	Rating					
		Cotton	Soybeans	Corn	Sugar Beet	B.L.*	Gr.**
CPTD—S	0.5	1.7	1.0	0.7	1.7	1.0	1.0
Treflan—S	0.5	2.0	2.7	1.0	2.0	2.3	3.7
CPTD—I	0.5	1.7	0.7	1.0	6.3	6.0	7.7
Treflan—I	0.5	0.3	3.3	2.3	6.7	7.3	7.7
CPTD—S	1.0	1.0	1.3	0.7	1.3	4.0	4.7
Treflan—S	1.0	5.3	5.7	2.3	4.0	4.7	6.3
CPTD—I	1.0	0.0	3.3	2.0	6.7	9.0	8.7
Treflan—I	1.0	0.33	2.7	3.0	9.7	9.0	9.0
CPTD—S	2.0	3.7	3.7	1.3	5.3	5.0	5.0
Treflan—S	2.0	3.7	3.7	0.7	4.0	5.0	5.7
CPTD—I	2.0	3.0	3.3	3.3	9.7	8.7	8.7
Treflan—I	2.0	0.7	5.0	7.0	10.0	9.0	9.0

CPTD = *N*-Cyclopropylmethyl-*N*-*n*-propyl-4-trifluoromethyl-2,6-di-nitroaniline.

*B.L. = broadleaved weeds.

S = surface application.

**Grassy weeds

I = soil incorporation.

EXAMPLE 23.

The effect of *N*-cyclopropylmethyl - *N* - *n*-propyl - 4 - trifluoromethyl - 2,6 - dinitro-aniline against a series of grass-type weeds in a pre-emergence soil incorporated herbicide test was carried out at a rate of 1.25 lbs./acre. The data is summarized below:

	Quack grass	Johnson grass	Annual Rye	Yellow foxtail	Barnyard grass	Crab- grass
1.25 lbs./acre	7	8	9	8	8	9

Examples 24 and 25, illustrate typical pesticidal compositions or formulations of this invention. Parts are by weight.

Wetting Agent (Sodium Alkyl Naphthalene Sulfate (Nekal BA—75'))
("NEKAL" is a Registered Trade Mark)

4 25

EXAMPLE 24.

A typical wettable powder concentrate that is diluted to the desired concentration by dispersing it in water has the following composition:

	Parts
Active Ingredient	50
Solid Carrier (e.g. Attapulgate)	42
Dispersant (Monocalcium salt of polymeric alkylaryl sulfonic acid)	4

EXAMPLE 25.

A liquid concentrate that is diluted in the field with water has the following composition:

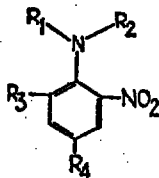
	Parts
Active Ingredient	45
Xylene	45
Emulsifier (blend of calcium dodecylbenzenesulfonate and alkyl aryl polyethylene oxide adduct)	10

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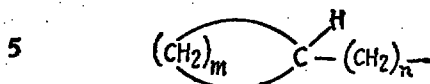
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WHAT WE CLAIM IS:—

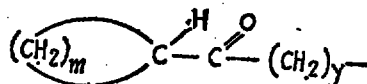
1. A compound of the formula:



wherein R_1 represents a



or a



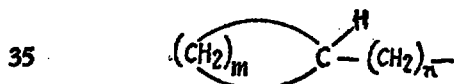
group in which the ring may be substituted or unsubstituted; m represents an integer from 2 to 4; n represents zero or an integer from 1 to 3; and y represents an integer from 1 to 3;

R_2 represents a hydrogen atom or a C_1 to C_{12} straight or branched chain monovalent aliphatic group, a C_3 to C_8 cycloalkyl group, a C_4 to C_{10} cycloalkylalkyl group, a C_2 to C_{12} alkoxyalkyl group, a C_1 to C_{12} haloalkyl group, a C_2 to C_{12} cyanoalkyl group, a C_2 to C_6 acyl group, or a C_2 to C_6 alkylmercaptoalkyl group or a sulfoxide or sulphone thereof;

R_3 represents a hydrogen or halogen atom or a nitro group, a C_1 to C_6 alkyl group, or a cyano group; and

R_4 represents a hydrogen or halogen atom or a C_1 to C_{12} alkyl group, a haloalkyl group, a cycloalkyl group, a nitro group, a cyano group, a substituted or unsubstituted phenyl group, a $C_6H_5-N=N-$ group, a C_1 to C_3 alkylmercapto group or a sulfoxide or sulphone thereof, or an $R_5R_6NSO_2-$ group in which R_5 and R_6 , which may be the same or different, each represent R_2 as hereinabove defined.

2. A compound according to claim 1 wherein R_1 represents a



group in m and n are defined in claim 1;

R_2 represents a hydrogen atom or a C_1 to C_{12} straight or branched chain monovalent aliphatic group, a C_3 to C_8 cycloalkyl group, a C_4 to C_{10} cycloalkylalkyl group, a C_2 to C_{12} alkoxyalkyl group or a C_1 to C_{12} haloalkyl group;

R_3 represents a nitro group; and

R_4 represents a hydrogen atom or a C_1 to C_{12} alkyl group, a haloalkyl group, a cyano

group, a substituted or unsubstituted phenyl group or a C_1 to C_3 alkylmercapto group or a sulfoxide or sulphone thereof.

3. A compound according to claim 1 wherein

R_1 represents a cyclopropylmethyl group;

R_2 represents a hydrogen atom or a methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, sec-butyl, isobutyl, cyclopropylmethyl, *n*-amyl, isoamyl, sec-amyl, allyl, propargyl, crotyl, methallyl, methoxyethyl, ethoxyethyl, *n*-propoxyethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-methylmercaptoethyl, 3-methylmercaptopropyl, trifluoromethyl, pentafluoroethyl, 3-chloropropyl, trichloromethyl or bromomethyl group;

R_3 represents a nitro group; and

R_4 represents a hydrogen, chlorine, bromine or fluorine atom or a methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, sec-butyl, isobutyl, *t*-butyl, *n*-pentyl, *n*-hexyl, trifluoromethyl, chloromethyl, trichloromethyl, bromomethyl, chloroethyl, bromoethyl, chloropropyl, bromopropyl, cyano, cyclopentyl, cyclohexyl, $C_6H_5N=N-$, unsubstituted or alkyl, halogen or nitro substituted phenyl, a C_1 to C_3 alkylmercapto group or a sulfoxide or sulphone thereof, or an $R_5R_6NSO_2-$ group in which R_5 and R_6 , which may be the same or different, each represent a hydrogen atom or an alkyl, alkenyl, alkynyl or cycloalkyl group.

4. A compound according to any of the preceding claims wherein R_1 is substituted with an alkyl, alkenyl or cyano group or a halogen atom.

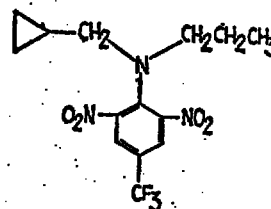
5. A compound according to any of the preceding claims wherein R_2 is a C_1 to C_{12} straight or branched chain alkyl, alkenyl or alkynyl group.

6. A compound according to any of the preceding claims wherein R_4 is a trifluoromethyl group.

7. A compound according to claim 1 specifically named herein.

8. A compound according to claim 1 substantially as hereinbefore described with reference to any of the specific Examples 1 to 16.

9. The compound:



10. A process for preparing a compound according to any of the preceding claims substantially as hereinbefore described.

11. A compound according to any of claims 1 to 9 whenever prepared by the process of claim 10.

- 5 12. A herbicidal composition comprising, as active ingredient, a herbicidally effective amount of a compound according to any of claims 1 to 9 or 11 in association with one or more inert carriers.
13. A composition according to claim 12 wherein the inert carrier is specifically named herein as such.
- 10 14. A composition according to claim 12 or 13 wherein the active ingredient comprises from 0.01% by weight to 90% by weight of the composition.
- 15 15. A composition according to claim 12, 13 or 14 substantially as hereinbefore described.
16. A method of combating the growth of undesired vegetation at a locus, which method comprises applying to the locus a herbicidally effective amount of a compound as claimed in any of claims 1 to 9 or 11.
- 20 17. A method according to claim 16 wherein the herbicidally effective amount of compound as claimed in any of claims 1 to 9 or 11 is contained in a composition according to any of claims 12, 13 or 14.
- 25 18. A method according to claim 16 or 17 wherein the locus is soil and the application is effected prior to emergence of the undesired vegetation.
- 30 19. A method according to any of claims 16, 17 or 18 substantially as hereinbefore described.

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