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3,663,594
N-SUBSTITUTED ARYL CARBAMATES

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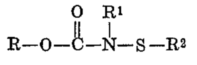
No Drawing. Continuation-in-part of application Ser. No. 764,299, Oct. 1, 1968. This application Sept. 4, 1969, Ser. No. 855,421
Int. Cl. C07c *149/40*
U.S. Cl. 260—470 5 Claims

ABSTRACT OF THE DISCLOSURE

Insecticidal carbamates of the formula



$$\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{R^1}{\overset{|}{N}}{-}S{-}R^2}$$

wherein R is aryl or aralkyl of 6 to 20 carbon atoms, R^1 is H or alkyl of 1 to 6 carbon atoms, and R^2 is alkyl of 1 to 10 carbon atoms or monocyclic aryl of 6 to 12 carbon atoms substituted with 0 to 2 alkyl in which the total number of carbon atoms in the alkyl groups combined is 1 to 6, 0 to 2 halogens of atomic number 17 to 35 or 0 to 2 trifluoromethyl.

CROSS REFERENCE TO RELATED APPLICATIONS

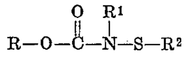
This application is a continuation-in-part of application Ser. No. 764,299, filed Oct. 1, 1968, now abandoned.

FIELD OF INVENTION

This invention is directed to novel aryl carbamates and their use as insecticides. More particularly, it is directed to a group of novel carbamates in which a proton of the nitrogen atom of the carbamyl group is replaced with an organic moiety derived from a sulfenyl halide.

DESCRIPTION OF INVENTION

The unique carbamates of this invention are represented by the formula:



$$\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{R^1}{\overset{|}{N}}{-}S{-}R^2}$$

wherein R is aryl or aralkyl of 6 to 20 carbon atoms, R^1 is hydrogen or alkyl of 1 to 6 carbon atoms and R^2 is alkyl of 1 to 10 carbon atoms or monocyclic aryl of 6 to 12 carbon atoms substituted with 0 to 2 alkyl in which the total number of carbon atoms in the alkyl groups combined is 1 to 6, halogen of atomic number 9 to 35, i.e., F, Cl, Br or trifluoromethyl. As used herein the term "aryl" means a radical derived either from benzene or a compound containing the benzene nucleus.

R in the above formula preferably contains 6 to 20 carbon atoms and is monocyclic or bicyclic aryl or aralkyl substituted with 0 to 2 halogen of atomic number 17 to 35, alkyl of 1 to 6 carbon atoms, alkoxy of 1 to 3 carbon atoms or alkylthio wherein the alkyl contains 1 to 3 carbon atoms; or 0 to 1 dialkylamino in which the alkyl groups contain individually 1 to 3 carbon atoms. The total number of substituents on these monocyclic or fused rings will be no more than 3. They may be the same or different.

Compounds in which R is benzyl, mono- or dichlorobenzyl, naphthyl, 3-alkylphenyl in which the alkyl is of 3 to 6 carbon atoms, 3,5-dialkyl-4-dialkylaminophenyl in which each alkyl is of 1 to 3 carbon atoms, alkoxyphenyl in which the alkyl is of 1 to 3 carbon atoms, 3-alkyl-4-alkylthiophenyl in which the alkyls individually contain 1 to 3 carbon atoms, 3,5-dialkyl-4-alkylthiophenyl in which the alkyls individually contain 1 to 3 carbon atoms, 3-alkyl-4-dialkylaminophenyl in which the alkyls individually contain 1 to 3 carbon atoms, 3-alkyl-4-alkoxyphenyl in which the alkyls individually contain 1 to 3 carbon atoms, 3,5-dialkyl-4-alkoxyphenyl in which the alkyls individually contain 1 to 3 carbon atoms or alkylthiophenyl in which the alkyl is of 1 to 3 carbon atoms; R^1 is methyl and R^2 is methyl, 4-chlorophenyl, tolyl or phenyl are particularly preferred.

Examples of radicals which R may represent are phenyl, 3-n-propylphenyl, 3-isopropylphenyl, 3-sec.butylphenyl, 3-tert.butylphenyl, 3-methyl-5-sec.butylphenyl, 3-propyl-5-sec.amylphenyl, 3-dodecylphenyl, 3-tetradecylphenyl, 3-amylphenyl, 3-hexylphenyl, benzyl, 4-tolyl, 3-tolyl, 3-methyl-5-hexylphenyl, 3,5-xylyl, 4-ethylphenyl, 4-cumyl, 4-butylbenzyl, 2,4-dichlorophenyl, 2,4,6-trichlorophenyl, 4-bromophenyl, 3,5-dibromophenyl, 2-chloro-5-tert.butylphenyl, naphthyl, 4-indanyl, 5-indanyl, 2-chloro-5-sec.amylphenyl, 5-chloronaphthyl, 4-methylthio-3-tolyl, 3-propylthiophenyl, 2-isopropoxyphenyl, 3,5-di(methylthio)phenyl, 2-ethoxyphenyl, 4-methoxyphenyl, 2-isopropoxy-3,5-dichlorophenyl, 4-dimethylamino-3-tolyl, 4-methylthio-3,5-xylyl, 4-dimethylamino-3,5-xylyl, 5-methoxynaphthyl, 2,4-dichloronaphthyl, 5,6,7,8-tetrahydronaphthyl, 4-propylthiophenyl, 5-bromonaphthyl, 4-diethylamino-3-tolyl, 4-dipropylamino-3-tolyl, 4-diethylaminophenyl, 2-chloro-4-dimethylaminophenyl and 4-methylethylamino-3,5-xylyl.

The alkyl groups which R^1 may represent include methyl, ethyl, isopropyl, n-propyl, butyl, isobutyl, amyl and hexyl.

R^2 in the above formula may represent methyl, ethyl, propyl, butyl, sec.butyl, amyl, hexyl, heptyl, decyl, phenyl, benzyl, 4-chlorobenzyl, 4-ethylbenzyl, 2-butylbenzyl, 2,4-dichlorophenyl, 2-bromophenyl, 3-chlorophenyl, 4-trifluoromethylbenzyl, 4-trifluoromethylphenyl, 3,5-dibromophenyl, 3-trifluoromethylphenyl, 4-trifluoromethyl-2-tolyl, tolyl, xylyl, 4-propyl-2-tolyl, 4-ethylphenyl, 2-ethylphenyl, 4-cumyl, trichlorovinyl, tribromovinyl, 1-chloro-2,2-dibromovinyl and the like.

Representative carbamates of the above formula are:

N-methylthiophenyl carbamate,
N-isopropylthio-N-methylbenzyl carbamate,
N-amylthio-N-butyl-3-isopropylphenyl carbamate,
N-ethyl-N-octylthio-3-sec.amylphenyl carbamate,
N-methyl-N-decylthio-4-tolyl carbamate,
N-methyl-N-trichlorovinylthio-3-sec.amylphenyl carbamate,
N-butyl-N-tribromoamylthio-4-dimethylamino-3,5-xylyl carbamate,
N-methylthio-N-methyl-2,4-dichlorophenyl carbamate,
N-hexylthio-N-hexyl-2,4,5-trichlorophenyl carbamate,
N-ethylthio-4-bromophenyl carbamate,
N-methylthio-N-methyl-2-chloro-3-isopropylphenyl carbamate,
N-octylthio-N-propyl-3-amyl-4-chlorophenyl carbamate,
N-decylthio-N-methyl-4-dimethylaminophenyl carbamate,
N-methylthio-4-dipropylamino-3,5-xylyl carbamate,
N-ethylthio-N-methyl-2-chloro-4-dimethylaminophenyl carbamate,
N-phenylthiophenyl carbamate,
N-phenylthio-N-methyl-benzyl carbamate,
N-phenylthionaphthyl carbamate,
N-methylthio-N-methylnaphthyl carbamate,
N-phenylthio-N-propyl-4-tolyl carbamate,
N-butyl-N-phenylthio-3-isopropylphenyl carbamate,
N-ethyl-N-phenylthio-4-dimethylamino-3,5-xylyl carbamate,
N-methyl-N-phenylthio-2,4-dibromophenyl carbamate,
N-ethyl-N-methylthio-4-bromophenyl carbamate,
N-4-chlorophenylthio-4'-methoxyphenyl carbamate,

N-4-chlorophenylthio-N-methyl-2-isopropoxyphenyl carbamate,
N-methyl-N-4-tolylthio-2'-isopropoxyphenyl carbamate,
N-4-bromophenylthio-N-ethyl-4'-dipropylamino-3,5-xylyl carbamate,
N-ethylthio-3,5-xylyl carbamate,
N-methyl-N-phenylthio-3-methyl-4-methylthiophenyl carbamate,
N-3,4-dichlorophenylthio-N-methyl-2'-propylthiophenyl carbamate,
N-methylthio-N-propyl-4-ethylthio-3-tolyl carbamate,
N-4-cumylthio-N-methyl-3'-ethyl-4'-dimethylaminophenyl carbamate,
N-2-methyl-4-chlorophenylthio-N-propyl-3',5'-dipropylphenyl carbamate,
N-butyl-N-4-trifluoromethylphenylthio-5'-bromo-1'-naphthyl carbamate,
N-4-chlorophenylthio-4'-chloro-1'-naphthyl carbamate,
N-butyl-N-4-tolylthio-5'-indanyl carbamate,
N-hexylthio-N-methyl-5'-propoxy-1-naphthyl carbamate,
N-methyl-N-phenylthio-2,4-dichloro-1-naphthyl carbamate,
N-butyl-N-4-clorophenylthio-1'-naphthyl carbamate,
N-methylthio-N-methyl-1-naphthyl carbamate,
N-3,5-dichlorophenylthio-N-methyl-5'-methylthio-1'-naphthyl carbamate,
N-methyl-N-4-trifluoromethylphenylthio-5'-ethyl-1'-naphthyl carbamate,
N-4-chlorophenylthio-N-methyl-4'-indanyl carbamate and
N-methylthio-N-propyl-1'-(5',6'7',8-tetrahydronaphthyl) carbamate.

Compounds of this invention may be made by reacting an aryl carbamate with a sulfenyl halide. The reaction proceeds according to the equation:

$$R-O-\overset{O}{\overset{\|}{C}}-\overset{R^1}{\overset{|}{N}}-M + XSR^2 \longrightarrow R-O-\overset{O}{\overset{\|}{C}}-\overset{R^1}{\overset{|}{N}}-SR^2 + MX$$

wherein X is halogen of atomic number 17 to 35, M is hydrogen or an alkali metal cation and R, R^1 and R^2 are as defined previously. This reaction may be carried out in pyridine, dimethylformamide with or without an acid acceptor or other solvents such as methylene chloride, chloroform, acetonitrile and dimethoxyethane using an acid acceptor. Acid acceptors which may be used with dimethylformamide and these other solvents include pyridine, alkylpyridines, quinoline and similar heterocyclic bases. Pyridine is a preferred acid acceptor. When pyridine is used alone it acts both as a diluent and acid acceptor. The preferred medium for carrying out this reaction is dimethylformamide with pyridine as an acid acceptor.

TABLE I

Ex. No.	Compound	Melting point, ° C.	Element analysis, percent N Calc.	N Found	S Calc.	S Found	Cl Calc.	Cl Found
2	N-p-chlorophenylthio-N-methyl-1-naphthyl carbamate	109-114			9.32	8.98	10.32	9.72
3	N-phenylthio-N-methyl-1-naphthyl carbamate	66-70	4.53	4.43	10.35	9.88		
4	N-methylthio-N-methyl-1-naphthyl carbamate	Liquid	5.66	5.49	12.95	12.72		
5	N-p-tolythio-N-methyl-1-naphthyl carbamate	96-99	4.33	4.28	9.90	9.81		
6	N-phenylthio-N-methyl-m-sec.butylphenyl carbamate	Liquid	4.44	4.64	10.18	10.45		
7	N-p-chlorophenylthio-N-methyl-m-sec.butylphenyl carbamate.	do			9.15	9.16	10.15	10.38
8	N-methylthio-N-methyl-m-sec.butylphenyl carbamate	do	5.53	5.50	12.65	10.58		
9	N-methylthio-N-methyl-m-2-pentylphenyl carbamate	do	5.24	5.00	11.97	10.67		
10	N-p-tolylthio-N-methyl-m-sec.butylphenyl carbamate	do	4.25	4.17	9.72	8.99		
11	N-p-chlorophenylthio-N-methylphenyl carbamate	76-78			10.81	10.92	12.02	12.12
12	N-methyl-N-p-chlorophenylthio-4-dimethylamino-3,5-xylyl carbamate.	Liquid			9.02	9.10	9.72	10.02
13	N-methyl-N-p-chlorophenylthio-o-isopropoxyphenyl carbamate.	do			9.10	8.58	10.10	9.52
14	N-methyl-N-trichlorovinylthio-1-naphthyl carbamate	do			8.83	8.90	29.30	29.58
15	N-methyl-N-p-chlorophenylthio-3,4-dichlorobenzyl carbamate.	do			8.41	9.00	27.9	28.65
16	N-methyl-N-p-chlorophenylthio-p-chlorobenzyl carbamate	do			9.35	9.61	20.8	21.08

The pressures and temperatures at which this reaction may be carried out are not critical. Temperatures ranging from ambient to about 60° C. will normally be used. However, lower temperatures or higher temperatures up to the decomposition temperature of the reactants and product may be used. For convenience, the pressure will usually be atmospheric or autogenous. However, subatmospheric or higher superatmospheric pressures may be used. The reaction will normally be complete within about 1 to 4 hours.

The carbamate reactant in the above equation may, and usually will, represent a commercial carbamate insecticide. Conventional methods for preparing such carbamates either in situ or beforehand may be used. Such reactants are disclosed in U.S. Pat. Nos. 3,062,707; 3,062,864; 3,062,865; 2,903,478; 3,084,096; 3,203,853; 3,167,472 and 3,256,145, British Pat. No. 982,235 and Pesticide Index, 3rd ed. D. E. H. Frear (1965).

EXAMPLES

The following examples illustrate methods which may be used to prepare the carbamates of this invention. These examples are in no way intended to limit the invention described herein. Unless otherwise indicated, percentages are by weight.

Example 1

5.5 g. of m-sec.amylphenyl-N-methyl carbamate in 40 ml. of dimethylformamide were mixed with 2.2 g. of pyridine in a vessel. To this mixture 4.9 g. of p-chlorophenylsulfenyl chloride was added. The combined mixture was stirred at ambient temperature for 2 hours, added to 500 ml. of ice water and the mixture was extracted with ethyl ether. The extract was washed with sodium bicarbonate and water and then dried. The ether was then removed to give an oily product. This oily product was chromatographed on silica gel with hexane and 5% ethyl ether in hexane. About 7 g. of N-p-chlorophenylthio-N-methyl-m-sec. amylphenyl carbamate was recovered. This material, an oil, had the following S and Cl analyses: S: calculated 8.80%; found 8.94%; Cl: calculated 9.75%; found 9.08%.

Other carabamates of this invention were made by the general technique described in Example 1. These carbamates along with their physical analyses are reported in Table I.

Utility

Carbamates of this invention may be used to control insects such as aphids, cockroaches, cabbage loopers, dock beetles, mosquitoes and the like. Insecticidal quantities of one or more of the carbamates are applied directly to the insect or their environment for such control. In many instances the carbamates of this invention exhibit significantly better insecticidal activity than the carbamate from which they were derived. The carbamates of this invention in which R represents an aralkyl group, especially those in which the aryl is nuclearly substituted with halogens, are herbicidal in both pre- and post-emergence application against weed grasses such as watergrass and crabgrass and broadleaved weeds such as mustard, pigweed and lamb's-quarters.

The following example illustrates the insecticidal activity of N-p-chlorophenylthio-N-methyl-1-naphthyl carbamate and its superiority as an aphicide over N-methyl-1-naphthyl carbamate.

Example 17

Each compound was dissolved in a suitable organic solvent and then diluted to a 1.9 p.p.m. concentration in water containing a small amount of surfactant. 4 replicate cucumber leaf sections infested with at least 20 cotton aphids (*Aphis gossypii* Glover) per section were dipped into this mixture. Excess mixture was drained from each section. Each section was then placed on a dish which was in turn placed in an incubator for 24 hrs. Mortality counts on 20 randomly selected aphids were then made on each replicate. A percent mortality based on the average of the 4 replicates was determined from these counts.

The mixture containing N-p-chlorophenylthio-N-methyl-1-naphthyl carbamate gave 100% mortality; whereas that containing N-methyl-1-naphthyl carbamate gave only 23.5% mortality.

Example 18

N-phenylthio-N-methyl-1-naphthyl carbamate and N-methyl-thio-N-methyl-1-naphthyl carbamate were tested at 0.98 p.p.m. and 1.9 p.p.m. respectively as aphicides by the general method described in Example 17.

N-phenylthio-N-methyl - 1 - naphthyl carbamate gave 98.5% mortality and N-methylthio-N-methyl-1-naphthyl carbamate gave 92.5% control.

Example 19

N-p-tolythio-N-methyl-1-naphthyl carbamate and N-p-chlorophenylthio-N-methyl-1-naphthyl carbamate were tested against dock beetle larvae (*Gastrophysa cyanea* Melsh.) by the following method. This method is designed to evaluate the extent to which leaves are protected from insect feeding.

Each test compound was dissolved in a suitable organic solvent and then diluted to a concentration of 15.6 p.p.m. with water containing a small amount of surfactant. 4 replicate sets of 20 mm. leaf disks (5 for each set) were cut from dock weed leaves. Each set of disks was dipped in the above-described mixture of the test compound, drained and placed in a dish. Each set was then dried of excess moisture and infested with 5 larvae. The sets were then incubated for 24 hrs. After this period, mortality counts were made on each replicate and a percent mortality based on the average of these counts was made. N-p-tolylthio-N-methyl - 1 - naphthylcarbamate provided 100% control; and N-p-chlorophenylthio - N - methyl-1-naphthyl carbamate gave 90% control.

Example 20

N-p-tolylthio-N-methyl - 1 - naphthyl carbamate was tested on cabbage looper larvae (*Trichoplusia ni*) at a concentration of 500 p.p.m. by the general method described in Example 19, using cucumber leaf disks. It gave 96% control.

Example 21

Representative carbamates of this invention were tested for activity against nymphal American cockroaches (*Periplaneta americana* L.) by the following method. Each test compound was dissolved in a suitable organic solvent and then diluted in water such that a 2.5 microliter dose gave 1250 ng. per insect. A random mixture of male and female roaches was anesthetized with CO_2 and 3 replicates of 10 roaches each were sorted out and placed in corrugated cardboard trays. A 2.5 microliter dose of the test compound mixture was applied to the abdomen of each roach with a micrometer syringe. Each replicate was placed in a recovery cage. After 24 hrs. mortality counts were made on each replicate and a percent mortality based on the average of these counts was made. The results of these tests appear below in Table II.

TABLE II

Compound:	Percent mortality
N - p - chlorophenylthio-N-methyl-m-sec.butylphenyl carbamate	70
N - phenylthio - N - methyl-m-sec.butylphenyl carbamate	78
N - methylthio - N - methyl-m-sec.butylphenyl carbamate	100
N - methylthio - N - methyl-m-2-pentylphenyl carbamate	100
N-methylthio-N-methyl-1-naphthyl carbamate	96

Example 22

Carbamates of this invention in which R represents m-alkylphenyl, R^1 is methyl and R^2 is phenyl optionally substituted with up to 2 halogens of atomic number 17 to 35 have shown excellent activity against mosquito larvae and adult mosquitoes. Representative carbamates of this type were tested as culicides against *Aedes. aegypti* 4th stage larvae by the following method:

A standard acetone solution of the test carbamate was prepared along with 3 replicate cups each filled with 100 ml. H_2O containing 10 larvae. Enough carbamate-acetone solution was mixed into each cup to give a desired carbamate concentration in the 100 ml. H_2O. Immediately after this mixing the cups were covered and placed in a controlled environment at 80° F. 48 hrs. thereafter mortality readings were taken. The percent mortality, based on the averages of the 3 replicates, are reported in Table III.

TABLE III

Compound	Concentrate (p.p.m.)	Percent mortality
N-phenylthio-N-methyl-m-sec.-butylphenyl carbamate	0.25 0.05	100 100
N-p-chlorophenylthio-N-methyl-m-sec. butylphenyl carbamate	0.05	10
N-p-chlorophenylthio-N-methyl-m-2-pentylphenyl carbamate	0.05	7

Mammalian toxicity tests also indicate that the carbamates of this invention are significantly less toxic than their precursors. For instance, standard oral mammalian toxicity tests on rats showed that the N-methylthio, N-phenylthio and N-4-chlorophenylthio derivatives of 3-sec.butylphenyl-N-methyl carbamate were about 2 to 4 times less toxic than 3 - sec.butylphenyl-N-methyl carbamate.

As illustrated above, insecticidal dosages of carbamates of this invention are effective for controlling a variety of arthropodal pests. For application to such insect pests one or more of these carbamates may, in general, be formulated with the same materials and by the same techniques used to formulate the carbamates from which they are derived. Liquid formulations of the carbamates of this invention will contain one or more suitable solvents such as hydrocarbon solvents and polar solvents and one or more surface active agents. The surface active agent will desirably be nonionic. It permits the formulation to be readily dispersed in water for field use. Such liquid formulations may be applied as sprays or gas propelled sprays. Solid formulations of the normally solid carbamates of this invention may be made by mixing one or more of them with a solid diluent such as clay, talc, diatomaceous earth and the like. The normally liquid carbamates may be sprayed on absorbent solid diluents to form granular or dust compositions. These insecticidal compositions may also contain other compatible pesticides, fillers, stickers, adjuvants, stabilizers, synergists and the like.

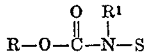
Certain carbamates of this invention such as the chlorinated benzyl carbamates are useful as herbicides in pre- and post-emergence applications. For pre-emergence control of undesirable vegetation these carbamates will be applied in herbicidal quantities to the environment, e.g., soil infested with seeds and/or seedlings of such vegetation. Such application will inhibit the growth of or kill the seeds, germinating seeds and seedlings. They are applied directly to the foliage and other plant parts in post-emergence applications. They are effective against weed grasses such as watergrass, crabgrass and wild oats as well as broadleaved weeds such as mustard, pigweed and lamb's-quarters.

The amount of carbamate administered will vary with the particular plant part or plant growth medium which is to be contacted, the general location of application, i.e., sheltered areas such as greenhouses as compared to exposed areas such as fields, as well as the desired type of control. For pre-emergent control of most plants dosages in the range of about 0.5 to 20 lbs. per acre will be used. Such administration will give a concentration of about 2 to 80 p.p.m. carbamate distributed throughout 0.1 acre-foot. For post-emergence application, such as foliar spray application, compositions containing about 0.5 to 8 lbs. carbamate per 100 gal. spray will be used. Such application is equivalent to about 0.5 to 20 lbs. carbamate per acre.

The herbicidal compositions of this invention comprise a herbicidal amount of one or more of the above described carbamates intimately admixed with a biologically inert carrier. The carrier may be a liquid diluent such as water or acetone or a solid. The solid may be in the form of dust, powder or granules. These compositions will also usually contain adjuvants such as a wetting or dispersing agent to facilitate their penetration into the plant growth media or plant tissue and generally enhance their effectiveness. These compositions may also contain other pesticides, stabilizers, conditioners, fillers and the like.

What is claimed is:

1. Carbamates of the formula



$$R-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{R^1}{|}}{N}-S-R^2$$

wherein R has 6 to 20 carbon atoms and is monocyclic or bicyclic aryl or aralkyl substituted with 0 to 2 halogens of atomic number 17 to 35, 0 to 2 alkyl of 1 to 6 carbon atoms, 0 to 2 alkoxy of 1 to 3 carbon atoms or 0 to 2 alkylthio in which the alkyl is of 1 to 3 carbon atoms, or 0 to 1 dialkylamino in which the alkyl groups individually contain 1 to 3 carbon atoms, with the proviso that the total number of substituents is not greater than 3, R^1 is hydrogen or alkyl of 1 to 6 carbon atoms, and R^2 is monocyclic aryl of 6 to 12 carbon atoms substituted with 0 to 2 alkyl in which the total number of carbon atoms in the alkyl groups combined is 1 to 6, 0 to 2 halogens of atomic number 9 to 35 or 0 to 2 trifluoromethyl.

2. The carbamates of claim **1** wherein R^1 is methyl.

3. The carbamates of claim **1** wherein R is naphthyl, 3-alkylphenyl in which the alkyl is of 3 to 6 carbon atoms, alkoxyphenyl in which the alkyl is of 1 to 3 carbon atoms, 3-alkyl-4-alkylthiophenyl in which the alkyls individually contain 1 to 3 carbon atoms, 3,5-dialkyl-4-alkylthiophenyl in which the alkyls individually contain 1 to 3 carbon atoms, 3-alkyl-4-dialkylaminophenyl in which the alkyls individually contain 1 to 3 carbon atoms, 3-alkyl-4-alkoxyphenyl in which the alkyls individually contain 1 to 3 carbon atoms, 3,5-dialkyl-4-alkoxyphenyl in which the alkyls individually contain 1 to 3 carbon atoms, alkylthiophenyl in which the alkyl is of 1 to 3 carbon atoms, or 3,5-dialkyl-4-dialkylaminophenyl in which each alkyl is of 1 to 3 carbon atoms, R^1 is methyl and R^2 is 4-chlorophenyl, tolyl or phenyl.

4. The carbamates of claim **1** wherein R^2 is phenyl substituted with 0 to 2 alkyl groups in which the total number of carbon atoms in the alkyl groups is 1 to 6, 0 to 2 halogens of atomic number 9 to 35 or 0 to 2 trifluoromethyl.

5. The carbamate of claim **1** wherein R is 3-sec.butylphenyl, R^1 is methyl and R^2 is phenyl or 4-chlorophenyl.

References Cited

UNITED STATES PATENTS

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1,493,581 9/1967 France.

LORRAINE A. WEINBERGER, Primary Examiner

J. F. TERAPANE, Assistant Examiner

U.S. Cl. X.R.

71—98; 260—479 C; 424—300

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,663,594 Dated May 16, 1972

Inventor(s) Melancthon S. Brown and Gustave K. Kohn

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

Col. 3 (Table I, Ex. 5), "tolythio" should read --tolylthio--.

Col. 4, line 36, "9.08%" should read --9.80%--.

Col. 4 (Table I, Ex. 16), "21.08" should read --21.0--.

Col. 5, line 32, "tolythio" should read --tolylthio".

Col. 6, line 38, "1^0" should read --100--.

Col. 6, line 40, "7" should read --70--.

Signed and sealed this 29th day of August 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents