

PATENT SPECIFICATION

NO DRAWINGS

1306334

- (21) Application No. 30415/71 (22) Filed 29 June 1971
 (31) Convention Application No. P 20 32 076.7
 (32) Filed 29 June 1970
 (31) Convention Application No. P 21 10 056.1
 (32) Filed 3 March 1971 in
 (33) Germany (DT)
 (44) Complete Specification published 7 Feb. 1973
 (51) International Classification C07C 69/14, 69/24; A01N 9/24
 (52) Index at acceptance
 C2C 1E3K3 1E3K7 1Q11G 1Q4 1Q6B1 1Q7B 1Q8C
 1Q9D1

A5E 1A3B 1A3C 1A3F 1A5B2 1C15B2 1C15D1
 1C15D2 1C15D3 1C8A

- (72) Inventors WERNER MEISER, WOLFGANG BEHRENZ,
 and KARL-HEINZ BUCHEL

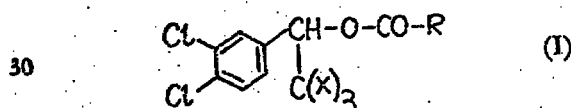
(54) NOVEL ACYLATED α -PHENYL ETHANOLS AND THEIR
 "USE AS INSECTICIDES"

- (71) We, BAYER AKTIENGESSELL-
 SCHAFT formerly known as Farbenfabriken
 Bayer Aktiengesellschaft, a body corporate
 organised under the laws of Germany, of
 5 Leverkusen, Germany, 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:—

- 10 The present invention relates to the use as
 insecticides of certain acylated β,β,β - trihalo-
 α - [3,4 - dichlorophenyl] - ethanol, which are
 new with one exception.

- It is already known that β,β,β - trichloro-
 15 α - [3,4 - dichlorophenyl] - ethanol exhibits
 insecticidal properties (R. Riemschneider,
 Monatshefte für Chemie, Vol. 82 (1951), pages
 600—606; Swiss Patent Specification
 20 251 120). Furthermore, it is known that
 β,β,β - trichloro - α - (4 - chlorophenyl)-
 ethanol and its acetyl derivative exhibit in-
 secticidal properties (German Patent Speci-
 fications 673 246 and 706 111). These com-
 pounds, however, are not particularly effective
 25 (cf: Läger, Martin, Müller, Helv. Chim.
 Acta, Vol. 27, page 892 (1944)).

It has now been found that the acylated
 β,β,β - trihalo - α - [3,4 - dichlorophenyl]-
 ethanol of the general formula:—



in which
 X is bromine, chlorine or fluorine, and
 R is methyl, ethyl, propyl, isopropyl, butyl,

[Price 25p]

tert.-butyl or 1-ethylpropyl
 exhibit excellent insecticidal properties.

The invention therefore provides an insecti-
 cidal composition containing as active ingredi-
 ent a compound of formula (I) in admixture
 with a solid diluent or carrier or in admixture
 with a liquid diluent or carrier containing a
 surface-active agent.

The invention also provides a method of
 combating insects which comprises applying to
 the insects or a habitat thereof a compound of
 formula (I) alone or in the form of a com-
 position containing as active ingredient a com-
 pound of formula (I) in admixture with a
 solid or liquid diluent or carrier.

The invention also provides crops protected
 from damage by insects by being grown in
 areas in which, immediately prior to and/or
 during the time of the growing, a compound
 of formula (I) was applied alone or in ad-
 mixture with a solid or liquid diluent or
 carrier. By this means the usual methods of
 providing harvested crops may be improved.

Surprisingly, the acylated carbinols of the
 formula (I), especially β,β,β - trichloro - α -
 (3,4 - dichlorophenyl) - ethanol - acetate, com-
 pared with the known, non-acylated β,β,β -
 trichloro - α - chlorophenyl - substituted car-
 binols and β,β,β - trichloro - α - (4 - chloro-
 phenyl) - ethanol - acetate, possess a far
 superior insecticidal effectiveness, especially
 against flies, mosquitoes and bugs. The effect
 sets in very rapidly and is long-lasting.

The compounds can therefore be used with
 good results for the control of insects, particu-
 larly Diptera, their low toxicity to warm-
 blooded animals being of particular advantage.
 Thus, tests indicate that β,β,β - trichloro - α

- (3,4 - dichlorophenyl) - ethanol - acetate has a median toxicity value (LD_{50}) greater than 2500 mg/kg rat (oral). Furthermore, the compounds to be used according to the invention, compared with the standard preparation dichlorodiphenyltrichloroethane, possess the advantage of better and more rapid effectiveness as well as higher vapour pressure, so that fewer residue problems result. They can therefore replace DDT which is losing more and more in importance. The substances to be used according to the invention therefore represent in many respects a genuine enrichment of the art.
- 15 The compounds to be used according to the invention are unambiguously defined generally by the formula (I). As examples, there are mentioned in particular:

- 20 β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol - acetate,
 β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol - propionate,
 β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol - butyrate,
 25 β,β,β - trichloro - α [3,4 - dichlorophenyl] - ethanol - 2 - methylpropionate,
 β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol - 2 - dimethyl - propionate,
 β,β,β - tribromo - α - [3,4 - dichlorophenyl] - ethanol - acetate,
 30 β,β,β - tribromo - α - [3,4 - dichlorophenyl] - ethanol - propionate,
 β,β,β - tribromo - α - [3,4 - dichlorophenyl] - ethanol - 2 - methyl - propionate,
 35 β,β,β - tribromo - α - [3,4 - dichlorophenyl] - ethanol - 2 - dimethyl propionate,
 β,β,β - trifluoro - α - [3,4 - dichlorophenyl] - ethanol - acetate,
 β,β,β - trifluoro - α [3,4 - dichlorophenyl] - ethanol propionate,
 40 β,β,β - trifluoro - α - [3,4 - dichlorophenyl] - ethanol - 2 - methyl - propionate,
 β,β,β - trifluoro - α - [3,4 - dichlorophenyl] - ethanol - 2 - dimethyl - propionate,
 45 β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol - 2 - ethyl - butyrate.

One of the active compounds to be used according to the invention is already known as such, namely β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol - acetate (compare R. Riemschneider, Monatshefte für Chemie, Vol. 82, (1951), page 600—606).

The invention accordingly provides as new compounds the other compounds of formula (I).

55 These compounds can be prepared according to known processes, especially by acylation of the appropriate carbinols by means of acid anhydride or chloride, possibly in the presence of acid-binding agents or in the presence of catalytic amounts of acid, as for example sulphuric acid. The reaction product may be isolated by destroying the excess acid chloride or anhydride by hydrolysis, separating the

aqueous layer and purifying the resulting organic phase by distillation or crystallisation.

Preparation of the carbinols to be used as starting materials may be effected either by Friedel-Crafts acylation of the appropriate hydrocarbons with trihaloacetaldehydes with catalytic assistance of $AlCl_3$, $FeCl_3$, BF_3 , conc. H_2SO_4 (comp. J. W. Howard, J. Amer. Chem. Soc. Vol. 57, page 2317 (1937); T. C. Chen, W. T. Sumerford, J. Amer. Chem. Soc. Vol. 72, pages 5124—5 (1950); P. Crooy, Ind. Chim. Belge, Vol. 32, pages 268—271 (1967) or according to other processes (cf. J. W. Howard, G. N. Stephens, J. Amer. Chem. Soc. Vol. 60, pages 228 (1938); R. Riemschneider, Monatshefte für Chemie, Vol. 82, pages 600—606 (1951), Swiss Patent Specification 258 755).

As already mentioned, the substances which can be used according to the invention are distinguished by outstanding insecticidal properties. They possess a good effectiveness against both sucking and biting insects, as well as, above all, against Diptera.

The products are therefore used with success in crop protection and the protection of stored products as well as in the hygiene field against the most diverse animal pests.

To the sucking insects there belong, in the main, aphids (Aphidae) such as the green peach aphid (*Myzus persicae*), the bean aphid (*Voridis fabae*), the bird cherry aphid (*Rhopalosiphum padi*), the pea aphid (*Macrosiphum pisi*) and the potato aphid (*Macrosiphum solanifolii*), the currant gall aphid (*Cryptomyzus korschelti*), the rosy apple aphid (*Sappaphis mali*), the mealy plum aphid (*Hyalopterus arundinis*) and the cherry blackfly (*Myzus cerasi*); in addition, scales and mealybugs (Coccinea), for example the oleander scale (*Aspidiotus hederæ*) and the soft scale (*Lecanium hesperidum*) as well as the grape mealy-bug (*Pseudococcus maritimus*); thrips (Thysanoptera), such as *Hercinothrips femoralis*, and bugs, for example the beet bug (*Piesma quadrata*), the red cotton bug (*Dysdercus intermedius*), the bed bug (*Cimex lectularius*), the assassin bug (*Rhodnius prolixus*) and Chagas' bug (*Triatoma infestans*) and, further, cicadas, such as *Euscelis bilobatus* and *Nephotettix bipunctatus*.

In the case of the biting insects, above all there should be mentioned butterfly caterpillars (Lepidoptera) such as the diamond-back moth (*Plutella maculipennis*), the gipsy moth (*Lymantria dispar*), the brown-tail moth (*Euproctis chrysorrhoea*) and tent caterpillar (*Malacosoma neustria*); further, the cabbage moth (*Mamestra brassicae*) and the cutworm (*Agrotis segetum*), the large white butterfly (*Pieris brassicae*), the small winter moth (*Choristobia brumata*), the green oak tortrix moth (*Tortrix viridana*), the fall armyworm (*Laphygma frugiperda*) and cotton worm

ing 65
on.
sed
by
ate
ith 70
nc.
m.
en,
Vol
ad. 75
57)
W.
m.
32, 80
ci-

ich
are
ial 85
ess
as

ess
ed 90
nst

the
ich
or-
si-
um
um
to-
id 100
id
ck-
nd
ler
ale 105
pe
ips
or-
ug
ug 110
ug
ri-
as
ct- 115

all
er-
ck
oth 120
oth
lar
ge
m
fly 125
th
ix
m
m

- (*Prodenia litura*), the ermine moth (*Hypomomeuta padella*), the Mediterranean flour moth (*Ephestia kuehniella*) and greater wax moth (*Galleria mellonella*).
- Also to be classed with the biting insects are beetles (Coleoptera), for example the granary weevil (*Sitophilus granarius* = *Calandra granaria*), the Colorado beetle (*Lepidotarsa decemlineata*), the dock beetle (*Gastrophysa viridula*), the mustard beetle (*Phaedon cochleariae*), the blossom beetle (*Meligethes aeneus*), the raspberry beetle (*Byturus tomentosus*), the bean weevil (*Bruchidius* = *Acanthoscelides obtectus*), the leather beetle (*Dermestes frischeri*), the khapra beetle (*Trogoderma granarium*), the flour beetle (*Tribolium castaneum*), the northern corn billbug (*Calandra or Sitophilus zeamais*), the drugstore beetle (*Stegobium paniceum*), the yellow mealworm (*Tenebrio molitor*) and the saw-toothed grain beetle (*Oryzaephilus surinamensis*), but also species living in the soil, for example wireworms (*Agriotes spec.*) and larvae of the cockchafer (*Melolontha melolontha*); cockroaches, such as the German cockroach (*Blattella germanica*), American cockroach (*Periplaneta americana*), Madeira cockroach (*Leucophaea or Rhyparobia madeirae*), oriental cockroach (*Blatta orientalis*), the giant cockroach (*Blaberus giganteus*) and the black giant cockroach (*Blaberus fuscus*) as well as *Henschoutedenia flexivitta*; further, Orthoptera, for example the house cricket (*Acheta domestica*); termites such as the eastern subterranean termite (*Reticulitermes flavipes*) and Hymenoptera such as ants, for example the garden ant (*Lasius niger*).
- The Diptera comprise essentially the flies, such as the vinegar fly (*Drosophila melanogaster*), the Mediterranean fruit fly (*Ceratitis capitata*), the house fly (*Musca domestica*), the little house fly (*Fannia canicularis*), the black blow fly (*Phormia aegina*) and bluebottle fly (*Calliphora erythrocephala*) as well as the stable fly (*Stomoxys calcitrans*); further, gnats, for example mosquitoes such as the yellow fever mosquito (*Aedes aegypti*), the northern house mosquito (*Culex pipiens*) and the malaria mosquito (*Anopheles stephensi*).
- The active compounds according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents.
- In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.
- As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes or benzene, chlorinated aromatic

hydrocarbons, such as chlorobenzenes, paraffins, such as mineral oil fractions, alcohols, such as methanol or butanol, or strongly polar solvents, such as dimethyl formamide or dimethyl sulphoxide, as well as water.

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc or chalk, or ground synthetic minerals, such as highly-dispersed silicic acid or silicates.

Preferred examples of emulsifying agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates and aryl sulphonates; and preferred examples of dispersing agents include lignin, sulphite waste liquors and methyl cellulose.

The active compounds to be used according to the invention may be present in the formulations in admixture with other active compounds.

The formulations contain, in general, from 0.1 to 95, preferably 0.5 to 90, per cent by weight of active compound.

The active compounds may be applied as such or in the form of their formulations or in the application forms prepared therefrom, such as ready-to-use solutions, emulsifiable concentrates, emulsions, suspensions, spray powders, pastes, soluble powders, dusting agents and granulates. Application may take place in the usual manner, for example by squirting, spraying, atomising, dusting, scattering, fumigation, vaporisation, watering, dressing or incrustation.

The concentrations of active compound in the ready-to-apply preparations can be varied within fairly wide ranges. In general, they are from 0.0001 to 10%, preferably 0.01 to 1%, by weight.

The active compounds can also be used with good results in the ultra-low-volume (ULV) process, where it is possible to apply formulations of up to 95% or even the 100%-strength active compound alone.

The invention is illustrated by the following Examples. In Tables A, B and C, h means hours and ' means minutes.

Example A

LT₁₀₀ test for Diptera
Test animals: *Musca domestica*
Solvent: acetone

The test animals, the active compounds, the dissolved in 1000 parts by volume of solvent. The solution so obtained is diluted with further solvent to the desired lower concentrations.

2.5 ml of the solution of active compound are pipetted into a Petri dish. On the bottom of the Petri dish there is a filter paper with a diameter of about 9.5 cm. The Petri dish remains uncovered until the solvent has completely evaporated. The amount of active

compound per square metre of filter paper varies with the concentration of the solution of active compound used. About 25 test animals are then placed in the Petri dish and it is covered with a glass lid.

5

The condition of the test animals is continuously observed for up to 8 hours. The time

which is necessary for a 100% destruction is determined.

The test animals, the active compounds, the concentrations of the active compounds and the periods of time at which there is a 100% destruction can be seen from the following Table A.

TABLE A

(LT₁₀₀ test for Diptera)

Active compound	Concentration of active compound of the solution in %	LT ₁₀₀
<chem>CC(=O)OC(c1ccccc1)C(Cl)(Cl)Cl</chem> (known) (1)	0.2	8h = 0%
<chem>CC(=O)OC(c1ccc(Cl)cc1)C(Cl)(Cl)Cl</chem> (known) (2)	0.2	8h = 90%
<chem>CC(=O)OC(c1ccc(Cl)c(Cl)c1)C(Cl)(Cl)Cl</chem> (3)	0.2 0.04 0.008	30' 75' 8h
<chem>CCOC(=O)C(c1ccc(Cl)c(Cl)c1)C(Cl)(Cl)Cl</chem> (4)	0.2 0.04	75' 7h
<chem>CCCC(=O)OC(c1ccc(Cl)c(Cl)c1)C(Cl)(Cl)Cl</chem> (5)	0.2 0.04 0.008	75' 6h 8h = 50%

Example BLT₁₀₀ test for DipteraTest animals: *Aedes aegypti*

Solvent: acetone

- 5 2 parts by weight of active compound are dissolved in 1000 parts by volume of solvent. The solution so obtained is diluted with further solvent to the desired lower concentrations.

- 10 2.5 ml of the solution of active compound are pipetted into a Petri dish. On the bottom of the Petri dish there is a filter paper with a diameter of about 9.5 cm. The Petri dish remains uncovered until the solvent has completely evaporated. The amount of active com-

pound per square metre of filter paper varies with the concentration of the solution of active compound used. About 25 test animals are then placed in the Petri dish and it is covered with a glass lid.

The condition of the test animals is continuously observed for up to 4 hours. The time which is necessary for a 100% destruction is determined.

The test animals, the active compounds, the concentrations of the active compounds and the periods of time at which there is a 100% destruction can be seen from the following Table B.

TABLE B

(LT₁₀₀ test for Diptera)

Active compound	Concentration of active compound of the solution in %	LT ₁₀₀
<chem>Clc1ccc(cc1)C(CCl)(Cl)COCC(=O)C</chem> (known) (2)	0.2 0.04 0.008 0.0016	15' 15' 75' 4h = 20%
<chem>c1ccccc1C(CCl)(Cl)COCC(=O)C</chem> (known) (1)	0.2	4h = 0%
<chem>Clc1ccc(cc1)C(CCl)(Cl)C(c2ccc(Cl)cc2)C</chem> (known) (6)	0.2 0.04 0.008	45' 60' 4h = 80%
<chem>Clc1cc(C(CCl)(Cl)COCC(=O)CC)ccc1Cl</chem> (3)	0.2 0.04 0.008 0.0016	15' 15' 45' 4h = 80%

Example CLT₁₀₀ test for DipteraTest animals: *Anopheles atroparvus*

Solvent: acetone

- 30 2 parts by weight of active compound are dissolved in 1000 parts by volume of solvent. The solution so obtained is diluted with further solvent to the desired lower concentrations.

2.5 ml of the solution of active compound are pipetted into a Petri dish. On the bottom of the Petri dish there is a filter paper with a diameter of about 9.5 cm. The Petri dish remains uncovered until the solvent has completely evaporated. The amount of active compound per square metre of filter paper varies with the concentration of the solution of

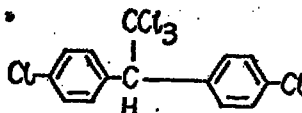
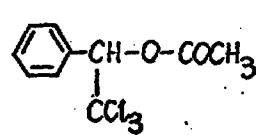
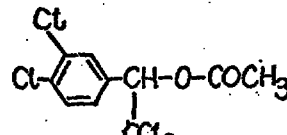
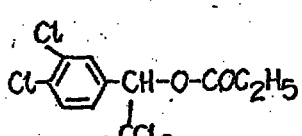
active compound used. About 25 test animals are then placed in the Petri dish and it is covered with a glass lid.

- 5 The condition of the test animals in continuously observed for 2 hours. The time which is necessary for a 100% destruction is determined.

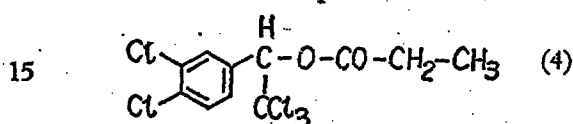
The test animals, the active compounds, the concentrations of the active compounds and the periods of time at which there is a 100% destruction can be seen from the following Table C.

TABLE C

LT₁₀₀ test for Diptera

Active compound	Concentration of active compound of the solution in %	LT ₁₀₀
 (known) (6)	0.2 0.04 0.008	60' 60' 90'
 (known) (1)	0.2	105'
 (3)	0.2 0.04 0.008	15' 30' 45'
 (4)	0.2 0.04 0.008	15' 30' 75'

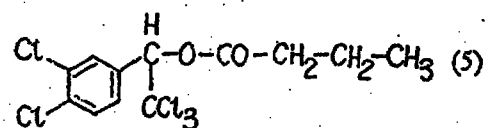
Example 1



150 ml propionic anhydride are added to 147 g β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol in 100 ml glacial acetic acid, and to this mixture 102 g concentrated sulphuric acid are added dropwise at 80° C. The reaction mixture is then heated on a water-bath for an hour; after cooling, it is poured into ice water; one hour later, it is taken up in methylene chloride and the organic

phase is dried. After the solvent has been distilled off, there is obtained by distillation 115 g of the propionate of β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol of b.p. 144-148° C/0.5 mm Hg.

Example 2



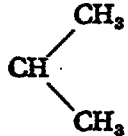
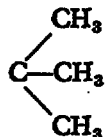
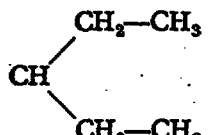
118 g butyric anhydride are added to 94 g

he
nd
% 10
ng

- β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol in 65 ml glacial acetic acid, and to this mixture 65 g of concentrated sulphuric acid are added dropwise at about 80° C. The mixture is then heated on a water-bath for an hour; after pouring into 1 litre of ice water, it is extracted with methylene chloride one hour later and the organic layer is dried. The solvent is evaporated under reduced

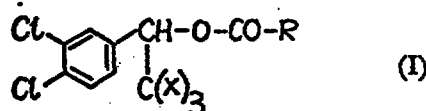
pressure, the residue is distilled, and the butyrate of β,β,β - trichloro - α - [3,4 - dichlorophenyl] - ethanol is obtained in an amount of 95 g with the b.p. 145° C/0.4 m Hg.

The compounds listed in the following table can be obtained in a manner analogous to that of the above Examples. The compounds have the general formula (I), the meaning of X and R being shown in the Table.

Compound	X	R	B.p.[°C] at [mm Hg]
(7)	F	CH ₃	120/0.3
(8)	Br	CH ₃	160/0.3
(9)	Cl		145/0.5
(10)	Cl		150/0.4
(11)	Cl		142/0.2

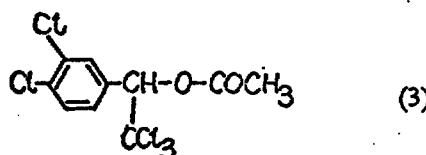
20 WHAT WE CLAIM IS:—

1. An insecticidal composition containing as active ingredient an acylated carbinol of the general formula:—



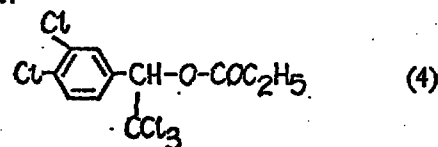
- 25 in which
X is bromine, chlorine or fluorine, and
R is methyl, ethyl, propyl, isopropyl, butyl,
tertiary butyl, or 1-ethylpropyl,
in admixture with a solid diluent or carrier or
30 in admixture with a liquid diluent or carrier
containing a surface-active agent.

2. An insecticidal composition containing as active ingredient an acylated carbinol of the formula:—



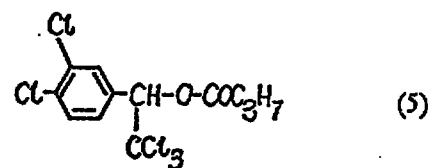
- in admixture with a solid diluent or carrier
or in admixture with a liquid diluent or carrier
containing a surface-active agent.

3. An insecticidal composition containing as active ingredient an acylated carbinol of the formula:—



- in admixture with a solid diluent or carrier
or in admixture with a liquid diluent or carrier
containing a surface-active agent.

4. An insecticidal composition containing as active ingredient an acylated carbinol of the formula:—



- in admixture with a solid diluent or carrier
or in admixture with a liquid diluent or carrier
containing a surface-active agent.

5. A composition according to claim 1 in which the acylated carbinol is any of those of formula (I) which are hereinbefore specifically identified.

cen 30
ion
ro-
p.p.

35

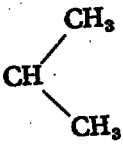
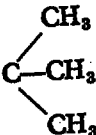
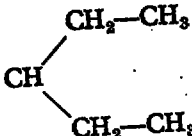
5)

g

6
the
and
00%
wing 10

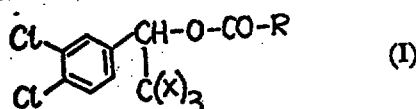
- 7
5 β, β, β - trichloro - α - [3,4 - dichlorophenyl] - ethanol in 65 ml glacial acetic acid, and to this mixture 65 g of concentrated sulphuric acid are added dropwise at about 80° C. The mixture is then heated on a water-bath for an hour; after pouring into 1 litre of ice water, it is extracted with methylene chloride one hour later and the organic layer is dried. The solvent is evaporated under reduced

10 pressure, the residue is distilled, and the butyrate of β, β, β - trichloro - α - [3,4 - dichlorophenyl] - ethanol is obtained in an amount of 95 g with the b.p. 145° C/0.4 m Hg.
The compounds listed in the following table can be obtained in a manner analogous to that of the above Examples. The compounds have the general formula (I), the meaning of X and R being shown in the Table.

Compound	X	R	B.p.[°C] at [mm Hg]
(7)	F	CH ₃	120/0.3
(8)	Br	CH ₃	160/0.3
(9)	Cl		145/0.5
(10)	Cl		150/0.4
(11)	Cl		142/0.2

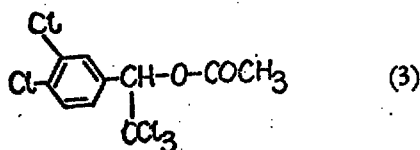
20 WHAT WE CLAIM IS:—

1. An insecticidal composition containing as active ingredient an acylated carbinol of the general formula:—



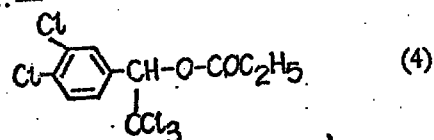
- 25 in which
X is bromine, chlorine or fluorine, and
R is methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, or 1-ethylpropyl,
in admixture with a solid diluent or carrier or
30 in admixture with a liquid diluent or carrier containing a surface-active agent.

2. An insecticidal composition containing as active ingredient an acylated carbinol of the formula:—



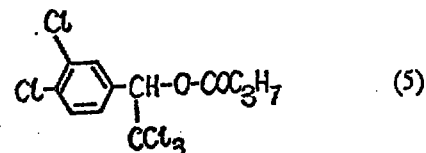
in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

3. An insecticidal composition containing as active ingredient an acylated carbinol of the formula:—



in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

4. An insecticidal composition containing as active ingredient an acylated carbinol of the formula:—



in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

5. A composition according to claim 1 in which the acylated carbinol is any of those of formula (I) which are hereinbefore specifically identified.



* C L M S *

been
ation
loro-
b.p. 30

35

(5)

94 g

6. A composition according to any of claims 1—5 containing from 0.1 to 95% of the active compound, by weight.
7. A method of combating insects which combating applying to the insects or a habitat thereof an acylated carbinol as defined in any of claims 1—5 alone or in the form of a composition containing the acylated carbinol as active ingredient in admixture with a solid or liquid diluent or carrier.
8. A method according to claim 7 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight.
9. A method according to claim 7 or 8 in which the insects are flies, mosquitoes or bugs.
10. A method according to any of claims 7—9 in which the acylated carbinol is one of those mentioned in Example A.
11. Crops protected from damage by insects by being grown in areas in which immediately prior to and/or during the time of the growing, an acylated carbinol as defined in any of claims 1 to 5 was applied alone or in admixture with a solid or liquid diluent or carrier.
12. A composition according to claim 6 in which the acylated carbinol is defined in claim 2, 3 or 4.
13. A method according to any of claims 7 to 9 in which the acylated carbinol is defined in claim 2, 3 or 4.
14. Crops according to claim 11, in which the protective acylated carbinol is defined in claim 2, 3 or 4.
15. Acylated carbinols of the general formula:
- $$\text{Cl} \begin{array}{c} \text{Cl} \\ \text{C}_6\text{H}_3 \end{array} \text{CH}(\text{C}(\text{X})_3)\text{O-CO-R} \quad (I)$$
- in which
X is bromine, chlorine or fluorine and
R is methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl or 1-ethylpropyl, provided that X is not chlorine when R is methyl.
16. The acylated carbinols according to claim 15 which are hereinbefore specifically identified.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24, Southampton Buildings,
Chancery Lane,
London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *