[Second Edition.]

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in Polysubstituted Ureas

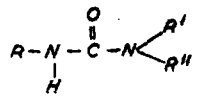
We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 10th and Market Streets, Wilmington, Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a new class of organic nitrogen compounds. More particularly, it relates to a new class of substituted ureas.

The enormous economic losses caused annually by weeds has, to some extent, been relieved in recent years with the advent of 2,4-dichlorophenoxyacetic acid (2,4-D) and related synthetic chemicals. These products, however, fail completely in the control of obnoxious grasses such as Johnson, quack and crab grasses. This problem is still acute and unsolved in spite of the tremendous number of various other types of compounds which have been investigated for the purpose.

It is an object of this invention to provide a new class of N,N^1-substituted ureas. A further object is to provide a new class of tri-substituted ureas. Another object is to provide new tri-substituted ureas possessing useful plant growth regulating properties, particularly in herbicidal applications against resistant grasses. Other objects will appear hereinafter.

The objects of this invention are accomplished by the new class of N,N^1-substituted ureas having a hydrogen atom directly attached to a urea nitrogen atom which is bonded to a nuclear carbon of a halogenoaryl radical, the other urea nitrogen atom being joined to two monovalent aliphatic hydrocarbon radicals. This new class of tri-substituted ureas is represented by the formula

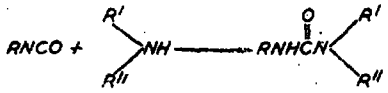


wherein R is a halogenoaryl radical, and R^1 and R^{11} each represent monovalent aliphatic hydrocarbon radicals, i.e., acyclic aliphatic and cycloaliphatic hydrocarbon radicals. Those ureas are preferred where R is a halogenated aryl radical containing one or two nuclei, particularly halogenophenyl. Those ureas are also preferred wherein R^1 and R^{11} are monovalent saturated aliphatic hydrocarbon radicals, particularly alkyl radicals. This latter class of ureas can be designated as 3-halogenoaryl-1,1-dialkylureas of which the 3-halogenophenyl - 1,1 - dialkylureas are especially preferred.

A convenient method for preparing the new ureas of this invention is illustrated by the following general equation (1) in which halogenoaryl isocyanate, RNCO (R being a halogenoaryl radical), is reacted with a secondary aliphatic amine, i.e., acyclic aliphatic and cycloaliphatic secondary amines of the formula,

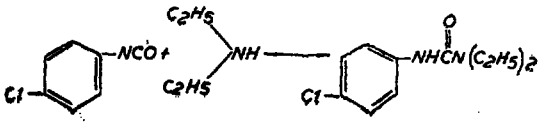


wherein R^1 and R^{11} have the same meaning previously designated for these symbols in the formula of the new ureas of the invention:—

(1) 

A specific reaction for the preparation of 3 - (*p*-chloropheny) - 1,1 - diethylurea is illustrated in the following equation (2):—

(2)



The reaction is accomplished by bringing in contact a halogenoaryl isocyanate and secondary aliphatic amine, usually in chemically equivalent amounts, and, if necessary, heating the mixture to reaction temperature. A suitable procedure consists in dropwise addition at a temperature from 0 to 100° C., preferably 25—75° C., of the halogenoaryl isocyanate to the secondary amine, preferably in a molal excess of 10—20% over the isocyanate employed, dissolved or suspended in an inert liquid media, for example, dry dioxane, dry benzene, and continuing the reaction until completed. Ordinarily, the reaction is complete in a relatively short time, usually two hours or less, after the reactants have been thoroughly mixed at the specified temperature. Two to twenty parts of inert reaction media to each part of secondary aliphatic amine will ordinarily be satisfactory.

The urea obtained can be isolated by crystallization, extraction or other suitable means, depending to a large extent on whether the urea is solid or liquid and the nature of the reaction media employed. For example, when dioxane or other inert water-soluble reaction media is employed, solid ureas of a satisfactory degree of purity can usually be isolated by cooling or diluting the reaction mixture with water and removing the precipitated urea by filtration. If necessary, further purification can be achieved through recrystallization, in most instances from dioxane or benzene or a mixture of these solvents.

The halogenoaryl isocyanates used as starting materials can be prepared by the general method described in the literature [Vittenet, Bull. Soc. Chim. [3] [21, 586,954 (1899); *Organic Syntheses*, Collective, Vol. II, page 453] which consists in heating the halogenoaryl carbamyl chloride first obtained by treating the halogenoaryl primary amine with phosgene at ordinary temperature in the presence of an appropriate solvent or reaction media. The invention is illustrated in greater detail by the following examples in which parts, unless otherwise specified, are by weight.

EXAMPLE 1.

To a stirred solution of 36.5 parts of diethylamine in 258 parts of dry dioxane was added dropwise 77 parts of *p*-chlorophenyl isocyanate with the evolution of heat. The temperature was maintained at 20—30° C. After cooling the reaction mixture to 15° C., the solid, white crystalline product which separated was filtered and dried in a vacuum (30 mm.) oven at 50° C. The 3-(*p*-chlorophenyl)-1,1-diethylurea thus obtained melted at 116.5—117° C. and amounted to 80 parts. A second crop of the above urea, melting point 116—117° C., was obtained by pouring the filtrate into 500 parts of water, and filtering and drying the resulting precipitate. The combined yield amounted to 98% of the theory.

Annal. Calc'd for $C_{11}H_{15}ClN_2O$: C, 58.40; H, 6.68. Found: C, 58.19, 58.45. H, 6.73, 6.72.

EXAMPLE 2.

A solution of 500 parts of *p*-chlorophenyl isocyanate in 102 parts of dry dioxane was added dropwise to a stirred solution of 262 parts of diethylamine in 507 parts of dry dioxane at a rate sufficient to produce refluxing from the heat liberated in this exothermic reaction. After the addition was completed, stirring was continued until the temperature of the reaction mixture had dropped to 25° C. The white crystals which had separated were filtered, washed with water and dried at 50° C. in a vacuum (30 mm.) oven. The first crop of 3-(*p*-chlorophenyl)-1,1-diethylurea melting at 116.5—117° C. amounted to 596 parts. A second crop of 116.8 parts of this urea melting point 115.5—116° C., was obtained on pouring the filtrate into 2,000 parts of water and filtering and drying the resulting precipitate.

EXAMPLE 3.

A solution of 19.5 parts of *m*-fluorophenyl isocyanate in 61 parts of dry dioxane was added dropwise to a stirred solution of 21 parts of di-*n*-butylamine and 51 parts of dry dioxane. There was an immediate liberation of heat. The rate of addition was controlled so that the temperature did not rise above 35° C. When the addition was completed, the reaction mixture was stirred for 20 minutes and then poured in 1,000 parts of water. The resulting precipitate was removed by filtration, washed with water and dried in a vacuum (30 mm.) oven at 25° C. The 3-(*m*-fluorophenyl)-1,1-di-*n*-butylurea thus obtained amounted to 36

parts (95% of the theoretical yield) and melted at 70.5—71° C.

Anal. Calc'd for $C_{15}H_{23}FN_2O$: C, 67.70; H, 8.70. Found: C, 67.74; H, 9.11.

EXAMPLE 4.

A solution of 57.5 parts of *p*-chlorophenyl isocyanate in 51 parts of dry dioxane was added slowly to 74 parts of dicyclohexylamine in 102 parts of dry dioxane while stirring, the temperature of this exothermic reaction being maintained at 25—35° C. The reaction mixture was stirred for one hour, after mixture of the reactants, and then poured into 1,000 parts of water. The resulting white 3-*p*-chlorophenyl) - 1,1 - dicyclohexylurea was filtered, washed and dried in a vacuum (30 mm.) oven at 50° C. It melted at 183—186° C. Recrystallization from hot benzene yielded 103 parts (86% of the theoretical yield) of white crystalline 3-(*p*-chlorophenyl)-1,1-dicyclohexylurea, melting point 184.5—185° C.

Anal. Calc'd. for $C_{19}H_{27}ClN_2O$: C, 68.25; H, 8.14. Found: C. 68.51; H, 8.09.

EXAMPLE 5.

A solution of 19.2 parts of *p*-chlorophenyl isocyanate and 51 parts of dry dioxane was slowly added at 25—35° C. to a stirred solution of 33 parts of di-*n*-octylamine in 102 parts of dry dioxane. Heat was liberated on mixing the reactants. After completion of the reaction, the mixture was poured into 1,000 parts of water, whereupon an oil separated. This oil was extracted with diethyl ether and the ether extract dried over anhydrous magnesium sulfate and filtered to remove the drying agent. The white solid remaining after evaporation of the ether was dried at 25° C. in a vacuum (30 mm.) oven. Forty-nine and five-tenths (49.5) parts of white 3-(*p*-chlorophenyl)-1,1-di-*n*-octylurea, melting point, 36—37° C., was thus obtained.

Anal. calc'd for $C_{23}H_{39}ClN_2O$: C, 70.00; H, 9.95. Found: C, 69.91; H, 10.10.

EXAMPLE 6.

o-Chlorophenyl isocyanate (30.6 parts) was added dropwise to a solution of 16 parts of diethylamine and 258 parts of dry dioxane with stirring. Heat was liberated on contact of the reactants and the temperature was maintained at 25—35° C. On pouring the reaction mixture into 500 parts of water, a light-colored oil separated. This oil was extracted with diethyl ether, and the ether extract was then dried over anhydrous magnesium sulfate. Distillation yielded a fraction (37 parts) of 3-(*o*-chlorophenyl)-1,1-diethylurea boiling at 137—139° C./0.5 mm.

Anal. Calc'd for $C_{11}H_{15}ClN_2O$: C, 58.35; H, 6.67. Found: C, 58.19; H, 6.86.

Additional examples of the new class of ureas prepared by the foregoing methods are given in the following Table:—

TABLE.

Name of Urea, $RNHCONR^1R^{11}$	Reactants: Halogenoaryl Isocyanate RNCO	Reactants: Secondary Aliphatic Amine $R^1R^{11}NH$
EXAMPLE 7.		
3-(*m*-fluorophenyl)-1,1-diethylurea m.p. 90.5—91.0° C., yield 87.5% Calc'd. for $C_{11}H_{15}FN_2O$: C, 62.90, H,7.20 Found: C, 62.89, H, 7.33	*m*-fluorophenyl	diethyl
EXAMPLE 8.		
3-(*o*-chlorophenyl)-1,1-dimethylurea m.p. 94.1—95.4° C., yield 89% Calc'd. for $C_9H_{11}ClN_2O$: Cl, 17, 87 Found: Cl, 17.90, 17.95	*o*-chlorophenyl	dimethyl

TABLE—*cont.*

Name of Urea, $RNHCONR^1R^{11}$	Reactants: Halogenoaryl Isocyanate RNCO	Reactants: Secondary Aliphatic Amine $R^1R^{11}NH$
EXAMPLE 9.		
3-(*o*-chlorophenyl)-1,1-diisopropyl-urea m.p. 75.0—75.5°C., yield 98% Calc'd. for $C_{13}H_{19}ClN_2O$: C, 61.40; H, 7.52 Found: C, 61.40; H, 7.59	*o*-chlorophenyl	diisopropyl
EXAMPLE 10.		
3-(*m*-chlorophenyl)-1,1-dimethylurea m.p. 144.3—144.8°C., yield 96.5% Calc'd. for $C_9H_{11}ClN_2O$: Cl, 17, 87 Found: Cl, 17.90, 17.97	*m*-chlorophenyl	dimethyl
EXAMPLE 11.		
3-(*m*-chlorophenyl)-1,1-diethylurea m.p. 89.5—90.0° C., yield 99% Calc'd. for $C_{11}H_{15}ClN_2O$: C, 58.35; H, 6.67 Found: C, 58.01; H, 6.50	*m*-chlorophenyl	diethyl
EXAMPLE 12.		
3-(*m*-chlorophenyl)-1,1-diisopropylurea m.p. 123.5—124.5° C., yield 100% Calc'd for $C_{13}H_{19}ClN_2O$: C, 61.40; H, 7.52 Found: C, 61.48; H, 7.34	*m*-chlorophenyl	diisopropyl
EXAMPLE 13.		
3-(*m*-chlorophenyl)-1,1-dicyclohexylurea m.p. 166.5—167.0° C., yield 100% Calc'd. for $C_{19}H_{27}ClN_2O$: C, 68.20; H, 8.14 Found: C, 68.13; H, 8.17	*m*-chlorophenyl	dicyclohexyl
EXAMPLE 14.		
3-(*p*-chlorophenyl)-1,1-dimethylurea m.p. 169.8—170.4° C., yield 85% Calc'd for $C_9H_{11}ClN_2O$: Cl, 17.90 Found: Cl, 17.83	*p*-chlorophenyl	dimethyl
EXAMPLE 15.		
3-(*p*-chlorophenyl)-1-methyl-1-ethylurea m.p. 149.0—149.5° C., yield 87%. Calc'd for $C_{10}H_{13}ClN_2O$: C, 56.50; H, 6.15 Found: C, 56.67; H, 6.03	*p*-chlorophenyl	methyl ethyl
EXAMPLE 16.		
3-(*p*-chlorophenyl)-1,1-diisopropylurea m.p. 152.4—153.2° C., yield 84% Calc'd for $C_{13}H_{19}ClN_2O$: Cl, 13.95 Found: Cl, 13.77	*p*-chlorophenyl	diisopropyl

TABLE—*cont.*

5 Name of Urea, $RNHCONR^1R^{11}$	Reactants: Halogenoaryl Isocyanate RNCO	Secondary Aliphatic Amine $R^1R^{11}NH$
EXAMPLE 17.		
3-(*p*-chlorophenyl)-1,1-di-*n*-butylurea m.p. 129.0—129.5° C., yield 100% Calc'd for $C_{15}H_{23}ClN_2O$: C, 63.75; H, 8.19 Found: C, 63.75; H, 8.32	*p*-chlorophenyl	di-*n*-butyl
EXAMPLE 18.		
3-(*p*-chlorophenyl)-1,1-diallylurea m.p. 77.5—78.0° C., yield 98% Calc'd for $C_{13}H_{15}ClN_2O$: C, 62.10; H, 6.01 Found: C, 62.37; H, 5.96	*p*-chlorophenyl	diallyl
EXAMPLE 19.		
3-(2,4-dichlorophenyl)-1,1-diethylurea m.p. 50—52.5° C., yield 84% Calc'd for $C_{11}H_{14}Cl_2N_2O$: Cl, 27.2 Found: Cl, 26.96	2,4-dichlorophenyl	diethyl
EXAMPLE 20.		
3-(2,4,6-trichlorophenyl)-1,1-diethylurea m.p. 151.5—152.0° C., yield 95% Calc'd for $C_{11}H_{13}Cl_3N_2O$: C, 44.70; H, 4.44 Found: C, 44.86; H, 4.70	2,4,6-trichlorophenyl	diethyl
EXAMPLE 21.		
3-(2,4,6-trichlorophenyl)-1,1-di-*n*-butylurea m.p. 88.5—89.2° C., yield 96% Calc'd. for $C_{15}H_{21}Cl_3N_2O$: C, 51.38; H, 6.02 Found: C, 51.10; H, 6.02	2,4,6-trichlorophenyl	di-*n*-butyl
EXAMPLE 22.		
3-(4-chloro-1-naphthyl)-1,1-dimethylurea m.p. 149.5—150.5° C., yield 98% Calc'd for $C_{13}H_{13}ClN_2O$: C, 62.80; H, 5.27 Found: C, 62.98; H, 5.39	4-chloro-1-naphthyl	dimethyl
EXAMPLE 23.		
3-(4-chloro-1-naphthyl)-1,1-diethylurea m.p. 145.5—146.0° C., yield 96.5% Calc'd for $C_{15}H_{17}ClN_2O$: C, 65.15; H, 6.20 Found: C, 65.29; H, 6.06	4-chloro-1-naphthyl	diethyl
EXAMPLE 24.		
3-(*p*-bromophenyl)-1,1-diethylurea m.p. 121° C., yield 81% Calc'd. for $C_{11}H_{15}BrN_2O$: C, 48.75; H, 5.58 Found: C, 48.85; H, 5.57	*p*-bromophenyl	diethyl

TABLE—*cont.*

Name of Urea, RNHCONR^{1}R^{11}	Reactants: Halogenoaryl Isocyanate RNCO	Reactants: Secondary Aliphatic Amine R^{1}R^{11}NH
EXAMPLE 25.		
3-(*p*-bromophenyl)-1,1-di-*n*-butylurea m.p. 123° C., yield 95% Calc'd for $C_{15}H_{23}BrN_2O$: C, 55.20; H, 7.08 Found: C, 55.00; H, 6.97	*p*-bromophenyl	di-*n*-butyl
EXAMPLE 26.		
3-(*p*-iodophenyl)-1,1-dimethylurea m.p. 185.5—186.0° C., yield 95% Calc'd. for $C_9H_{11}IN_2O$: C, 37.22; H, 3.82 Found: C, 37.49; H, 3.99	*p*-iodophenyl	dimethyl
EXAMPLE 27.		
3-(*p*-iodophenyl)-1,1-diethylurea m.p. 118.0—118.5° C., yield 99% Calc'd. for $C_{11}H_{15}IN_2O$: C, 41.50; H, 4.75 Found: C, 41.68; H, 4.84	*p*-iodophenyl	diethyl
EXAMPLE 28.		
3-(*p*-iodophenyl)-1,1-di-*n*-butylurea m.p. 110—111° C., yield 98% Calc'd for $C_{15}H_{23}IN_2O$: C, 48.15; H, 6.18 Found: C, 48.38; H, 6.37	*p*-iodophenyl	di-*n*-butyl

This invention is not limited to the specific ureas described in the Examples but embraces broadly the tri-substituted ureas having but one halogenoaryl radical nuclearly bonded through carbon to one of the urea nitrogen atoms which nitrogen atom also bears a hydrogen atom, and two monovalent aliphatic hydrocarbon radicals, i.e., hydrocarbon radicals of the acyclic and alicyclic series, on the other urea nitrogen atom. The halogenoaryl radicals can be any of the monovalent halogenated aromatic hydrocarbon radicals but, because of availability of the preparative raw materials, those ureas having halogenated aryl radicals containing one to two nuclei such as halogenated phenyl, tolyl, xylyl, xenyl, naphthyl, methylnaphthyl, are preferred. Particularly preferred ureas are those having a halogenophenyl radical containing from one to three halogen substituents. The halogens can be fluorine, chlorine, bromine or iodine as shown by the examples.

The two monovalent aliphatic hydrocarbon radicals attached to the same nitrogen atom of the new ureas of the invention are preferably saturated aliphatic hydrocarbon radicals and can be the same or different radicals of from 1 to 18 or more carbon atoms, including in addition to those illustrated in the Examples oleyl, dodecyl, octadecyl, methylcyclohexyl, decahydronaphthyl.

Because of their higher activity as plant growth regulants and the lower cost, in general, of the secondary aliphatic amines from which the ureas are prepared, the preferred ureas of the invention are those in which the monovalent aliphatic hydrocarbon radicals are from one to eight carbon atoms, and preferably saturated aliphatic hydrocarbon radicals. Those ureas wherein the monovalent aliphatic hydrocarbon radicals are acyclic, especially alkyl, and contain from one to four carbon atoms are particularly preferred.

The new ureas of the invention are,

for the most part, white crystalline and practically odorless solids which are insoluble, or only slightly soluble, in water and cold benzene and, in general, appreciably soluble in dioxane, acetone, ethyl acetate, ethanol and hot benzene. Those ureas containing long chain aliphatic hydrocarbon groups are usually oils and are also appreciably oil-soluble, e.g., in the mineral oils.

They have plant growth regulating properties and are especially useful in herbicidal applications, being unusually active herbicides particularly against the hitherto highly resistant grasses such as quack, nut and Bermuda grasses.

For example, a one per cent. acetone-water (50/50) solution of the urea described in Example I, i.e., 3-(*p*-chlorophenyl)-1,1-diethylurea, was sprayed on the aerial parts of a healthy stand of quack grass. At the end of three weeks, this highly resistant grass was killed and after two months, no resprouting from the sod had occurred. Similar results were obtained with 3-(*p*-chlorophenyl)-1,1-dimethylurea.

A three per cent. acetone solution of 3 - (*p*-chlorophenyl)-1,1-diethylurea was sprayed on the aerial parts of nut grass and Bermuda grass. At the end of three weeks, these grasses were dead and after two months, no resprouting from the sod had occurred. In contrast, a three per cent. acetone-water (50/50) solution of one of the current commercial herbicides, sodium trichloroacetate, failed to kill either of these grasses when sprayed in a similar manner.

The new ureas of this invention are useful chemical intermediates. They may be nitrated, sulphonated or converted to the N-methylol derivatives which are modifiers for urea-formaldehyde polymers. Moreover certain of these new ureas also possess insecticidal and bacteriostatic properties.

What we claim is:—

1. An N,N^1-substituted urea having a hydrogen atom directly attached to a urea nitrogen atom which is bonded to a nuclear carbon of a halogenoaryl radical and having the other urea nitrogen atom joined to two monovalent aliphatic hydrocarbon radicals.

2. An N,N^1-substituted urea having a hydrogen atom directly attached to a urea nitrogen atom which is bonded to a nuclear carbon of a halogenophenyl radical and having the other urea nitrogen atom joined to two monovalent aliphatic hydrocarbon radicals.

3. An N,N^1-substituted urea having a hydrogen atom directly attached to a urea nitrogen atom which is bonded to a nuclear carbon of a halogenophenyl radical and having the other urea nitrogen atom joined to two monovalent acyclic aliphatic hydrocarbon radicals.

4. An N,N^1-substituted urea having a hydrogen atom directly attached to a urea nitrogen atom which is bonded to a nuclear carbon of a halogenophenyl radical and having the other urea nitrogen atom joined to two monovalent alkyl radicals.

5. The N,N^1-substituted urea, 3-(*p*-chlorophenyl)-1,1-diethylurea.

6. The N,N^1-substituted urea, 3-(*p*-chlorophenyl)-1,1-dimethylurea.

7. The N,N^1-substituted urea, 3-(*m*-chlorophenyl)-1,1-dimethylurea.

8. An N,N^1-substituted urea according to claim 4, wherein the halogenophenyl radical contains from one to three chlorine substituents and the alkyl radicals each contain from one to four carbon atoms.

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* C L M S *

for the most part, white crystalline and practically odorless solids which are insoluble, or only slightly soluble, in water and cold benzene and, in general, appreciably soluble in dioxane, acetone, ethyl acetate, ethanol and hot benzene. Those ureas containing long chain aliphatic hydrocarbon groups are usually oils and are also appreciably oil-soluble, e.g., in the mineral oils.

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3. An N,N^1-substituted urea having a hydrogen atom directly attached to a urea nitrogen atom which is bonded to a nuclear carbon of a halogenophenyl radical and having the other urea nitrogen atom joined to two monovalent acyclic aliphatic hydrocarbon radicals.

4. An N,N^1-substituted urea having a hydrogen atom directly attached to a urea nitrogen atom which is bonded to a nuclear carbon of a halogenophenyl radical and having the other urea nitrogen atom joined to two monovalent alkyl radicals.

5. The N,N^1-substituted urea, 3-(*p*-chlorophenyl)-1,1-diethylurea.

6. The N,N^1-substituted urea, 3-(*p*-chlorophenyl)-1,1-dimethylurea.

7. The N,N^1-substituted urea, 3-(*m*-chlorophenyl)-1,1-dimethylurea.

8. An N,N^1-substituted urea according to claim 4, wherein the halogenophenyl radical contains from one to three chlorine substituents and the alkyl radicals each contain from one to four carbon atoms.

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